Synthesis and Structure of a Novel Cyclic Polysulfide, 2,4,6-Tris[bis(trimethylsilyl)methyl]phenyloctathionane

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A novel cyclic polysulfide, octathionane $TbtCHS_8$ (**7**; Tbt=2,4,6-tris[bis(trimethylsilyl)methyl]phenyl) was synthesized by thermal reaction of the corresponding diazomethane $TbtCHN_2$ with cyclooctasulfur (S_8) in benzene in the dark. Molecular structure of **7** was determined by X-ray crystallographic analysis and the geometry of the CS_8 ring was compared with that of theoretically optimized cyclononasulfur (S_9). Desulfurization of **7** by triphenylphosphine afforded the corresponding pentathiane $TbtCHS_5$.

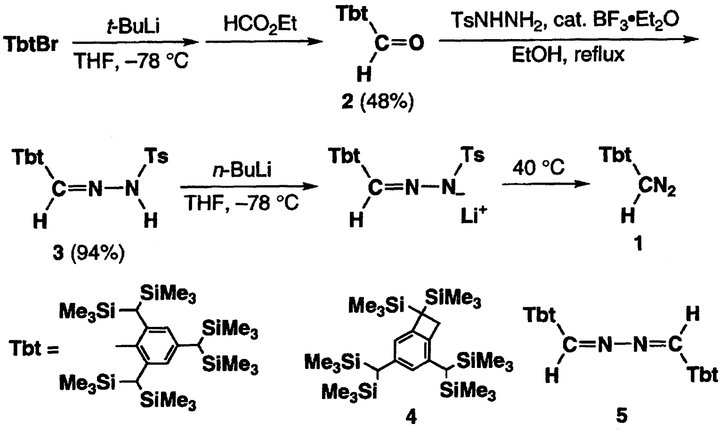
Recently, much attention has been paid to the chemistry of cyclic polysulfides because of their unique structures and reactivities as well as their biological activities.[1] Although most of the cyclic polysulfides so far studied are restricted to 1,2,3-trithiole and 1,2,3,4,5-pentathiepin ring systems, some cyclic polysulfides containing a ring system of CS_n (n=2, 5—34) type have been reported.[1a,2] For example, the structure of dithiirane (CS_2),[2i] pentathiane (CS_5),[2d] hexathiepane (CS_6),[2d] and heptathiocane (CS_7)[2h] have been elucidated by X-ray crystallographic analysis, although other cyclic polysulfides (CS_n; n=8—34) have been only detected by HPLC. In the meantime, we recently succeeded in the synthesis of novel cyclic tetrachalcogenides containing group 14 metals such as $Tbt(Ar)MY_4$ (M=Si, Ge, Sn, Pb; Y=S, Se; Ar=mesityl or 2,4,6-triisopropylphenyl)[3] by taking advantage of an efficient steric protection group, 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl[4] (denoted as Tbt in this paper). We became interested in the syntheses of cyclic polysulfides with a CS_n ring system using the Tbt group, and previously reported the first synthesis and X-ray crystallographic analysis of stable octathionane $TbtCHS_8$ (**7**) in a preliminary form.[5] In this paper we delineate a detailed account of the synthesis of the octathionane and its desulfurization reaction.

Results and Discussion

For the synthesis of cyclic polysulfides, we chose the reaction of Tbt-substituted diazomethane $TbtCHN_2$ (**1**) with sulfur. It is known that the reaction of diazo compounds (or carbenes) with sulfur gives thiiranes or thiocarbonyl compounds,[6] while that with disulfides affords S–S insertion products.[7] It has recently been reported by us that the reactions of sulfur with the carbene analogues of heavier group 14 elements having Tbt group, Tbt(Ar)M: (M=Si, Ge, Sn, Pb; Ar=mesityl or 2,4,6-triisopropylphenyl), afford the corresponding cyclic tetrasulfides.[3b,3c,3f,3g] It occurred to us that the reaction of sulfur with a highly hindered (and hence less reactive) diazo compound like $TbtCHN_2$ (**1**) (or the corresponding carbene) might give a polysulfide which is not available from a reaction using a reactive substrate. We found that indeed the reaction of **1** with sulfur resulted in the formation of the corresponding octathionane, a novel cyclic polysulfide.

Synthesis of Tbt-Substituted Diazomethane $TbtCHN_2$ (1). The diazo compound **1** was prepared by the Bamford–Stevens reaction,[8] i.e., by thermolysis of the lithium salt of the corresponding tosylhydrazone TbtCHNNHTs (**3**) obtained from TbtBr via TbtCHO (**2**) (Scheme 1). The aldehyde **2** was synthesized from ethyl formate and TbtLi, prepared by treatment of TbtBr with t-BuLi in THF, and converted to **3** by reaction with $TsNHNH_2$ (Ts=p-toluenesulfonyl) in the presence of $BF_3 \cdot Et_2O$ catalyst in ethanol. Reaction of **3** with n-BuLi at −78 °C in THF gave white precipitates which were presumably TbtCHNNTsLi, and heating of the reaction mixture at 45 °C for 10 h afforded diazomethane **1** as a mixture with benzocyclobutene **4**, the purity of **1** being determined to be 80% by ^1H NMR. Since **1** was gradually decomposed to the corresponding azine **5** even at 4 °C, **1** was used in the next reaction immediately after the preparation without further purification.

Thermal Reaction of Diazomethane 1. Com-



Scheme 1.

pound **1** was thermally decomposed in refluxing benzene for 4 h to give benzocyclobutene **4** (73%), which was undoubtedly formed by the thermal denitrogenation of **1** followed by an intramolecular C–H insertion of the resulting carbene **6** toward the *ortho*-bis(trimethylsilyl)methyl group, together with azine **5** (0.8%) (Scheme 2).

Benzocyclobutene **4** and azine **5** showed satisfactory spectral and analytical data. The molecular structure of **4** was definitively determined by X-ray crystallographic analysis. An ORTEP drawing and selected bond lengths and angles are shown in Fig. 1 and Table 2, respectively. The crystallographic data are summarized in Table 1.[9] The fused cyclobutene ring was coplanar to the benzene ring. No appreciable Mills–Nixon effect[10] was observed in the benzene ring of **4**.

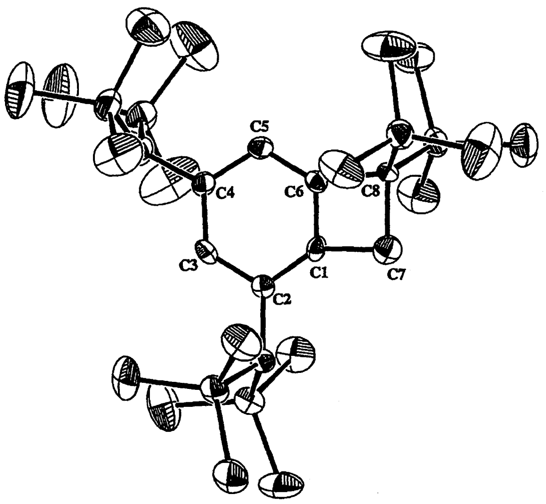


Fig. 1. ORTEP drawing of benzocyclobutene **4**.

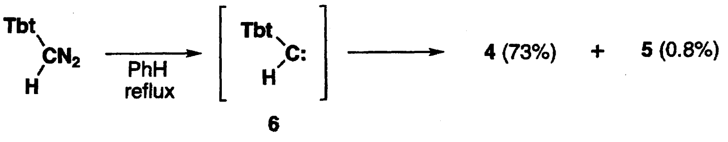
Table 1. Crystal Data for **4** and **7**

	4	7
Empirical formula	$C_{28}H_{60}Si_6$	$C_{28}H_{60}S_8Si_6$
Fw	565.29	821.78
Cryst syst	Monoclinic	Monoclinic
Space group	$P2_1/a$	$P2_1/c$
a/Å	12.604(5)	9.951(1)
b/Å	18.396(3)	13.075(1)
c/Å	16.513(4)	35.076(5)
β/deg	94.92(2)	97.4969(6)
V/Å^3	3815(2)	4544.7(1.0)
Z	4	4
D_{calcd}/g cm^{-3}	0.984	1.2005
μ/cm^{-1}	2.27	50.61
Cryst size/mm	0.60×0.20×0.08	0.4×0.3×0.07
R	0.056	0.092
R_w	0.053	0.094

Table 2. Selected Bond Lengths (Å) and Angles (deg) for **4**

C(1)–C(2)	1.351(9)	C(4)–C(5)	1.396(9)
C(1)–C(6)	1.375(9)	C(5)–C(6)	1.376(9)
C(1)–C(7)	1.513(9)	C(6)–C(8)	1.531(9)
C(2)–C(3)	1.402(9)	C(7)–C(8)	1.59(1)
C(3)–C(4)	1.398(9)		
C(2)–C(1)–C(6)	123.6(7)	C(4)–C(5)–C(6)	117.6(7)
C(6)–C(1)–C(7)	92.3(7)	C(1)–C(6)–C(5)	121.7(7)
C(1)–C(2)–C(3)	114.6(7)	C(1)–C(6)–C(8)	95.7(6)
C(2)–C(3)–C(4)	124.1(7)	C(1)–C(7)–C(8)	88.1(6)
C(3)–C(4)–C(5)	118.3(7)	C(6)–C(8)–C(7)	83.9(6)

Reaction of Diazomethane 1 with Elemental Sulfur. When a benzene solution of **1** was added dropwise into a refluxing benzene suspension of an excess amount of cyclooctasulfur (S_8) purified by a liter-

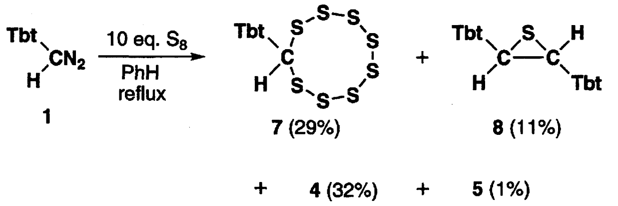


Scheme 2.

ature method[11] during 4.5 h and the reaction mixture was refluxed for further 0.5 h in the dark, octathionane **7** (29%) and episulfide **8** (11%) were isolated as sulfurization products along with benzocyclobutene **4** (32%) and azine **5** (1%) (Scheme 3). Octathionane **7** was stable in refluxing benzene or ethanol–chloroform.

The mechanism for the formation of **7** and **8** in the reaction of **1** with cyclooctasulfur can be interpreted in terms of the initial addition of the intermediary carbene **6** to cyclooctasulfur followed by a competitive ring expansion and S_7 extrusion of the resulting sulfonium ylide **9** leading to octathionane **7** and thioaldehyde **10**, respectively (Scheme 4). Episulfide **8**, the configuration of which is tentatively assigned as trans for steric reason, might be formed by the reaction of thioaldehyde **10** with co-existing carbene **6** and/or diazomethane **1**, as shown in Scheme 4. Reaction of **1** under fluorescent light with elemental sulfur purified by usual recrystallization from benzene gave a mixture of cyclic polysulfides TbtCHS_n (n=5—8), probably owing to the reaction of **1** with cyclopolysulfurs (S_{5-8}) which might be contained in elemental sulfur, suggesting the importance of the purity of sulfur in the formation of **7**.

It has been reported that the reaction of a diazomethane such as diphenyldiazomethane with elemental sulfur afford the corresponding episulfide in good yield.[6a,6b] The formation of **7** in the present reaction can be ascribed to steric demand due to the Tbt group which retards a further reaction of **7** with **1**.

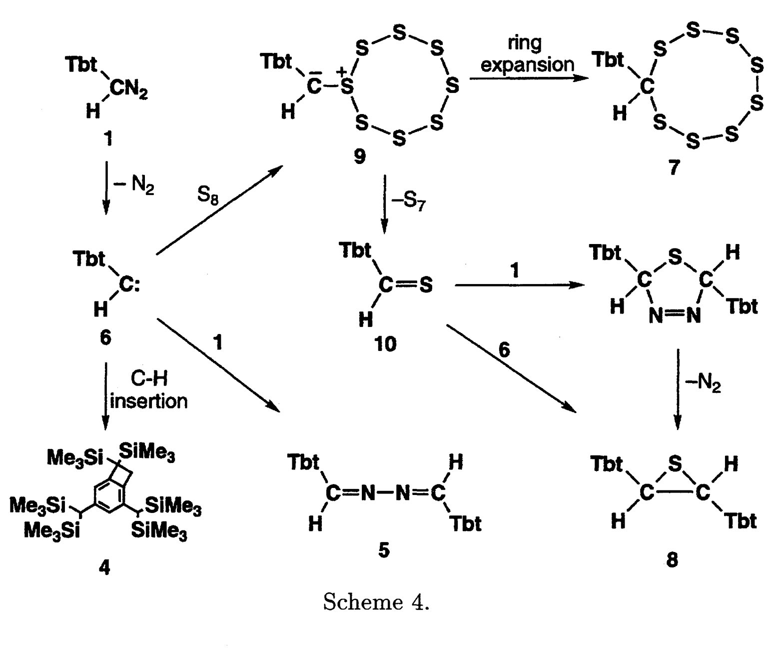


Scheme 3.

Crystal Structure of Octathionane 7. Octathionane **7** showed satisfactory spectral and analytical data. The molecular structure of **7** was established by X-ray crystallographic analysis. The ORTEP drawing is shown in Fig. 2; selected bond lengths and angles and torsion angles are listed in Table 3. The crystallographic data are summarized in Table 1.

Since S_9 is the only cyclopolysulfide, among S_6—S_{12}, whose geometry has not been experimentally determined,[12] the structure analysis of **7** is worthy of note from the viewpoints of not only the first example of an octathionane derivative but also a comparative study on the structure of nine-membered cyclopolysulfide rings. As shown in Fig. 2, the octathionane ring of **7** is of C_1 symmetry. In contrast to **7**, cyclononasulfur (S_9) has been concluded to be of C_1 or C_2 symmetry from Raman spectral data[13] and C_2 symmetry in the ground state from theoretical calculations,[12] while a 1,2,3,4,5,6,7-heptathionane (C_2S_7) ring in *exo*-3,4,5,6,7,8,9-heptathiatricyclo[9.2.1.$0^{2,10}$]tetradecane was presumed to have C_s symmetry from spectral data.[1h]

MMP2 calculations[14] revealed that replacement of one sulfur atom of S_9 by TbtCH unit (the *p*-bis(trimethylsilyl)methyl group was excluded to simplify the calculations) gave the lowest converged ground state geometry with no symmetry factor which was almost identical with the crystal structure of **7**. Since the MMP2 calculations indicate that octathionane CH_2S_8 is unstable in the C_1 symmetry form which is the optimized one in the CS_8 ring of **7**, the difference in the ground state geometry between the octathionane ring in **7** and cyclononasulfur is probably due to the steric repulsion between the bulky Tbt group and the polysulfur linkage. However, the geometry of the polysulfur linkage, i.e., the atom stacking mode of the octathionane ring moiety, is essentially identical with that of S_9, the S–S bonds being neither unusually long nor short as in the



Scheme 4.

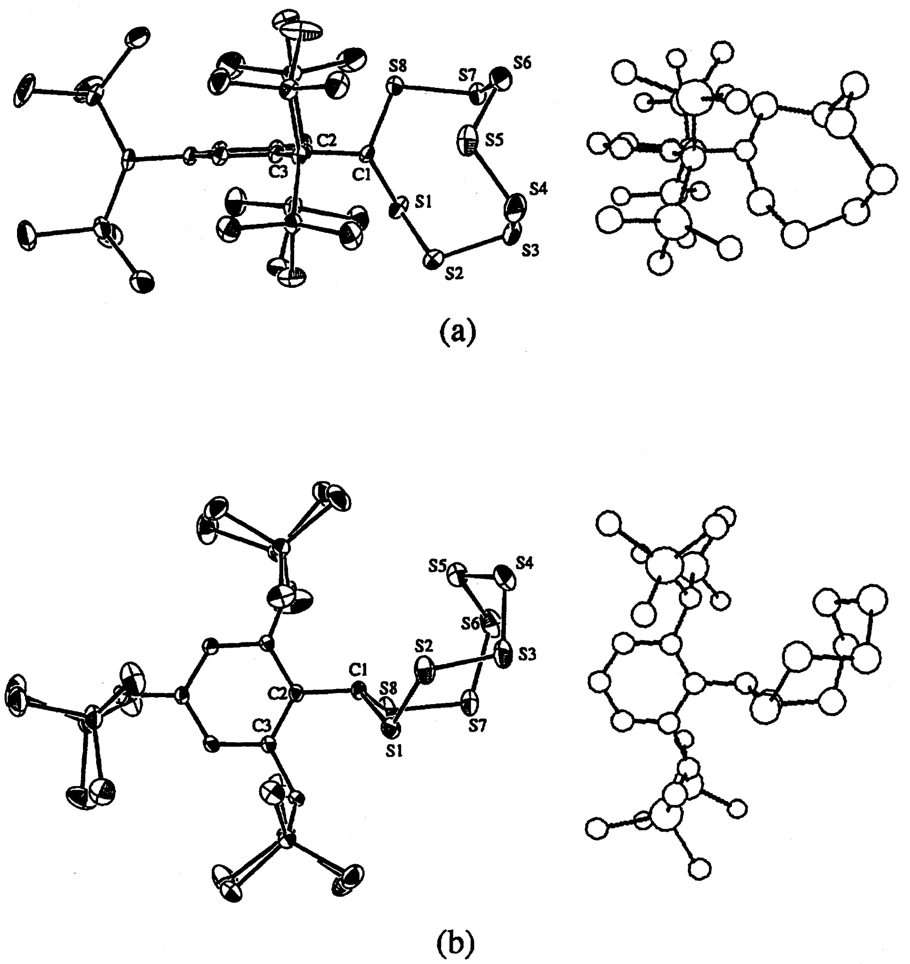


Fig. 2. ORTEP drawing of TbtCHS$_8$ **7** together with the optimized structure of **7** by MMP2 calculation; a) top view and b) side view.

Table 3. Selected Bond Lengths (Å), Bond Angles (deg), and Tortion Angles (deg) for **7**

S(1)–S(2)	2.022(3)	S(5)–S(6)	2.046(4)
S(1)–C(1)	1.832(6)	S(6)–S(7)	2.066(4)
S(2)–S(3)	2.045(3)	S(7)–S(8)	2.016(3)
S(3)–S(4)	2.029(4)	S(8)–C(1)	1.845(6)
S(4)–S(5)	2.034(4)	C(1)–C(2)	1.519(9)
S(2)–S(1)–C(1)	105.9(2)	S(6)–S(7)–S(8)	108.4(2)
S(1)–S(2)–S(3)	108.4(1)	S(7)–S(8)–C(1)	104.7(2)
S(2)–S(3)–S(4)	108.6(2)	S(1)–C(1)–S(8)	111.9(3)
S(3)–S(4)–S(5)	108.7(2)	S(1)–C(1)–C(2)	115.9(4)
S(4)–S(5)–S(6)	109.1(2)	S(8)–C(1)–C(2)	108.9(4)
S(5)–S(6)–S(7)	106.0(1)		
C(1)–S(1)–S(2)–S(3)	−87.9(2)	S(5)–S(6)–S(7)–S(8)	66.8(2)
S(2)–S(1)–C(1)–S(8)	121.0(3)	S(6)–S(7)–S(8)–C(1)	−88.8(2)
S(2)–S(1)–C(1)–C(2)	−113.3(4)	S(7)–S(8)–C(1)–S(1)	−52.5(3)
S(1)–S(2)–S(3)–S(4)	111.8(2)	S(7)–S(8)–C(1)–C(2)	178.2(4)
S(2)–S(3)–S(4)–S(5)	−66.8(2)	S(1)–C(1)–C(2)–C(3)	−52.8(7)
S(3)–S(4)–S(5)–S(6)	−64.4(2)	S(8)–C(1)–C(2)–C(3)	74.3(6)
S(4)–S(5)–S(6)–S(7)	78.7(2)		

case of calculated S$_9$ molecule.

Desulfurization of Cyclic Polysulfides. In the hope of synthesizing the corresponding heptathiocane TbtCHS$_7$ (**11**), the reaction of **7** with equimolar triphenylphosphine in THF at −78 °C was attempted. The products were, however, an inseparable mixture of **11**, hexathiepane $TbtCHS_6$ (**12**), and pentathiane $TbtCHS_5$ (**13**) along with some sulfur, the relative ratio of the polysulfides being estimated by ^{1}H NMR to be 4 : 10 : 5 (Scheme 5). The number of sulfur contained in the cyclic polysulfides was determined by ^{1}H NMR measurement of the relative ratios of the polysulfides yielded in the desulfurizations of **7** with 1, 3, and 4 equivalents of triphenylphosphine, although **11** and **12** could not be isolated. Desulfurization with 3 and 4 equivalents of the phosphine will be described later.

The formation of a mixture of **11**, **12**, and **13** even in the reaction with one equivalent of triphenylphosphine at low temperature like −78 °C suggests concomitant occurrence of cyclization paths a, b, and c in the intermediary zwitter ion **14**, as shown in Scheme 6.

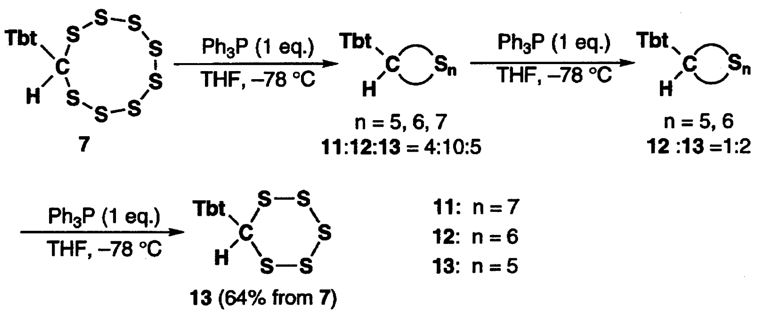
The reaction of the mixture of **11**, **12**, and **13** thus obtained with one equivalent of triphenylphosphine at −78 °C again afforded a mixture of **12** and **13** (1 : 2), which was subjected to similar desulfurization with the phosphine to give **13** as a sole polysulfide (64% from **7**). Interestingly, treatment of **13** with the phosphine under conditions similar to those of the above desulfurizations resulted in the recovery of 56% of **13** although the phosphine was quantitatively converted into the corresponding sulfide. This finding indicates that a reaction product from **13** and the phosphine is more reactive than the starting **13**, thus undergoing a further reaction with the phosphine to give the phosphine sulfide. The reaction product containing the TbtCH unit is most likely a cyclic sulfide of type $TbtCH(S_x)(S_y)CHTbt$ judging from the retention time in gel permeation liquid chromatography although the exact structure could not be determined. The absence of tetrathiolane $TbtCHS_4$ in the desulfurization products of **13** is in keeping with the fact that there has been known no stable tetrathiolane (R_2CS_4) probably because of its ring distortion.

Desulfurization of **7** with 3 equivalents of triphenylphosphine at −78 °C did not give **13**, but a mixture of **12** and **13**. The use of 4 equivalents of the phosphine also resulted in the formation of a mixture of **12** and **13** instead of the expected tetrathiolane $TbtCHS_4$.

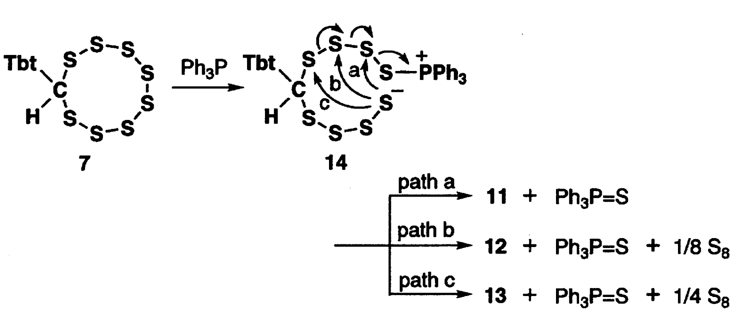
Experimental

All melting points were uncorrected. All solvents used in reactions were purified by the reported methods. THF was purified by distillation from sodium diphenylketyl before use. All reactions were carried out under an argon atmosphere. Preparative gel permeation liquid chromatography (GPLC) was performed on an LC-908 or an LC-908-C60 instrument with JAI gel 1H+2H columns and JAI gel 1H-40+2H-40 columns (Japan Analytical Industry) and chloroform as solvent. Dry column chromatography (DCC), preparative thin-layer chromatography (PTLC), and wet column chromatography (WCC) were performed with ICN silica DCC 60A, Merck Kieselgel 60 PF_{254} (Art. No. 7747), and Wakogel C-200, respectively. The ^{1}H NMR (500 MHz) and ^{13}C NMR spectra (125 or 68 MHz) were measured in $CDCl_3$ with a Bruker AM-500 or a JEOL EX-270 spectrometer using $CHCl_3$ as internal standard. Infrared spectra were recorded on a Horiba FT-200 spectrophotometer. Elemental analyses were performed by the Microanalytical Laboratory of the Department of Chemistry, Faculty of Science, The University of Tokyo.

Preparation of 2,4,6-Tris[bis(trimethylsilyl)methyl]benzaldehyde (2). To a THF solution (160 ml) of 1-bromo-2,4,6-tris[bis(trimethylsilyl)methyl]benzene (12.6 g, 20.0 mmol) was added at −78 °C *t*-BuLi (1.33 M solu-



Scheme 5.



Scheme 6.

tion in pentane, 1 M=1 mol dm^{-3}, 36 ml, 50.0 mmol), and the solution was stirred for 30 min. After ethyl formate (2.4 ml, 30 mmol) was added to the resulting solution of TbtLi, the reaction mixture was warmed to room temperature and quenched with aq NH_4Cl. To the reaction mixture was added 100 ml of hexane, and the organic layer was washed with aq NH_4Cl (100 ml×3). The water layer and washings were extracted with $CHCl_3$ (100 ml) and the extract was combined with the organic layer. After filtration of precipitated TbtH, the solution was dried with $MgSO_4$ and the solvent was evaporated. The residue was dissolved in hot $CHCl_3$ and the solution was cooled to room temperature. After filtration of precipitated TbtH, the filtrate, after evaporation of $CHCl_3$, was subjected to WCC (hexane and then hexane : CH_2Cl_2=1 : 1) to give **2**, which was recrystallized from EtOH–$CHCl_3$ to give pure **2** (5.59 g, 9.62 mmol, 48%). **2**: White crystals; mp 260.0—265.0 °C (decomp); ^{1}H NMR (500 MHz, $CDCl_3$) δ=0.01 (s, 18H), 0.02 (s, 18H), 0.05 (s, 18H), 1.41 (s, 1H), 2.70 (s, 1H), 2.85 (s, 1H), 6.32 (s, 1H), 6.44 (s, 1H), 10.38 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ=0.4 (q), 0.66 (q), 0.70 (q), 23.1 (d×2), 31.7 (d), 122.9 (d), 127.7 (d), 128.6 (s), 147.9 (s), 148.1 (s), 148.7 (s), 194.7 (d); IR (KBr) 1678 cm^{-1} ($\nu_{C=O}$). Found: C, 57.89; H, 10.52%. Calcd for $C_{28}H_{60}Si_6$: C, 57.85; H, 10.40%.

Preparation of 2,4,6-Tris[bis(trimethylsilyl)methyl]benzaldehyde Tosylhydrazone (3). To an EtOH solution (80 ml) of **2** (8.96 g, 15.4 mmol) and $TsNHNH_2$ (3.02 g, 16.2 mmol) was added $BF_3\cdot Et_2O$ (0.95 ml, 7.7 mmol), and the solution was heated to reflux for 4 h. Aq $NaHCO_3$ (50 ml) was added to the reaction mixture, which was extracted with $CHCl_3$ (100 ml). The extract was washed with aq $NaHCO_3$ (50 ml×3), dried with $MgSO_4$, and the solvent was evaporated. The residue was recrystallized from EtOH to give **3** (10.9 g, 14.5 mmol, 94%). **3**: White crystals; mp 190.5—195.0 °C (decomp); ^{1}H NMR (500 MHz, $CDCl_3$) δ=−0.09 (s, 36H), 0.02 (s, 18H), 1.32 (s, 1H), 1.93 (s, 1H), 1.97 (s, 1H), 2.36 (s, 3H), 6.25 (s, 1H), 6.37 (s, 1H), 7.24 (d, 2H, $^3J_{HH}$=8 Hz), 7.82 (d, 2H, $^3J_{HH}$=8 Hz), 7.84 (s, 1H), 8.31 (brs, 1H, NH); ^{13}C NMR (125 MHz, $CDCl_3$) δ=0.2 (q), 0.4 (q), 0.6 (q), 21.5 (q), 24.6 (d×2), 30.5 (d), 121.7 (d), 125.3 (s), 126.5 (d), 128.1 (d), 129.6 (d), 135.4 (s), 143.6 (s), 143.7 (s), 143.9 (s), 144.0 (s), 150.4 (d). Found: C, 55.89; H, 8.98; N, 3.98; S, 4.44%. Calcd for $C_{35}H_{68}N_2O_2SSi_6$: C, 56.09; H, 9.14; N, 3.74; S, 4.28%.

Preparation of 2,4,6-Tris[bis(trimethylsilyl)methyl]phenyldiazomethane (1). To a THF solution (180 ml) of **3** (4.80 g, 6.41 mmol) was added at −78 °C *n*-BuLi (1.65 M hexane solution, 3.9 ml, 6.4 mmol) and the solution was stirred for 2.5 h. The reaction mixture was gradually warmed to 45 °C (bath temperature) and stirred for 10 h at the same temperature. After evaporation of the solvent, hexane (10 ml) was added to the reaction mixture and evaporated to remove the remaining THF. The residual orange solid was again dissolved in hexane (10 ml). Insoluble material (TsLi) was filtered off and the solvent was evaporated from the filtrare to give an orange solid (3.90 g). This contained about 80% of **1** as judged from ^{1}H NMR, the impurity being mostly benzocyclobutene **4**. This mixture was used for the next reactions without further purification immediately after the preparation. **1**: Orange solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ=−0.00 (s, 36H), 0.03 (s, 18H), 1.32 (s, 1H), 1.93 (s, 1H), 2.01 (s, 1H), 4.26 (s, 1H), 6.33 (s, 1H), 6.46 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ=0.5 (q), 0.7 (q), 26.2 (d×2), 30.2 (d), 39.5 (d, CN$_2$), 119.3 (s), 121.7 (d), 126.5 (d), 142.9 (s), 144.8 (s×2); IR (KBr) 2056 cm^{-1} ($\nu_{C=N=N}$). **4**: White crystals; mp 213.5—214.5 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ=−0.04 (s, 18H), 0.01 (s, 18H), 0.02 (s, 18H), 1.29 (s, 1H), 1.33 (s, 1H), 2.77 (s, 2H), 6.23 (s×2, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ=−1.6 (q), 0.4 (q), 0.6 (q), 23.0 (d), 30.5 (d), 31.3 (s), 31.9 (t), 115.5 (d), 125.0 (d), 135.1 (s), 137.0 (s), 141.8 (s), 150.4 (s). Found: C, 59.19; H, 10.43%. Calcd for $C_{28}H_{60}Si_6$: C, 59.49; H, 10.70%.

Thermal Reaction of Diazomethane 1. A benzene solution (10 ml) of **1** (prepared from 117 mg, 0.157 mmol of **3**) was added dropwise over 75 min into refluxing benzene (5 ml), and the mixture was refluxed for additional 3 h. After removal of the solvent, the residue was separated with GPLC followed by PTLC (hexane) to afford 3,5-bis[bis(trimethylsilyl)methyl]-1,1-bis(trimethylsilyl)benzocyclobutene (**4**) (65 mg, 0.114 mmol, 73% from **3**) and 2,4,6-tris[bis(trimethylsilyl)methyl]benzaldehyde azine (**5**) (0.7 mg, 0.0006 mmol, 0.8% from **3**). **5**: White crystals; mp >300 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ=0.02 (s, 72H), 0.06 (s, 36H), 1.37 (s, 2H), 2.42 (s, 2H), 2.67 (s, 2H), 6.34 (s, 2H), 6.47 (s, 2H), 8.77 (s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ=0.5 (q), 0.7 (q), 24.5 (d×2), 30.6 (d), 122.2 (d), 126.5 (s), 126.9 (d), 144.0 (s), 144.2 (s), 144.3 (s), 163.2 (d). Found: C, 57.84; H, 10.30; N, 2.51%. Calcd for $C_{56}H_{120}N_2Si_{12}$: C, 58.05; H, 10.44; N, 2.42%.

Reaction of Diazomethane 1 with Cyclooctasulfur. To a refluxing benzene suspension (90 ml) of cyclooctasulfur (16.8 g, 65.5 mmol), purified by recrystallization three times from benzene in the dark,[11)] was added dropwise a solution of **1** (prepared from 4.80 g, 6.41 mmol of **3**) in benzene (250 ml) over 4.5 h in the dark. The pale yellow mixture was refluxed for additional 0.5 h and cooled to room temperature. After filtration of precipitated sulfur, the benzene was evaporated from the filtrate, and the residue was dissolved in hot $CHCl_3$. After the solution was cooled to room temperature, precipitated sulfur was filtered off. The filtrate was separated with GPLC to afford two fractions, one containing one Tbt group and another containing two Tbt groups. The former fraction was dissolved in hot $CHCl_3$–EtOH, and the solution was cooled to room temperature. After the filtration of 2,4,6-tris[bis(trimethylsilyl)methyl]phenyloctathionane (**7**) (1.54 g, 1.88 mmol, 29%) precipitated as yellow crystals, the filtrate, after evaporation of the solvent, was separated with WCC (hexane) to afford benzocyclobutene **4** (1.16 g, 2.06 mmol, 32%) and an inseparable yellow solid (671 mg) which was presumably a mixture of cyclic polysulfides, TbtCHS$_n$ (n=5—8) judging from ^{1}H NMR, the spectral data of the cyclic polysulfides TbtCHS$_n$ (n=5—7) being shown below. The latter fraction containing two Tbt groups was separated with DCC (hexane) to afford 2,3-bis{2,4,6-tris[bis(trimethylsilyl)methyl]phenyl}thiirane (**8**) (417 mg, 0.358 mmol, 11%) and azine **5** (41 mg, 0.036 mmol, 1%). **7**: Yellow crystals; mp 200.5—201.5 °C (decomp); ^{1}H NMR (500 MHz, $CDCl_3$, 82 °C) δ=0.08 (s, 18H), 0.12 (s, 18H), 0.14 (s, 18H), 1.38 (s, 1H), 2.04 (s, 1H), 2.16 (s, 1H), 6.34 (brs, 1H, –S–CH(Tbt)–S–), 6.41 (s, 1H), 6.45 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$, 80 °C) δ=0.9 (q), 1.7 (q), 1.8 (q), 26.0 (d), 27.8 (d), 31.1 (d), 67.7 (d), 123.6 (d), 125.6 (s), 127.8 (d), 144.5 (s), 144.7 (s), 146.6 (s). Found: C, 41.10; H, 7.11; S, 31.36%. Calcd for $C_{28}H_{60}S_8Si_6$: C, 40.92; H, 7.36; S, 31.21%. **8**: White crystals; mp 224.5—226.0 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ=0.03 (s, 18H), 0.06 (s, 36H), 0.09 (s, 18H), 0.10 (s, 36H), 1.28 (s, 2H), 2.02 (s, 2H), 2.30 (s, 2H), 4.39 (s, 2H), 6.31 (s, 2H), 6.43 (s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$, 57 °C) δ=0.5 (q), 1.0 (q), 1.5 (q), 2.0 (q), 25.9 (d×2), 29.9 (d), 48.3 (d), 123.0 (d), 128.1 (d), 130.3 (s), 140.3 (s), 140.5 (s), 146.4 (s). Found: C, 57.65; H, 10.19; S, 3.01%. Calcd for $C_{56}H_{120}SSi_{12}$: C, 57.85; H, 10.40; S, 2.76%.

Desulfurization of Octathionane 7. To a THF solution (15 ml) of **7** (61.5 mg, 0.0748 mmol) was added at −78 °C Ph_3P (19.7 mg, 0.0751 mmol). The reaction mixture was stirred for 10 min at −78 °C, and warmed to room temperature. After removal of the solvent, the residue was separated with GPLC to afford a mixture of 2,4,6-tris[bis(trimethylsilyl)methyl]phenylheptathiocane (**11**) and 2,4,6-tris[bis(trimethylsilyl)methyl]phenylhexathiepane (**12**), and 2,4,6-tris[bis(trimethylsilyl)methyl]phenylpentathiane (**13**) (53.5 mg, **11**:**12**:**13**=4:10:5 by ^{1}H NMR) and Ph_3P=S (20.3 mg, 0.0690 mmol, 92%). The number of sulfur contained in the cyclic polysulfides was determined by ^{1}H NMR measurement of the relative ratios of the polysulfides yielded in the desulfurizations of **7** with 1, 3, and 4 equivalents of Ph_3P, although **11** and **12** could not be isolated. Reaction of this mixture of **11**, **12**, and **13** (53.5 mg) with Ph_3P (19.6 mg, 0.0747 mmol) in THF (15 ml) under similar conditions gave a mixture of **12** and **13** (45.6 mg, **12**:**13**=1:2 by ^{1}H NMR) together with Ph_3P=S (20.2 mg, 0.0686 mmol, 92%). Further Desulfurization of this mixture of **12** and **13** (45.6 mg) by Ph_3P (19.5 mg, 0.0743 mmol) in THF (15 ml) under the same conditions gave **13** (34.7 mg, 0.0478 mmol, 64% from **7**) and Ph_3P=S (19.8 mg, 91%).

11: ^{1}H NMR (500 MHz, $CDCl_3$) δ=0.03 (s, 18H), 0.12 (s, 36H), 1.32 (s, 1H), 1.65 (s, 1H), 1.82 (s, 1H), 5.87 (s, 1H, -S-C*H*(Tbt)-S-), 6.26 (s, 1H), 6.42 (s, 1H).

12: ^{1}H NMR (500 MHz, $CDCl_3$) δ=0.03 (s, 18H), 0.07 (s, 18H), 0.08 (s, 18H), 1.32 (s, 1H), 1.69 (s, 1H), 1.74 (s, 1H), 6.31 (s, 1H), 6.38 (s, 1H), 6.51 (s, 1H, -S-C*H*(Tbt)-S-).

13: Yellow crystals, mp 227.0—230.0 °C (decomp); ^{1}H NMR (500 MHz, $CDCl_3$, 67 °C) δ=0.05 (s, 18H), 0.12 (s, 18H), 0.15 (s, 18H), 1.33 (s, 1H), 1.99 (s, 1H), 2.60 (s, 1H), 6.32 (s, 1H), 6.40 (s, 1H), 6.73 (s, 1H, -S-C*H*(Tbt)-S-); ^{13}C NMR (68 MHz, $CDCl_3$, 60 °C) δ=0.8 (q), 1.8 (q), 26.6 (d), 27.6 (d), 30.7 (d), 59.4 (d), 123.3 (d), 127.0 (d), 131.4 (s), 143.4 (s), 144.4 (s), 144.8 (s). Found: C, 46.15; H, 8.33; S, 21.90%. Calcd for $C_{28}H_{60}S_5Si_6$: C, 46.35; H, 8.33; S, 22.10%.

Desulfurization of Octathionane 7 by 3 Equivalents of Ph_3P. To a THF solution (5 ml) of **7** (15.1 mg, 0.0184 mmol) was added at −78 °C the phosphine (14.8 mg, 0.0564 mmol), and the reaction mixture was gradually warmed to room temperature. After removal of the solvent, the residue was separated with GPLC to afford a mixture of **12** and **13** (12.7 mg, 0.017 mmol, 93%, **12**:**13**=5:6 by ^{1}H NMR) and Ph_3P=S (15.9 mg, 0.054 mmol, 96%).

Desulfurization of Octathionane 7 by 4 Equivalents of Ph_3P. To a THF solution (15 ml) of **7** (42.4 mg, 0.0516 mmol) was added at −78 °C Ph_3P (54.5 mg, 0.208 mmol), and the reaction mixture was gradually warmed to room temperature. After removal of the solvent, the residue was separated with GPLC to afford a mixture of **12** and **13** (28.0 mg, 0.038 mmol, 73%, **12**:**13**=3:4 by ^{1}H NMR) and Ph_3P=S (61.3 mg, 0.208 mmol, 100%).

Desulfurization of Pentathiane 13. To a THF solution (30 ml) of **13** (91.6 mg, 0.126 mmol) was added at −78 °C Ph_3P (33.1 mg, 0.126 mmol), and the reaction mixture was gradually warmed to room temperature. After removal of the solvent, the residue was separated with GPLC to afford **13** (160.0 mg, 0.0835 mmol, 66%), a mixture of cyclic polysulfides containing two Tbt units (18.6 mg), and Ph_3P=S (35.7 mg, 0.121 mmol, 96%).

Conformation Analysis of 7 by Molecular Mechanics Calculations. A conformational analysis of cyclononasulfur (S_9) by MMP2 calculation gave the two stable conformations of C_1 and C_2 symmetry with energy minimum. Conformational optimization was performed for all of the structures (14 patterns) where one sulfur atom of S_9 in the two conformations was replaced by a CH_2 unit. Conformational analysis for sterically possible structures (15 patterns) where one hydrogen atom in these 14 conformations of octathionane CH_2S_8 was displaced by a Tbt unit, whose *p*-bis(trimethylsilyl)methyl group was excluded for simplification, afforded a structure with no symmetry factor as the lowest ground state geometry (Fig. 2).

Crystal and Experimental Data for 4 and 7. (a) 4: Single crystals were grown by the slow evaporation of its saturated solution in $CHCl_3$. The intensity data ($2\theta \leq 55°$) were collected on a Rigaku AFC5R diffractometer with graphite monochromated Mo $K\alpha$ radiation (λ=0.71069 Å), and the structure was solved by direct methods. All calculations were performed using TEXSAN crystallographic software package of Molecular Structure Corporation. The non-hydrogen atoms were refined anisotropically and all hydrogen atoms were located by calculation. The final cycle of full-matrix least-squares refinement was based on 1948 observed reflections ($I>3\sigma$) and 307 variable parameters.

(b) 7: Single crystals were grown by the slow evaporation of its saturated solution in $CHCl_3$. The data were collected on a Enraf–Nonius CAD4 diffractometer with graphite monochromated Cu $K\alpha$ radiation (λ=1.5418 Å). Unique reflections ($|F_o| \geq 3\sigma|F_o|$, 6561) were observed ($4° < 2\theta \leq 120°$). The total loss in intensity was 5.8%. A linear decay correction and empirical absorption correction were applied. The structure was solved by direct method (MULTAN 78). The 8 hydrogen atoms were introduced from D-Fourier maps in the course of refinement and the other hydrogen atoms were located by calculation. Refinement on F was performed by full-matrix least-squares method with anisotropic temperature factors for non hydrogen atoms and isotopic temperature factors for hydrogen atoms. Positional and thermal parameters of hydrogen atoms were fixed. The larger temperature factor for S atoms, S2, S3, S4, S5, and S6, should be due to disorder. Data reduction was calculated using molen package and other calculations were performed using UNICS III.

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