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Three syntheses of *trans*-cyclooctane-1,2-dithiol by ring opening of *cis*-cyclooctene episulfoxide with ammonium thiocyanate followed by reduction and reductions of *trans*-1,2-di(thiocyanato)cyclooctane and *trans*-1,2-cyclooctyl trithiocarbonate

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Three syntheses of *trans*-cyclooctane-1,2-dithiol by ring opening of *cis*-cyclooctene episulfoxide with ammonium thiocyanate followed by reduction and reductions of *trans*-1,2-di(thiocyanato)cyclooctane and *trans*-1,2-cyclooctyl trithiocarbonate

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This paper is dedicated to Professor Juzo Nakayama on the occasion of his 65th birthday and retirement.

trans-Cyclooctane-1,2-dithiol was synthesized by three methods: (i) ring opening of *trans*-cyclooctene episulfoxide with NH_4SCN in THF followed by a stepwise reduction with diisobutylaluminum hydride (DIBAH) in hexane and then $LiAlH_4$ in ether; (ii) a stepwise reduction of *trans*-1,2-di(thiocyanato)cyclooctane **11** with DIBAH and then $LiAlH_4$; and (iii) the reduction of *trans*-1,2-cyclooctyl trithiocarbonate with $LiAlH_4$ in refluxing ether. The course of reactions of method (i) was investigated in detail.

Keywords: episulfoxide; ring opening; thiocyanation; reduction; 1,2-dithiol; trithiocarbonate

1. Introduction

Recently, tetradentate [O−S−S−O]-type diphenolate ligands **1** (*1*) and **2** (*2*), involving a 1,2-alkanediylbis(thio) core, have attracted considerable attention because their Group 4 metal (Ti, Zr, Hf) complexes, a single-site post-metallocene catalyst (*3*), have effective catalytic activities for alkene polymerization. The optically active complexes of **1** catalyzed the copolymerization of stylene and 1-hexene to give the corresponding optically active copolymer (*1a, b*). Several ligands belonging to **3** and **4** have been reported so far, and their transition metal complexes were studied in detail in the viewpoint of structural chemistry (*4–8*). Sellmann and coworkers synthesized Ni (*4a*), Fe (*4b*), Ru (*4c, d*), and Rh (*4e*) complexes using [S−S−S−S]-type ligands (**3**, X=S) as the

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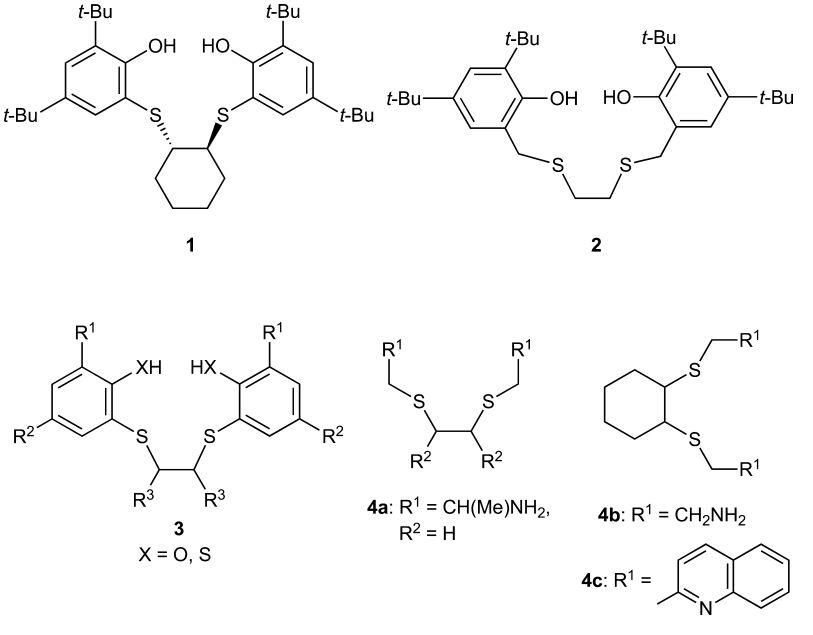
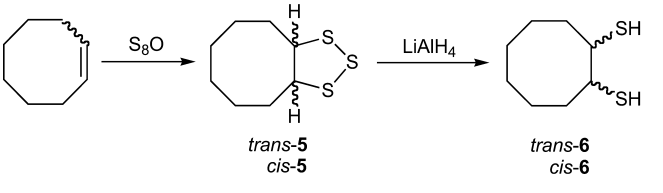
nitrogenase models. Studies on Co(III) complexes with ligands **4a** (*5*) and **4b** (*6*) and Cu(I) and Cu(II) complexes with ligand **4c** (*7*), which are [N−S−S−N]-type ligands, have been reported. Synthetically, compounds **3** are derived from 2-mercaptophenols or arene-1,2-dithiols (*1*, *4*), and compounds **4** are prepared from alkane-1,2-dithols (*2*, *5–7*).



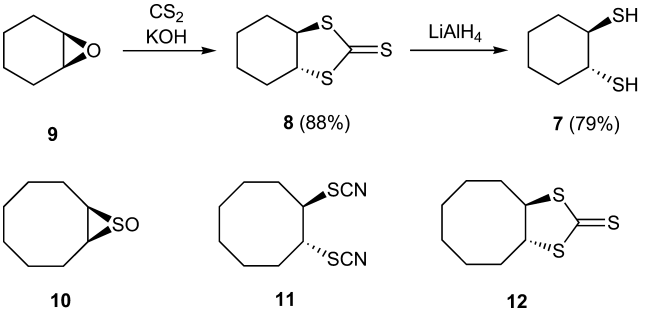
We have reported the reaction of *cis*- and *trans*-cyclooctenes with S_8O to give the corresponding 1,2,3-trithiolanes **5** stereospecifically (*9*, *10*). Reduction of **5** with $LiAlH_4$ (*11*) provided *cis*- and *trans*-cyclooctane-1,2-dithiols **6**, respectively, in high yields (Equation (1)) (*10*). A drawback of this synthetic route for *trans*-**6** was the low overall yield from commercially available *cis*-cyclooctene.



(1)

trans-Cycloalkane-1,2-dithiols are chiral, owing to the *C*2 symmetry, and are promising as chiral sources (*1*). They can be synthesized by the reduction of *trans*-connected trithiocarbonates (*12*), the ring opening of *cis*-connected episulfides with sulfur nucleophiles (*13*), or the reduction of *trans*-1,2-di(thiocyanato) compounds (*14*). *trans*-Cyclohexane-1,2-dithiol (**7**) was prepared by the reduction of trithiocarbonate **8** prepared from epoxide **9** about half a century ago (Equation (2)) (*12a*). On the other hand, while ring-opening reactions of episulfides (*13*) and episulfones (*15*) with sulfur nucleophiles and those of episulfoxides with oxygen nucleophiles (*16*) have been reported, there is little precedent on the reactions of episulfoxides with sulfur nucleophiles as far as we know (*16a*). In this article, we report the ring-opening reactions of *cis*-cyclooctene episulfoxide **10** with sulfur nucleophiles, followed by reduction to lead to *trans*-cyclooctane-1,2-dithiol (*trans*-**6**). In addition, we report the reduction reactions of *trans*-di(thiocyanato) compound **11**

and trithiocarbonate **12** for the synthesis of *trans*-**6**.

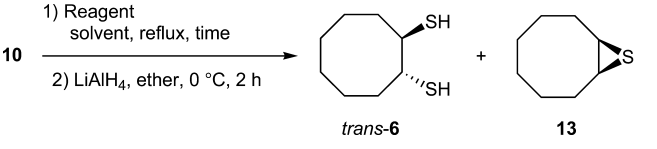


(2)

2. Results and discussion

2.1. *Reaction of cis-cyclooctene episulfoxide (10) with sulfur nucleophiles*

As shown in Equation (3) and Table 1, the reactions of **10** with $NaSH{\cdot}nH_2O$ (Entry 1), $H_2NC(S)NH_2$ (Entry 2), AcSK (Entry 3), $NaBH_2S_3$ in EtOH (Entry 5), or NH_4SCN (Entries 6, 8–10) followed by reduction of the reaction mixture with $LiAlH_4$ gave the desired 1,2-dithiol *trans*-**6** in 2–20% yields. NH_4SCN was better than other reagents, but episulfide **13** was also formed (Entries 6, 8–10). Incidentally, the reaction of *cis*-cyclooctene episulfide (**13**) with $NaSH{\cdot}nH_2O$ in DMF at 65 °C, $Na_2S{\cdot}9H_2O$ in refluxing ethanol, or AcSK in refluxing ethanol, gave a complex mixture. The reaction of **13** with the Lalancette reagent ($NaBH_2S_3$) followed by treatment with $LiAlH_4$ (*13a*), $NaSH{\cdot}nH_2O{-}H_2S$ in methanol at room temperature (*13b*), or NH_4SCN in THF under reflux, resulted in no reaction.



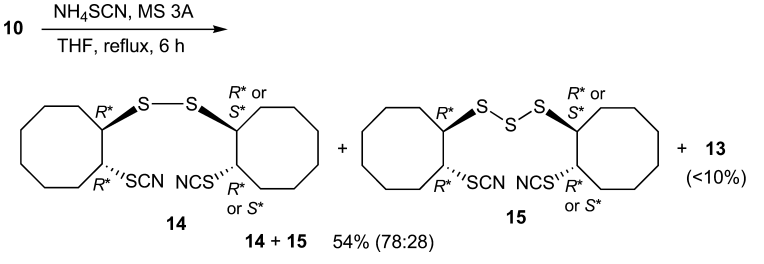
(3)

To clarify the course of the reaction and to improve the yield of *trans*-**6**, we carried out the structure elucidation of intermediates in Entry 6 (NH_4SCN in THF) and optimization of the reaction conditions. Thus, the reaction of **10** with NH_4SCN was performed in refluxing THF in the presence

Table 1. Yields of 1,2-dithiol *trans*-**6** by the reactions of episulfoxide **10** with sulfur nucleophiles followed by reduction with $LiAlH_4$.

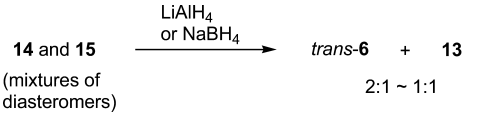
Entry	Reagent	Solvent	Time/h	Products (yield/%)
1	$NaSH{\cdot}nH_2O$	THF	3	*trans*-**6** (13)
2	$H_2NC(S)NH_2$	THF	3	*trans*-**6** (2)
3	AcSK	Et_2O	14	*trans*-**6** (4)
4	KSCN	THF	3	No reaction
5	$NaBH_2S_3$	EtOH	3	*trans*-**6** (10)
6	NH_4SCN	THF	3	*trans*-**6** (20), **13** (5)
7	NH_4SCN	Et_2O	14	No reaction
8	NH_4SCN	DME	1.5	*trans*-**6** (17), **13** (13)
9	NH_4SCN	CH_3CN	1.5	*trans*-**6** (6), **13** (3)
10	NH_4SCN	DMF	3	*trans*-**6** (2), **13** (4)

of molecular sieves (MS-3A) to give a 72:28 mixture of *trans*-(2-thiocyanato)cyclooctyl disulfide **14** and trisulfide **15** in 54% combined yield (Equation (4)). Episulfide **13** was formed in less than 10% in this stage. The mixture of **14** and **15** could be separated by gel permeation liquid chromatography (GPC), and their structures were elucidated by ^{1}H and ^{13}C NMR, IR, MS, and elemental analysis. In the nuclear magnetic resonance (NMR) data of **14** and **15**, two sets of signals were observed to indicate that they consist of respective diastereomers; (*R**,*R**,*R**,*R**)-**14** (**15**) and (*R**,*R**,*S**,*S**)-**14** (**15**). The diastereomers could not be separated.



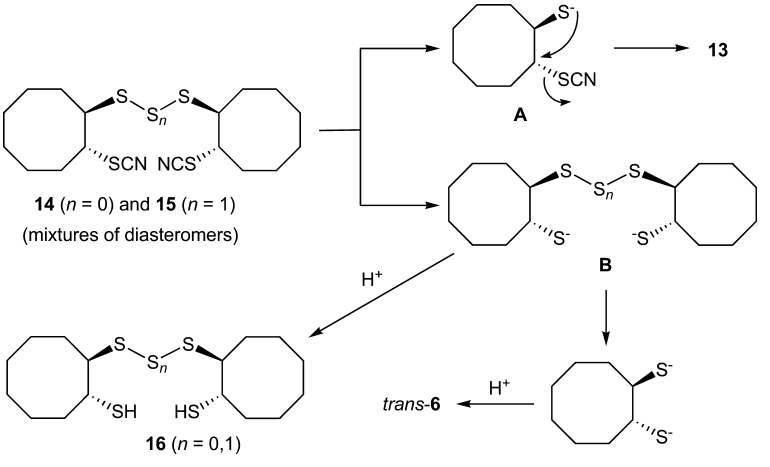
(4)

Reduction of a mixture of **14** and **15** was investigated to optimize the reaction conditions. The reduction with $LiAlH_4$ in THF or $NaBH_4$ in ethanol gave a 2:1 to 1:1 mixture of *trans*-**6** and episulfide **13** (Equation (5)). $LiBH_4$ in ether and $LiEt_3BH$ in THF resulted in the formation of a complex mixture.



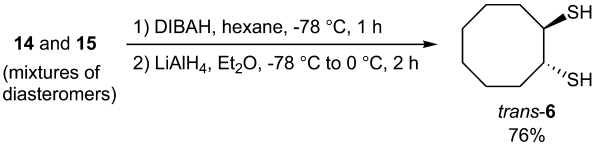
(5)

The formation pathways for *trans*-**6** and **13** were speculated as shown in Scheme 1. Treatment with a hydride reagent reduces both of the S−S and S−CN bonds to give the intermediates **A** and **B**, respectively; the former gives episulfide **13** by an intramolecular S_N2 reaction and the latter is led to dithiol *trans*-**6** by the following S−S bond reduction and quenching with acid. Thus, control of the formation of **A** was the key to improve the yield of *trans*-**6**, which was accomplished by the treatment of diisobutylaluminum hydride (DIBAH) in hexane. Thus, when the mixture was first treated with DIBAH in hexane at −78 °C and next with $LiAlH_4$ in ether, the formation of



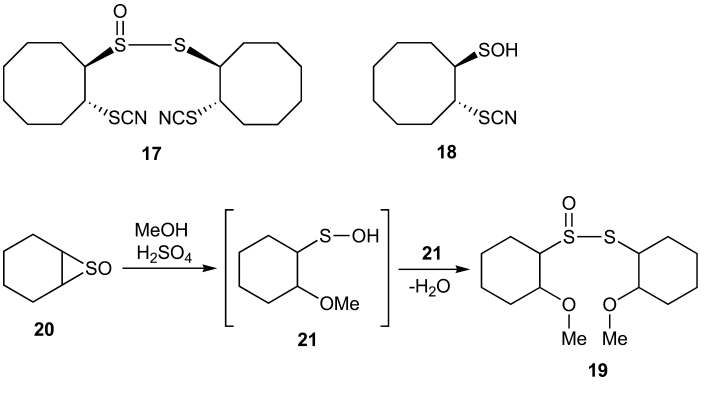
Scheme 1. Reaction pathways of the reduction of di- and trisulfides **14** and **15**.

episulfide **13** was suppressed completely to provide *trans*-**6** in 76% yield (Equation (6)). The formation of intermediate **B** was evidenced by the isolation of **16** ($n = 0$) when the reaction on **14** ($n = 0$) was quenched without treatment with $LiAlH_4$. **16** ($n = 0$) was obtained as a mixture of two diastereomers: ^{1}H NMR δ 1.40–2.40 (m, 26H + 26H), 3.01–3.06 (m, 2H), 3.09–3.14 (m, 2H), 3.15–3.22 (m, 2H), 3.22–3.38 (m, 2H) (the SH protons were observed at δ 2.31–2.34). Reduction of **16** ($n = 0$) with $LiAlH_4$ yielded *trans*-**6** quantitatively.



(6)

In the reaction of episulfoxide **10** with NH_4SCN, one might expect the formation of thiosulfinate **17** through **18** in analogy of the formation of **19** in the reaction of episulfoxide **20** with MeOH under acidic conditions giving sulfenic acid **21** as the intermediate (Equation (7)) (*16b*). A similar ring-opening reaction was also reported by Kondo (*16a*). However, we did not observe **17** or **18** in the reaction mixture. Oxidation of isolated disulfide **14** with *m*-chloroperoxybenzoic acid (*m*-CPBA) or dimethyldioxirane gave a complicated mixture. An attempt to trap sulfenic acid **18** with methyl propiolate resulted in failure because NH_4SCN reacted with the trapping reagent preferentially. We also examined the reaction of disulfide **14** with NH_4SCN to give no trisulfide **15**. Although it is considered that **14** and **15** would be derived from initially generated **18** or its ammonium salt, we have no experimental evidence at present. The oxygen atom in episulfoxide **10** would be removed as water, which might take a part to decrease the yields of **14** and **15** since the combined yield of **14** and **15** was improved by addition of MS-3A. The overall yield of 1,2-dithiol *trans*-**6** from *cis*-cyclooctene was 30%.

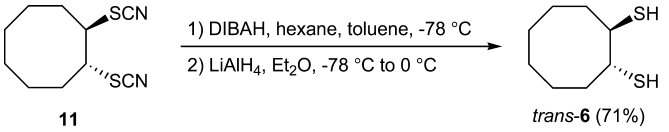


(7)

2.2. *Reduction of trans-1,2-di(thiocyanato)cyclooctane (11)*

When *trans*-1,2-di(thiocyanato)cyclooctane **11** (*17*) was treated with $LiAlH_4$ or $NaBH_4$, we encountered again the formation of episulfide **13** in addition to *trans*-**6**. Therefore we examined the reduction of **11** with a combination of DIBAH and $LiAlH_4$ as the case of **14** and **15**. Thus, **11** was first treated with DIBAH and then $LiAlH_4$ at $-78\,^{\circ}C$ to give *trans*-**6** in 71% yield without **13** (Equation (8)). When the reduction was interrupted at the stage of DIBAH, we obtained

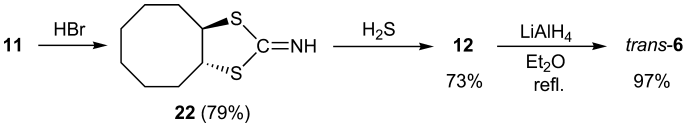
a complex mixture of unidentifiable materials.



11 *trans*-**6** (71%) (8)

2.3. *Reduction of trans-cyclooctyl trithiocarbonate (12)*

trans-1,2-Cyclooctyl trithiocarbonate (**12**) was prepared by the reaction of imine **22**, prepared from **11** (79%), with hydrogen sulfide (73%) (*17*). Trithiocarbonate **12** was not obtained by the reaction of *cis*-cyclooctene oxide with CS_2 under basic conditions, unlike the reaction shown in Equation (2) (*12b*). Reduction of **12** with $LiAlH_4$ in refluxing ether gave *trans*-**6** almost quantitatively (Equation (9)).



(9)

3. Conclusion

trans-Cyclooctane-1,2-dithiol (*trans*-**6**) was synthesized by three methods: (i) ring opening of episulfoxide **10** with NH_4SCN in THF in the presence of molecular sieves followed by a stepwise reduction with DIBAH in hexane and then $LiAlH_4$ in ether; (ii) a stepwise reduction of *trans*-1,2-di(thiocyanato)cyclooctane **11** with DIBAH and then $LiAlH_4$; and (iii) the reduction of trithiocarbonate **12** with $LiAlH_4$ in refluxing ether. In the study of method (i), we found that the stepwise treatment with DIBAH and $LiAlH_4$ to the intermediates **14** and **15** is quite effective to prevent the intramolecular S_N2 reaction leading to the formation of episulfide **13**. This procedure was successfully applied to the reduction of **11** (method (ii)). The overall yields from *cis*-cyclooctene are (i) 30%, (ii) 47%, and (iii) 37%. Thus, method (ii) is the best of the three, in which *trans*-**6** was synthesized from commercially available *cis*-cyclooctene in two pots.

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 analyses were performed by the Molecular Analysis and Life Science Center of Saitama University. Column chromatography was performed with silica gel (70–230 mesh) and the eluent is shown in parentheses. Preparative GPC was performed on an LC-918 (Japan Analytical Industry Co., Ltd.) equipped with JAIGEL 1H and 2H columns (eluent: $CHCl_3$).

4.2. *Materials*

cis-Cyclooctene oxide was prepared by oxidation with *m*-CPBA (*18*) in 94% and *cis*-cyclooctene episulfide was obtained by the reaction of *cis*-cyclooctene oxide with potassium thiocyanate (*19*) in 95% yield. *trans*-1,2-Di(thiocyanato)cyclooctane **11** was prepared by the reaction of *cis*-cyclooctene with $(SCN)_2$ (*17*), prepared by treatment of $Pb(SCN)_2$ with bromine in acetic acid (*20*), in 66% yield. *trans*-Cyclooctyl trithiocarbonate (**12**) was synthesized by the reaction of imine **22**, prepared by treatment of **11** with HBr in 79% yield, with H_2S (*17*) in 73% yield.

4.3. *cis-Cyclooctene episulfoxide (10)*

m-CPBA (95%, 64.1 mg, 0.35 mmol) was added to a solution of episulfide **13** (50.3 mg, 0.35 mmol) in dichloromethane (5 mL) at 0 °C. The mixture was stirred for 2 h and then aqueous Na_2SO_3 and aqueous $NaHCO_3$ were added. The mixture was extracted with dichloromethane, and the extract was washed with water, dried over anhydrous $MgSO_4$, and evaporated to dryness to give episulfoxide **10** (*21*) (51.2 mg, 93%): ^{1}H NMR δ 0.92–1.03 (m, 2H), 1.39–1.69 (m, 8H), 2.42–2.49 (m, 2H), 2.95–3.03 (m, 2H); ^{13}C NMR δ 23.0, 25.8, 27.7, 56.6; IR (neat) 1058 cm^{-1} (S=O).

4.4. *Reaction of cyclooctene episulfoxide (10) with NH_4SCN in THF*

A mixture of episulfoxide **10** (238 mg, 1.5 mmol), NH_4SCN (236 mg, 3.1 mmol), and 20 grains of molecular sieves (MS-3A) in THF (20 mL) was heated under reflux for 6 h under argon. Aqueous NH_4Cl was added and the mixture was extracted with dichloromethane. The extract was washed with water, dried over anhydrous $MgSO_4$, and evaporated to dryness. The residue was subjected to column chromatography (hexane-CH_2Cl_2 1:3) to give a 72:28 mixture of disulfide **14** and **15** (164.7 mg, 54%). The mixture of **14** and **15** could be separated with GPC.

4.5. *Di[trans-(2-thiocyanato)cyclooctyl] disulfide (mixture of two diastereomers) (14)*

Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.41–1.85 (m, 16H+16H), 2.06–2.40 (m, 8H+8H), 3.09–3.20 (m, 2H+2H), 3.55–3.63 (m, 2H+2H); ^{13}C NMR(100.6 MHz, $CDCl_3$) δ 25.23 (2C), 25.52, 25.58, 25.62, 25.66, 26.00, 26.26, 31.60, 31.66, 31.80, 31.90, 54.47, 54.89, 55.81, 56.10, 111.65, 111.69; IR (neat) 2149 cm^{-1}(CN); MS m/z 400 (M^+). Anal. Calcd for $C_{18}H_{28}N_2S_4$: C 53.95, H 7.04, N 6.99; found: C 53.89, H 6.98, N 6.93.

4.6. *Di[trans-(2-thiocyanato)cyclooctyl] trisulfide (mixture of two diastereomers) (15)*

Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.41–1.84 (m, 16H+16H), 2.10–2.30 (m, 4H+4H), 2.30–2.41 (m, 4H+4H), 3.27–3.28 (m, 2H+2H), 3.71–3.76 (m, 2H+2H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 25.22 (2C), 25.55 (2C), 25.72 (2C), 26.21 (2C), 31.36 (2C), 31.63, 31.64, 54.45, 54.49, 56.29, 56.37, 111.76 (2C); IR (neat) 2149 cm^{-1} (CN); MS m/z 432. Anal. Calcd for $C_{18}H_{28}N_2S_5$: C 49.96, H 6.52, N 6.47; found: C 50.21, H 6.55, N 6.39.

4.7. *Reduction of a mixture of 14 and 15 with DIBAH-$LiAlH_4$*

DIBAH (0.98 M hexane solution, 0.18 mL, 0.17 mmol) was added to a solution of a 3:1 mixture of **14** and **15** (34.4 mg, 0.086 mmol) in hexane (4 mL) at −78 °C under argon. The mixture was stirred for 1 h at −78 °C, and then a suspension of $LiAlH_4$ (21.3 mg, 0.56 mmol) in ether (4 mL)

was added dropwise at −78 °C. The mixture was warmed to 0 °C and stirred for 2 h. 1.2 M aq. HCl solution was added and the mixture was extracted with ether. The extract was washed with water, dried over anhydrous $MgSO_4$, and evaporated to dryness. The residue was subjected to column chromatography (pentane-CH_2Cl_2 4:1) to give *trans*-**6** (23 mg, 76%).

4.8. *Reduction of trans-1,2-di(thiocyanato)cyclooctane (11) with DIBAH-LiAlH$_4$*

A solution of *trans*-1,2-di(thiocyanato)cyclooctane (**11**) (313.6 mg, 1.4 mmol) in hexane (6 mL) and toluene (6 mL) was added to DIBAH (1.03 M hexane solution, 5.8 mL, 5.9 mmol) at −78 °C and the mixture was stirred for 2 h at this temperature. Then, a suspension of $LiAlH_4$ (222.6 mg, 5.9 mmol) in ether (12 mL) was added at −78 °C, and the mixture was warmed to 0 °C and stirred for 2 h. 1.2 M aq. HCl solution was added and the mixture was extracted with ether. The extract was washed with water, dried over anhydrous Na_2SO_4, and evaporated to dryness. The residue was purified by column chromatography (pentane-CH_2Cl_2 4:1) to give *trans*-**6** (173.3 mg, 71%).

4.9. *Reduction of trans-cyclooctyl trithiocarbonate (12) with LiAlH$_4$*

A mixture of *trans*-cyclooctyl trithiocarbonate **12** (39.3 mg, 0.18 mmol) and $LiAlH_4$ (28.1 mg, 0.83 mmol) in ether was refluxed for 2 days. 1.2 M aq. HCl solution was added and the mixture was extracted with ether. The extract was washed with water, dried over anhydrous Na_2SO_4, and evaporated to dryness. The residue was purified by column chromatography (pentane-CH_2Cl_2 4:1) to give *trans*-**6** (30.7 mg, 97%).

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