Synthesis and Physical Properties of Sterically Congested Cycloalkenes, 1,2-Di-*tert*-butyl-3,3,5,5-tetramethylcyclopentene and 1,2-Di-*tert*-butyl-3,3,6,6-tetramethylcyclohexene

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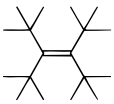
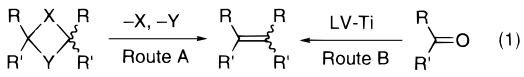
Two sterically congested cycloalkenes (**9** and **10**), congeners of tetra-*tert*-butylethylene, were synthesized and characterized. Oxidation of the bicyclic 1,3-dithietane **8** with dimethyldioxirane (DMD) gave the *endo*,*endo*-disulfoxide **13**, thermal isomerization of which to the *endo*,*exo*-disulfoxide **15** followed by oxidation with DMD gave the trioxide **18**. Heating **18** in refluxing 1,3-dimethyl-2-imidazolidinone furnished 1,2-di-*tert*-butyl-3,3,5,5-tetramethylcyclopentene (**9**) in 69% yield by a 2-fold extrusion process. The reaction of the 1,6-diketone dihydrazone **23** with Se_2Cl_2 gave the selenadiazoline **34** and the 1,3-diselenetane **35**. Heating **34** at 115−130 °C gave 1,2-di-*tert*-butyl-3,3,6,6-tetramethylcyclohexene (**10**), a "didehydro" derivative of tetra-*tert*-butylethylene, in 43% yield. The C═C bond in **10** is strained in degree comparable to those of most strained alkenes reported so far.

Introduction

The chemistry of sterically congested alkenes has been a most challenging subject in both synthetic chemistry[1−6] and theoretical chemistry[7] for the last several decades. An ultimate goal of this chemistry is the preparation of tetra-*tert*-butylethylene (**1**). Although the 2-fold extrusion process[1] (route A, eq 1) and the McMurry coupling[2] using low-valent Ti (route B, eq 1) have been satisfactorily applied to the synthesis of sterically congested alkenes, the compound **1** has never been synthesized despite extensive effort.[1−6]

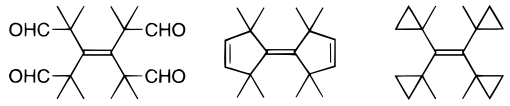


1



(1)

The preparation of tied-back cyclic alkenes as intermediates has been considered to be a potential strategy for the synthesis of **1**; the tying would facilitate the synthesis by moderating the steric hindrance between the adjacent *tert*-butyl groups, and untying might give **1**.[3−6] This approach led to the synthesis of tetrakis(2-formyl-2-propyl)ethylene (**2**) from bi-3,3,5,5-tetramethylcyclopentene-4-ylidene (**3**)[3h,4,5] and tetrakis(1-methylcyclopropyl)ethylene (**4**)[6] as the most successful examples, but the synthesis of sulfur-bridged tied-back alkenes **5**,[3h,i,4c] **6**,[3a] and **7**[3g] has not been accomplished yet.



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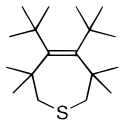

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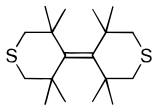

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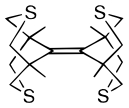

7

In the course of our study on sterically congested compounds,[8] we recently prepared a bicyclic 1,3-dithietane **8**.[9] This has now been converted to the cyclopentene derivative **9** by a series of reactions[10] involving a 2-fold extrusion reaction in the last step. We report here the synthesis and some physical properties of the cyclopen-

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(2) For reviews, see: McMurry, J. E. *Chem. Rev.* **1989**, *89*, 1513−1524. Lenoir, D. *Synthesis* **1989**, 883−897.

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(7) For a recent report: Sulzbach, H. M.; Bolton, E.; Lenoir, D.; Schleyer, P. v. R.; Schaefer, H. F., III. *J. Am. Chem. Soc.* **1996**, *118*, 9908−9914 and references therein.

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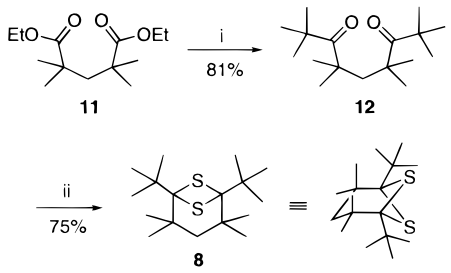
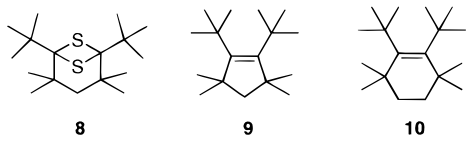
Scheme 1[a]



[a] i: i: *t*-BuLi (2 molar equiv), Et_2O, –50 °C; ii: Lawesson's reagent (2 molar equiv), $PhCH_3$, refl., 40 h.

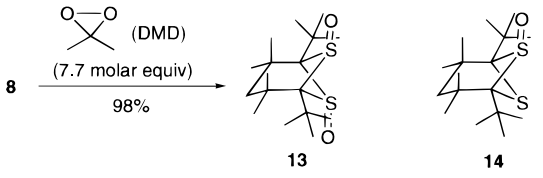
tene **9** and, in addition, the cyclohexene **10**, a tied-back derivative of **1**.



Results and Discussion

Synthesis of 1,2-Di-*tert*-butyl-3,3,5,5-tetramethylcyclopentene (9). The bicyclic 1,3-dithietane **8** was obtained by thionation of the 1,5-diketone **12**, prepared by reaction of the diester **11**[11,12] with *t*-BuLi (2 molar equiv), with Lawesson's reagent (LR)[13] (Scheme 1).[9]

Oxidation of **8** with dimethyldioxirane (DMD)[14] proceeded cleanly to produce the *endo*,*endo*-disulfoxide **13** quantitatively, whereas the oxidation with MCPBA (4.5 molar equiv) gave **13** in only 9% yield along with the *endo*-sulfoxide **14** (49%) and the 1,5-dicarbonyl compound **12** (29%). TLC indicated that the oxidation with DMD proceeded stepwise through the *endo*-sulfoxide **14**, and totally 7.7 molar equiv of DMD was necessary for the complete conversion to **13**. Further treatment with DMD provided neither the tri- nor tetraoxide of **8**.



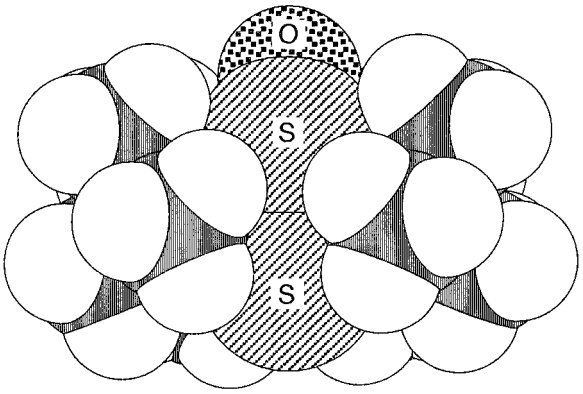
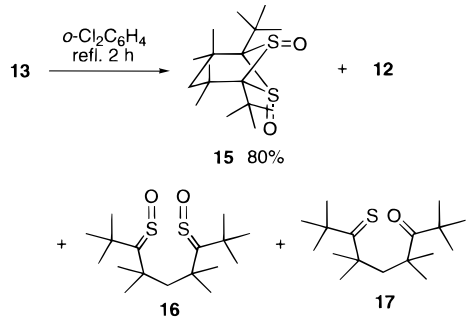


Figure 1. Space-filling model of the *endo*-sulfoxide **14**.

The structure of **13** was determined on the basis of the spectroscopic data and elemental analysis. The ^1H and ^{13}C NMR spectra showed that **13** has four equivalent ring methyls, two equivalent methylenes, and two equivalent *t*-Bu groups. The IR spectrum showed only one strong S=O stretching absorption. These spectral data indicate the symmetrical structure of **13**. The configuration of the sulfoxide groups is determined to be *endo*,*endo* and not *exo*,*exo*, with respect to the six-membered ring, on analyzing the ^1H NMR spectrum by taking the anisotropic effect of the sulfoxide groups into account.[10] The *endo*-sulfoxide structure of **14**, determined by X-ray crystallography, also supports the above assignment on **13**. Figure 1 shows a space-filling model of **14**, based on the X-ray analysis, which explains the stereoselective formation of the *endo*,*endo*-isomer **13** in terms of the sterically favorable *endo*-approach of oxidants.

The thermolysis of the *endo*,*endo*-disulfoxide **13** was examined with expectation of the formation of the cyclopentene **9** by extrusion of two SO molecules. Heating **13** in refluxing *o*-dichlorobenzene for 2 h, however, resulted in mainly isomerization to an isomer, the *endo*,*exo*-disulfoxide **15** (80%), in addition to decomposition to small amounts of **12**, the dithioketone *S*,*S*′-dioxide (disulfine) **16**, and the monothiodiketone **17**.[9]



The driving force for the *endo*-*exo* isomerization would originate from the reduction of the 1,3-diaxial repulsion between the sulfoxide oxygen atoms and the ring methyl groups in **13**. The formation of the disulfine **16** results from an intramolecular [2 + 2] cycloreversion of 1,3-dioxide **13** or **15**.[15] The configuration of the C=S=O moieties in **16** was determined to be *Z*,*Z* or *E*,*E* by ^1H and ^{13}C NMR analyses.

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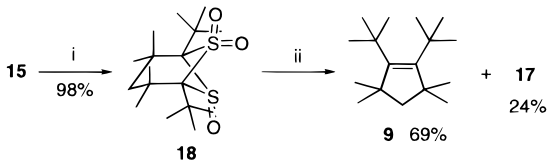
(15) Block, E.; Corey, E. R.; Penn, R. E.; Renken, T. L.; Sherwin, P. F.; Bock, H.; Hirabayashi, T.; Mohmand, S.; Solouki, B. *J. Am. Chem. Soc.* **1982**, *104*, 3119−3130.

Scheme 2[a]



[a] i: DMD (3 molar equiv), CH_2Cl_2, 0 °C; ii: DMI, refl. 1 h.

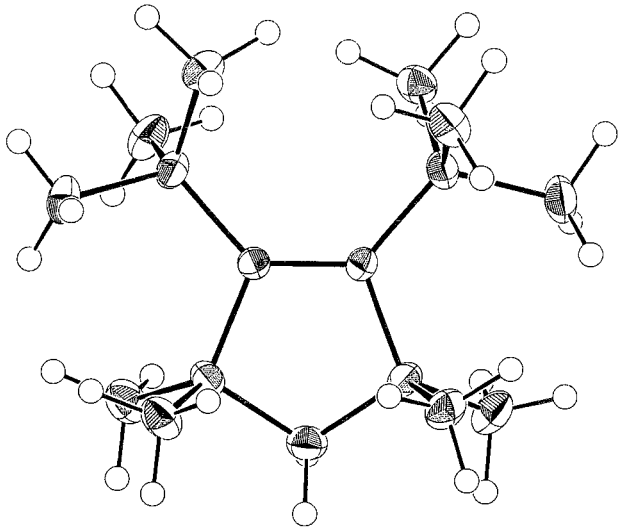


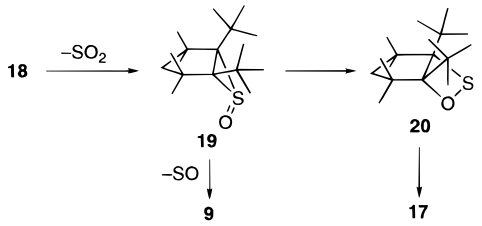
Figure 2. ORTEP drawing of the cyclopentene **9** (50% thermal ellipsoid).

The *endo*,*exo*-disulfoxide **15** opens the sterically favorable *endo* side to the attack of oxidants. In fact, **15** was oxidized with DMD to give the trioxide **18** quantitatively (Scheme 2). The trioxide **18** is more promising as the precursor for **9** than are the dioxides **14** and **15**. Thus the trioxide **18** was heated in refluxing *o*-dichlorobenzene for 1 day to give the desired cyclopentene **9** in addition to the monothiodiketone **17**. In this case, however, the high volatility of **9** precluded its efficient isolation. This trouble was overcome by carrying out the thermolysis in 1,3-dimethyl-2-imidazolidinone (DMI) (bp 224 °C), which is easily removed by shaking with water. The thermolysis conducted in refluxing DMI for 1 h furnished the cyclopentene **9** in 69% isolated yield along with the monothiodiketone **17** (24%) (Scheme 2). Heating **18** in refluxing DMSO for 23 h also yielded **9**, albeit in a lower yield (31%), and a white solid insoluble in common organic solvents. The structure of **9** was determined by the spectroscopic data and X-ray crystallography (Figure 2).

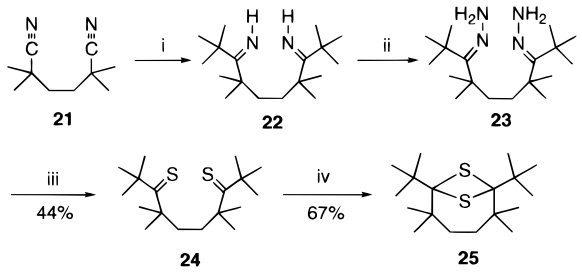
The formation of the cyclopentene **9** and the monothiodiketone **17** from the trioxide **18** is rationalized by Scheme 3. SO_2, which is a better leaving group than SO,[16] would be extruded from **18** initially to give the *endo*-episulfoxide **19**. Two reactions take place from **19**: (i) the extrusion of SO to furnish the cyclopentene **9** and (ii) the thermal sulfoxide−sulfenate isomerization,[17] which gives the 1,2-oxathietane intermediate **20** to provide the monothiodiketone **17** by a ring opening.[18]

Synthesis of 1,2-Di-*tert*-butyl-3,3,6,6-tetramethylcyclohexene (10). First we examined the synthesis of the cyclohexene **10** from the bicyclic 1,3-dithietane **25**. The dinitrile **21** was treated with *t*-BuLi to give the diimine **22**, the reaction of which with hydrazine hydrate yielded the dihydrazone **23**.[19] The dihydrazone **23** was treated with S_2Cl_2[20] to give the dithioketone **24**. An acid-catalyzed intramolecular cyclization[21] of **24** gave **25** (Scheme 4). Instead, the reaction of the 1,6-diketone **26** with LR did not yield **25**.

Scheme 3

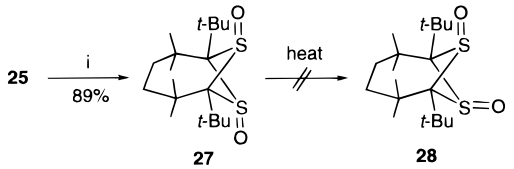


Scheme 4[a]

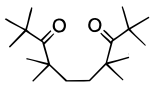


[a] i: *t*-BuLi (6 molar equiv), Et_2O, 0 °C; ii: $H_2NNH_2 \cdot H_2O$ (20 molar equiv), diethylene glycol, refl., 20 h; iii: S_2Cl_2 (2.1 molar equiv), Et_3N, PhH, 0 °C and then rt; iv: $MeSO_3H$ (excess), PhH, rt.

Scheme 5[a]



[a] i: DMD (2.3 molar equiv), CH_2Cl_2, 0 °C.



26

The 1,3-dithietane **25** was oxidized with DMD, MCPBA−Na_2CO_3, or $KMnO_4$ to give the *endo*,*endo*-disulfoxide **27** in high yields (Scheme 5). Heating **27** in toluene (reflux), diethylene glycol (100 °C in the presence of hydrochloric acid), or DMI (reflux), however, gave neither the *endo*,*exo*-disulfoxide **28** nor the cyclohexene **10**. This route was therefore abandoned at this stage.

Next, the reaction of the dihydrazone **23** with Se_2Cl_2 was investigated.[22] We previously observed that the diphenyl analogue **29** reacted with Se_2Cl_2 in the presence

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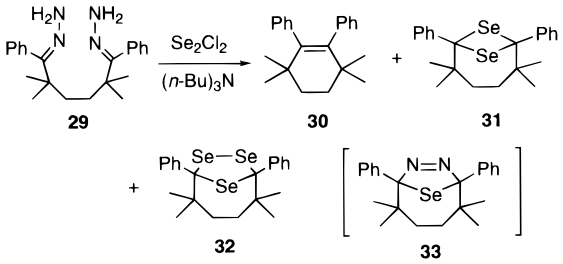
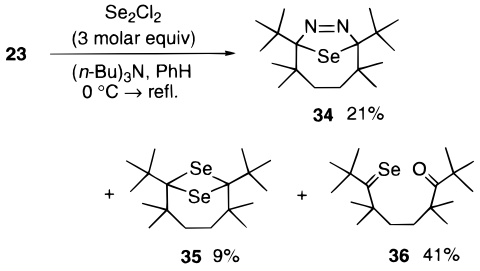
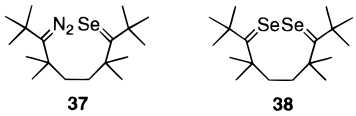
of (*n*-Bu)$_3$N to produce the cyclohexene **30** along with the bicyclic selenium compounds **31** and **32**. The 1,3,4-selenadiazoline **33** was proposed as the intermediate for **30**.[23]



In the present case, the dihydrazone **23** reacted with Se_2Cl_2 in the presence of *n*-Bu_3N to furnish the 1,3,4-selenadiazoline **34** and the 1,3-diselenetane **35** in 21% and 9% isolated yields, respectively, along with the monoselenodiketone **36** (41%). The former two compounds are light-sensitive and thus were treated in the dark as far as possible.



The formation of **34** was explained in terms of an intramolecular [3 + 2] cyclization of the diazoselenoketone **37**, while that of **35** was by an intramolecular [2 + 2] cyclization of the 1,6-diselenoketone **38** in a head-to-tail manner.[23] The formation of diazo compounds by the reaction of sterically hindered hydrazones with Se_2Cl_2 has been reported.[24]



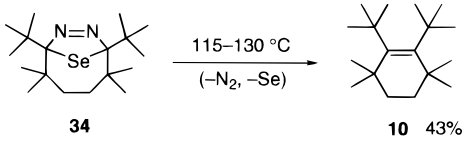
Several 1,3,4-selenadiazolines were obtained in reactions of selenoketones with diazo compounds.[1c,3e,g,5b] The selenadiazoline **34** is thermally stable up to 105 °C, its melting point in the dark. The structure of **34** was confirmed by X-ray crystallography.

Thermolysis of the selenadiazoline **34** without a solvent at 115−130 °C gave the desired cyclohexene **10** in 43% yield as colorless crystals. The thermolysis in refluxing DMI yielded **10** in a lower yield (7%). The structure of **10** was supported by the spectroscopic data and elemental analysis. In the ^{1}H NMR spectrum, only three singlets appear at δ 1.16 (ring methyls), 1.28 (*tert*-butyls), and 1.44 (methylene protons). Single crystals of **10** suitable for X-ray crystallographic analysis have not yet been obtained.

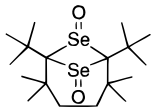
Table 1. Characteristic Spectral Data of Sterically Congested Alkenes

entry	alkenes	^{13}C NMR C=C, δ	UV nm (log ϵ)[a]	Raman C=C, cm^{-1}
1	**9**	149.6	210 (3.31)	1505
2	**10**	153.7	245 (3.72)	*b*
3	**2**[c,d]	150.1	241 (3.18)	1461
4	**4**[e]	142.3	217 (4.14)	1580
5	**40**[f]	147.2		1573
6	**41**[d]	147.4	210 (3.65)	1503
		152.8	225 (3.53)	
			251 (3.58)	
7	**42**[d]	152.2	245 (3.57)	1475
		154.5		

[a] Cyclohexane as the solvent. [b] Not determined because of overlapping with C−H bending vibrations. [c] References 3h, 4b. [d] Reference 4c. [e] Reference 6a. [f] Reference 3b.



In comparison, conversion of the 1,3-diselenetane **35** to the diselenoxide **39** was performed in a high yield by oxidation with DMD. However, thermolysis or photolysis of **39** resulted in the formation of the 1,6-diketone **26** and elemental selenium mainly, though only a trace amount of **10** was detected by ^{1}H NMR spectroscopy in the photolysis.



Physical Properties of the Cyclopentene 9 and the Cyclohexene 10. The geometry of the cyclopentene **9**, determined by X-ray crystallography, is summarized in Figure 3. The double bond length is 1.365(2) Å, being slightly longer than those of typical cyclopentenes (1.323 Å)[25] and hindered alkenes such as **2** (1.357 Å)[4b] and **4** (1.353 Å)[6b] (Figure 3a). Because of the intrinsically small interior angles of cyclopentenes (110.9° and 111.1° in **9**), the C=C−*t*-Bu angles enlarge (129.5° and 131.4°) to moderate the steric hindrance between the adjacent *t*-Bu groups (Figure 3b). The stretching of the four C−C bonds α to the double bond (1.556−1.566 Å) contributes to reduction of the steric hindrance as well. The C−C=C−C torsion angles (5.3° and 4.7°) are rather small compared with those of **2** (28.6°)[4b] and **4** (19.7°),[6b] and the cyclopentene ring takes a slightly distorted envelope conformation.

Table 1 summarizes characteristic spectroscopic data of **9** and **10**, with those of several hindered alkenes for comparison. ^{13}C NMR spectroscopy shows resonances due to the olefin carbons of **9** and **10** at δ 149.6 and 153.7, respectively, which are comparable to those of other hindered alkenes. The UV spectrum of the cyclohexene **10** exhibits a band at 245 nm, assignable to the $\pi \rightarrow \pi^*$

(22) Okazaki, R.; Ishii, A.; Inamoto, N. *J. Chem. Soc., Chem. Commun.* **1983**, 1429−1430. Ishii, A.; Okazaki, R.; Inamoto, N. *Bull. Chem. Soc. Jpn.* **1988**, *61*, 861−867.

(23) Ishii, A.; Ding, M.-X.; Nakayama, J.; Hoshino, M. *Chem. Lett.* **1992**, 2289−2292.

(24) Okazaki, R.; Tokitoh, N.; Ishii, A.; Ishii, N.; Matsuhashi, Y.; Matsumoto, T.; Suzuki, H. *Phosphorus, Sulfur Silicon Relat. Elem.* **1992**, *67*, 49−66.

(25) Allen, F. H.; Kennard, O.; Watson, D. G.; Brammer, L.; Orpen, A. G.; Taylor, R. *J. Chem. Soc., Perkin Trans. 2* **1987**, S1−S19.

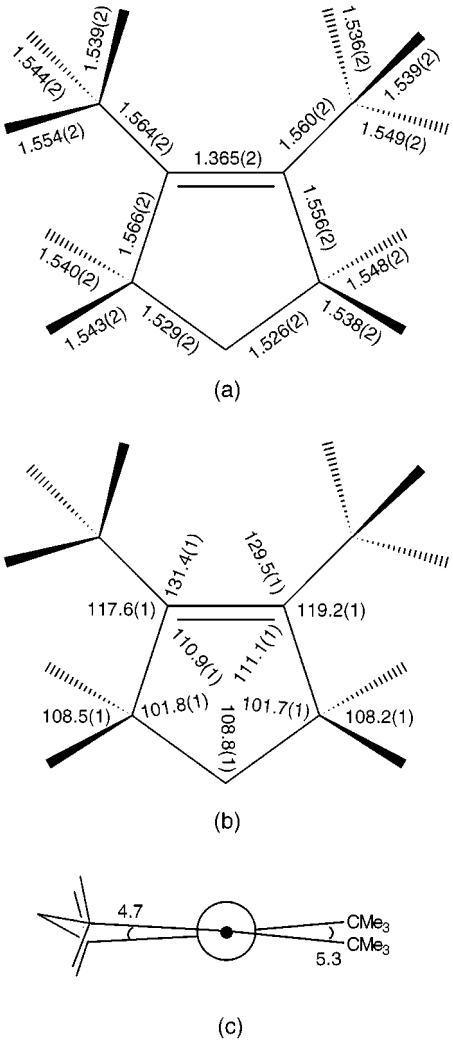
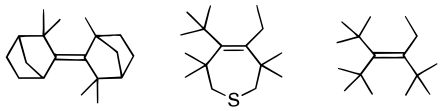


Figure 3. Selected (a) bond lengths (Å), (b) bond angles (deg), and (c) a torsion angle (deg) of the cyclopentene **9**.

transition of the C=C bond. The bathochromic shift is characteristic of highly hindered alkenes (entries 2, 6, and 7).[4c] The Raman spectrum of the cyclopentene **9** shows a strong band at 1505 cm^{-1} assignable to the C=C stretching vibration (Figure 4a), whereas that of the cyclohexene **10** does not show an isolated band due to the C=C stretching vibration, probably because of overlap with the CH_2 deformation bands centered at around 1440−1460 cm^{-1} (Figure 4b). If so, the C=C stretching band of **10** is comparable to those of **3** (1461 cm^{-1}) and **42** (1475 cm^{-1}) (entries 3 and 7). Judging from the data shown in Table 1, the cyclohexene **10** is clearly more strained than **9** and is comparable with **2**, **42**,[4c] and a tied-back cycloalkene **41**[4c] in terms of strain.



40 **41** **42**

In conclusion, we have succeeded in the syntheses of sterically congested cycloalkenes **9** and **10** by 2-fold extrusion processes. The C=C bond in the cyclohexene **10** is strained in degree comparable to those of most strained alkenes reported so far. The compound **10**, which

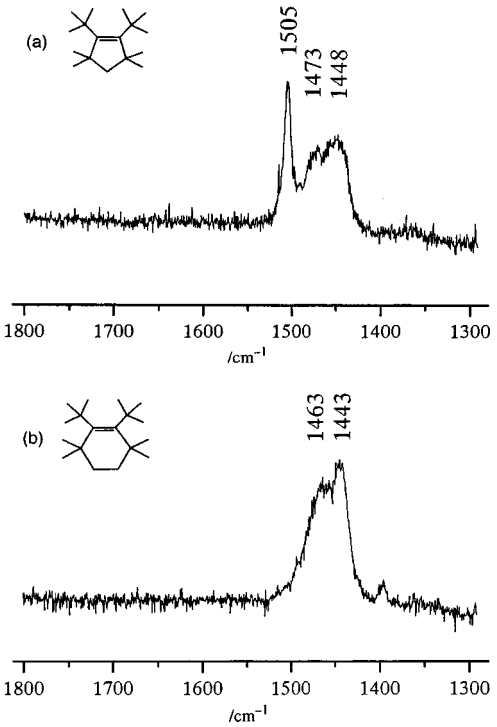


Figure 4. Raman spectra of (a) the cyclopentene **9** and (b) the cyclohexene **10**.

corresponds to a "didehydro" derivative of tetra-*tert*-butylethylene (**1**), possesses the molecular structure nearest to **1** among the so-called hindered alkenes so far synthesized.

Experimental Section

General. Melting points were determined on a capillary tube apparatus and are uncorrected. ^1H and ^{13}C NMR spectra were obtained in $CDCl_3$ as the solvent unless otherwise noted. ^{77}Se NMR spectra were obtained in $CDCl_3$ as the solvent using 0.1 M D_2SeO_3/D_2O as an external standard (δ 1282). Raman spectra were recorded by a triple-polychromator and a liquid N_2-cooled CCD detector. Mass spectra were determined at 70 eV in the EI mode. Elemental analyses were performed by the Chemical Analysis Center of Saitama University.

In workup of reactions, the extract was dried over anhydrous $MgSO_4$ after washing with water. Column chromatography was performed with silica gel, and the eluent is given in parentheses.

Diethyl 2,2,4,4-Tetramethylglutarate (11). The diester **11** was prepared by the reported method[12] with a small modification. To a solution of 2,2,4,4-tetramethylglutaric acid[26] (3.00 g, 13.3 mmol) in dimethyl sulfoxide (80 mL) was added aqueous sodium hydroxide (6.30 M, 7.8 mL, 49.2 mmol). The solution was stirred for 1 h, and ethyl iodide (10.3 mL, 128 mmol) was added. The mixture was stirred for 20.5 h, diluted with 1.2 M hydrochloric acid (180 mL), and extracted with diethyl ether twice. The combined extracts were washed with aqueous $NaHSO_3$, aqueous $NaHCO_3$, and water, in this order, and dried. The solvent was removed under reduced pressure, and the residual oil was distilled in vacuo (80 °C/1.1 Torr) (lit.[11] bp 96 °C/1.0 Torr) to give **11** (3.24 g, 83%) as a colorless oil: ^1H NMR (400 MHz) δ 1.12 (s, 12H), 1.26 (t, J = 7.2 Hz, 6H), 2.07 (s, 2H), 4.11 (q, J = 7.1 Hz, 4H); ^{13}C NMR (100.6 MHz) δ 14.1, 26.0, 41.6, 49.2, 60.4, 178.3; IR (neat, cm^{-1}) 1732.

2,2,4,4,6,6,8,8-Octamethylnonane-3,7-dione (12). To a solution of the diester **11** (972 mg, 3.98 mmol) in diethyl ether

(26) Maier, G.; Roth, C.; Schmitt, R. K. *Chem. Ber.* **1985**, *118*, 704−721.

(59 mL) cooled at −50 °C under argon was added *t*-BuLi (1.54 M, 5.2 mL, 7.96 mmol). After stirring for 1 h, the mixture was warmed to room temperature, diluted with aqueous NH_4Cl, and extracted with diethyl ether twice. The combined extracts were washed with water and dried, and the solvent was removed under reduced pressure. The residue was subjected to column chromatography (CH_2Cl_2−CCl_4 3:1) to give **12** (865 mg, 81%) as a colorless oil, which was further purified by bulb-to-bulb distillation at 70 °C under 0.85 Torr: ^{1}H NMR (400 MHz) δ 1.21 (s, 12H), 1.27 (s, 18H), 2.19 (s, 2H); ^{13}C NMR (100.6 MHz) δ 28.3, 28.9, 46.3, 49.2, 51.0, 218.5; IR (neat, cm^{-1}) 1684. Anal. Calcd for $C_{17}H_{32}O_2$: C, 76.06; H, 12.01. Found: C, 75.72; H, 12.14.

1,5-Di-*tert*-butyl-2,2,4,4-tetramethyl-6,7-dithiabicyclo-[3.1.1]heptane (8). A mixture of the diketone **12** (568 mg, 2.12 mmol) and Lawesson's reagent[13] (1.72 g, 4.24 mmol) in toluene (50 mL) was heated under reflux under argon for 40 h. The mixture was cooled to room temperature and diluted with aqueous $NaHCO_3$. The organic layer was separated, washed with water, dried, and evaporated to dryness. The residue was subjected to column chromatography (CCl_4) to give **8** (474 mg, 75%): colorless needles, mp 76.0−76.5 °C (MeOH). ^{1}H NMR (400 MHz) δ 1.13 (s, 18H), 1.42 (s, 12H), 1.95 (s, 2H); ^{13}C NMR (100.6 MHz) δ 28.7, 28.9, 40.6, 45.4, 66.7, 68.2; MS *m*/*z* (rel intensity) 300 (M^+, 29), 199 (100). Anal. Calcd for $C_{17}H_{32}S_2$: C, 67.93; H, 10.73. Found: C, 67.97; H, 10.78.

Oxidation of Bicyclic 1,3-Dithietane 8 with DMD. To a solution of **8** (49 mg, 0.163 mmol) in dichloromethane (19 mL) was added an acetone solution of DMD[14] (0.078 M) in small portions (2−3 mL) at 0 °C with monitoring of the progress of the reaction by TLC; the volume totaled 16 mL (1.25 mmol). The mixture was warmed to room temperature and stirred for an additional 1 h. The mixture was diluted with aqueous $NaHCO_3$ and water, and the organic layer was separated, dried, and evaporated to dryness to give the *endo,endo*-dioxide **13** (53 mg, 98%).

Di-*tert*-butyl-2,2,4,4-tetramethyl-6,7-dithiabicyclo[3.1.1]-heptane 6-*endo*,7-*endo*-Dioxide (13): colorless crystals; mp 140.0−141.5 °C (MeOH−H_2O). ^{1}H NMR (400 MHz) δ 1.45 (s, 18H), 1.65 (s, 12H), 2.52 (s, 2H); ^{13}C NMR (100.6 MHz) δ 30.8, 32.4, 40.8, 46.2, 57.0, 97.8; IR (KBr, cm^{-1}) 1064; MS *m*/*z* (rel intensity) 332 (M^+, 4), 57 (100). Anal. Calcd for $C_{17}H_{32}O_2S_2$: C, 61.40; H, 9.70. Found: C, 61.50; H, 9.80.

Oxidation of Bicyclic 1,3-Dithietane 8 with MCPBA. To a solution of **8** (103 mg, 0.333 mmol) in dichloromethane (20 mL) was added MCPBA (70%, 371 mg, 1.5 mmol) in small portions. The mixture was stirred for 2.5 h at room temperature and then was diluted with aqueous $NaHSO_3$. The organic layer was separated, washed with aqueous $NaHCO_3$ and water, dried, and evaporated to dryness. The residue was subjected to column chromatography (CH_2Cl_2) to give the *endo*-oxide **14** (52 mg, 49%), the *endo, endo*-dioxide **13** (9 mg, 9%), and the diketone **12** (26 mg, 29%).

Di-*tert*-butyl-2,2,4,4-tetramethyl-6,7-dithiabicyclo[3.1.1]-heptane 6-*endo*-Oxide (14): colorless needles, mp 102.5−103 °C (hexane). ^{1}H NMR (400 MHz) δ 1.05 (d, J = 14.4 Hz, 1H), 1.30 (s, 18H), 1.39 (s, 6H), 1.54 (s, 6H), 3.27 (d, J = 14.5 Hz, 1H); ^{13}C NMR (100.6 MHz) δ 30.8, 31.9, 40.9, 42.4, 57.8, 89.5; IR (KBr, cm^{-1}) 1080; MS *m*/*z* (rel intensity) 316 (M^+, 23), 57 (100). Anal. Calcd for $C_{17}H_{32}OS_2$: C, 64.50; H, 10.19. Found: C, 64.76; H, 10.29.

Thermal Isomerization of *endo,endo*-Dioxide 13 to *endo,exo*-Dioxide 15. A solution of **13** (186 mg, 0.56 mmol) in *o*-dichlorobenzene (10 mL) was heated under reflux for 2 h. The mixture was cooled to room temperature, and the solvent was removed under reduced pressure. The residue was subjected to column chromatography (CH_2Cl_2) to give the *endo,exo*-dioxide **15** (150 mg, 80%) along with small amounts of the dicarbonyl compound **12**, the disulfine **16**, and the monothiodiketone **17**.

1,5-Di-*tert*-butyl-2,2,4,4-tetramethyl-6,7-dithiabicyclo-[3.1.1]heptane 6-*endo*,7-*exo*-Dioxide (15): colorless crystals, mp 124−125 °C (MeOH−H_2O). ^{1}H NMR (400 MHz) δ 1.35 (s, 6H), 1.53 (s, 18H), 1.59 (d, J = 16 Hz, 1H), 1.72 (s, 6H), 1.85 (d, J = 16 Hz, 1H); ^{13}C NMR (100.6 MHz) δ 28.6, 31.5, 32.0, 42.0, 42.9, 55.6, 92.6; IR (KBr, cm^{-1}) 1086, 1072; MS *m*/*z* (rel intensity) 332 (M^+, 4), 57 (100). Anal. Calcd for $C_{17}H_{32}O_2S_2$: C, 61.40; H, 9.70. Found: C, 61.60; H, 9.86.

2,2,4,4,6,6,8,8-Octamethylnonane-3,7-dithione *S,S′*-Dioxide (16): colorless crystals, mp 152.5−153 °C (MeOH). ^{1}H NMR (400 MHz) δ 1.47 (s, 12H), 1.56 (s, 18H), 2.31 (s, 2H); ^{13}C NMR (100.6 MHz) δ 29.9, 31.2, 43.8, 45.3, 47.9, 216.7; IR (KBr, cm^{-1}) 1138, 1120, 1092, 1052, 976. Anal. Calcd for $C_{17}H_{32}O_2S_2$: C, 61.40; H, 9.70. Found: C, 61.41; H, 9.79.

2,2,4,4,6,6,8,8-Octamethyl-7-thioxononan-3-one (17): purple oil. ^{1}H NMR (400 MHz) δ 1.22 (s, 6H), 1.26 (s, 9H), 1.39 (s, 6H), 1.50 (s, 9H), 2.54 (s, 2H); ^{13}C NMR (100.6 MHz) δ 29.03, 29.09, 32.6, 33.7, 46.4, 50.1, 53.4, 54.3, 57.7, 218.7, 279.0; IR (neat, cm^{-1}) 1684; UV−vis (CH_2Cl_2, $c = 1.00 \times 10^{-2}$ M, nm) λ_{max} (ϵ) 537 (10); MS *m*/*z* (rel intensity) 284 (M^+, 5), 57 (100); HRMS calcd for $[C_{17}H_{32}OS]^+$ 284.2174, found 284.2197.

1,5-Di-*tert*-butyl-2,2,4,4-tetramethyl-6,7-dithiabicyclo-[3.1.1]heptane *S′*-*endo*-*S,S,S′*-Trioxide (18). To a solution of the *endo,exo*-dioxide **15** (49 mg, 0.147 mmol) in dichloromethane (10 mL) was added an acetone solution of DMD (62 mM, 3.6 mL, 0.22 mmol) at 0 °C. The mixture was stirred for 30 min at 0 °C and 30 min at room temperature, and then another portion of DMD (3.6 mL) was added. After stirring for 30 min at 0 °C and 30 min at room temperature, the mixture was diluted with aqueous $NaHCO_3$ and water, dried, and evaporated to dryness. The residue was subjected to column chromatography (CH_2Cl_2) to give the trioxide **18** (50 mg, 98%): colorless crystals, mp 158−159 °C (MeOH−H_2O). ^{1}H NMR (400 MHz) δ 1.517 (s, 6H), 1.522 (s, 18H), 1.69 (d, J = 15.0 Hz, 1H), 1.80 (s, 6H), 2.90 (d, J = 15.0 Hz, 1H); ^{13}C NMR (100.6 MHz) δ 26.8, 31.5, 34.4, 40.8, 44.4, 59.8, 106.9; IR (KBr, cm^{-1}) 1304, 1144, 1096; MS *m*/*z* (rel intensity) 348 (M^+, 3), 57 (100). Anal. Calcd for $C_{17}H_{32}O_3S_2$: C, 58.58; H, 9.25. Found: C, 58.38; H, 9.35.

Thermolysis of the Trioxide 18. A solution of **18** (91 mg, 0.26 mmol) in 1,3-dimethyl-3-imidazolidinone (DMI) (10 mL) was heated under reflux for 1 h. The mixture was cooled to room temperature, diluted with water, and extracted with pentane. The extract was washed with water several times to remove DMI completely and dried. The solvent was removed under reduced pressure, and the residue was subjected to column chromatography (pentane) to give the cyclopentene **9** (43 mg, 69%) and the monothiodiketone **17** (18 mg, 24%). The cyclopentene **9** was purified by sublimation under 31 mmHg on an oil bath warmed at 68−71 °C.

1,5-Di-*tert*-butyl-2,2,4,4-tetramethylcyclopentene (9): colorless crystals; mp 68−68.5 °C. ^{1}H NMR (400 MHz) δ 1.25 (s, 12H), 1.37 (s, 18H), 1.50 (s, 2H); ^{13}C NMR (100.6 MHz) δ 32.4, 35.0, 35.6, 46.7, 64.5, 149.6; MS (GC) *m*/*z* (rel intensity) 236 (M^+, 44), 123 (100); UV−vis (cyclohexane, $c = 7.2 \times 10^{-4}$ M, nm) λ_{max} (log ϵ) 210 (3.31). Anal. Calcd for $C_{17}H_{32}$: C, 86.36; H, 13.64. Found: C, 86.10; H, 13.78.

X-ray Crystal Structure Determination of 9: $C_{17}H_{32}$, monoclinic, $P2_1/a$, a = 11.303(2) Å, b = 8.3740(6) Å, c = 16.069-(2) Å, β = 87.482(6)°, V = 1519.5(3) Å^3, Z = 4, D_c = 1.031 g cm^{-3}, μ(Mo Kα) = 0.53 mm^{-1}. A colorless plate with dimensions 0.30 × 0.24 × 0.18 mm^3 was mounted on a Mac Science DIP3000 diffractometer with a graphite monochromator. Oscillation and nonscreen Weissenberg photographs were recorded on the imaging plates of the diffractometer by using Mo Kα radiation (λ = 0.71073 Å) at 153 K, and the data reduction was made by the MAC DENZO program system. Intensity data of 3623 independent reflections were collected in the range of $0 \le h \le 16$, $0 \le k \le 8$, $-22 \le l \le 22$. Cell parameters were determined and refined by using MAC DENZO for all observed reflections. The structure was solved by direct methods using SIR92[27] in the CRYSTAN-GM program system. The atomic coordinates and anisotropic thermal parameters of the non-H atoms were refined by full-matrix least-squares to minimize the functions, $\Sigma(|F_o| - |F_c|)^2$, for 2522 reflections [$I \ge 2\sigma(I)$] (282 parameters). The final R (R_w) =

(27) Altomare, A.; Cascarano, G.; Giacovazzo, C.; Guagliardi, A. *J. Appl. Crystallogr.* **1993**, *26*, 343−350.

0.057 (0.061) and GOF = 1.878; max/min residual electron density = 0.73/−0.37 e Å^{-3}.

2,2,4,4,7,7,9,9-Octamethyldecane-3,8-dione Diimine (22). To a solution of 2,5-dicyano-2,5-dimethylhexane[28] (553 mg, 3.36 mmol) in diethyl ether (20 mL) was added *t*-BuLi (1.64 M, 12.2 mL, 20 mmol) at 0 °C under argon. The mixture was stirred for 4 h at 0 °C and then diluted with water. The ethereal layer was separated, washed with water, dried, and evaporated to dryness to leave a pale yellow oil (969 mg). The diimine **22** was used in the next reaction without further purification because of high susceptibility to hydrolysis to give the 1,6-diketone **26**.

Diimine 22: ^{1}H NMR (300 MHz) δ 1.24 (s, 12H), 1.25 (s, 18H), 1.42 (s, 4H), 9.43 (br s, 2H); ^{13}C NMR (50 MHz) δ 28.2, 29.9, 37.3, 41.3, 44.6, 192.2.

2,2,4,4,7,7,9,9-Octamethyldecane-3,8-dione Dihydrazone (23). A mixture of the crude diimine **22** (969 mg) and hydrazine monohydrate (3.14 g, 68 mmol) in diethylene glycol (5 mL) was heated under reflux for 20 h. The mixture was cooled to room temperature, diluted with water, and extracted with dichloromethane. The extract was washed with water, dried, and evaporated to dryness. The residue was washed in hexane to give **23** (355 mg, 44% from 2,5-dicyano-2,5-dimethylhexane): colorless crystals; mp 177−177.5 °C (CH_2Cl_2-hexane). ^{1}H NMR (CD_2Cl_2, 400 MHz) δ 1.13 (s, 12H), 1.36 (s, 18H), 1.48 (s, 4H), 5.26 (br s, 4H); ^{13}C NMR (CD_2Cl_2, 100.6 MHz) δ 28.5, 29.2, 36.65, 36.68, 44.0, 173.5; IR (KBr, cm^{-1}) 3388, 3320, 3244; MS *m*/*z* (rel intensity) 310 (M$^+$, 16), 57 (100). Anal. Calcd for $C_{18}H_{38}N_4$: C, 69.62; H, 12.33; N, 18.04. Found: C, 69.55; H, 12.40; N, 17.89.

Reaction of the Dihydrazone 23 with S_2Cl_2. To a solution of the dihydrazone **23** (122 mg, 0.391 mmol) and triethylamine (0.45 mL, 326 mg, 3.22 mmol) in benzene (10 mL) under argon was added a benzene solution of S_2Cl_2 (0.88 M, 0.95 mL, 0.83 mmol) at 0 °C. The mixture was stirred for 2.25 h at room temperature and then diluted with aqueous NH_4Cl. The organic layer separated was washed with water, dried, and evaporated to dryness to give an orange oil. The residue was subjected to column chromatography (hexane) to give the dithioketone **24** (54 mg, 44%).

2,2,4,4,7,7,9,9-Octamethyldecane-3,8-dithione (24): pink oil. ^{1}H NMR (300 MHz) δ 1.410 (s, 18H), 1.413 (s, 12H), 1.65 (s, 4H); ^{13}C NMR (50 MHz) δ 31.2, 32.7, 40.3, 53.6, 57.0, 277.2; MS *m*/*z* (rel intensity) 314 (M$^+$, 71), 69 (100); HRMS calcd for $[C_{18}H_{34}S_2]^+$ 314.2102, found 314.2060.

1,6-Di-*tert*-butyl-2,2,5,5-tetramethyl-7,8-dithiabicyclo-[4.1.1]octane (25). To a solution of the dithioketone **24** (136 mg, 0.432 mmol) in benzene (10 mL) was added methanesulfonic acid (1 mL) at room temperature under argon. The mixture was stirred for 40 min and then diluted with aqueous $NaHCO_3$. The organic layer was separated, washed with water, dried, and evaporated to dryness. The pale yellow residue was recrystallized from MeOH to give **25** (91 mg, 67%) as colorless needles: mp 151−152 °C (MeOH−H_2O). ^{1}H NMR (400 MHz) δ 1.09 (br s, 6H), 1.21 (s, 18H), 1.34 (br s, 6H), 2.88 (br s, 4H). The two singlets at 1.09 and 1.34 coalesced at 305 K to give $\Delta G^{\ddagger} = 15.1$ kcal mol^{-1} for the ring inversion.[29] ^{13}C NMR (100.6 MHz) δ 24.3 (br s), 29.1 (br s), 29.7, 43.1, 45.0, 45.4, 59.3; MS *m*/*z* (rel intensity) 314 (M$^+$, 30), 203 (100). Anal. Calcd for $C_{18}H_{34}S_2$: C, 68.72; H, 10.89. Found: C, 68.57; H, 11.06.

1,6-Di-*tert*-butyl-2,2,5,5-tetramethyl-7,8-dithiabicyclo-[4.1.1]octane 7-*endo*,8-*endo*-Dioxide (27). To a solution of the 1,3-dithietane **25** (101 mg, 0.321 mmol) in dichloromethane (12.5 mL) was added an acetone solution of DMD (0.076 M, 9.5 mL, 0.73 mmol) at 0 °C. After 1 h of stirring, the solvent was removed, and the residue was purified by column chromatography (CH_2Cl_2) to give **27** (99 mg, 89%): colorless crystals, mp 151−152 °C (MeOH−H_2O). ^{1}H NMR (300 MHz) δ 1.27 (pseudo d, J = 13 Hz, 2H), 1.455 (s, 18H), 1.466 (s, 6H), 3.82 (pseudo d, J = 13 Hz, 2H); ^{13}C NMR (50 MHz) δ 28.3, 31.0, 35.2, 39.7, 43.1, 47.1, 96.5; IR (KBr, cm^{-1}) 1058. Anal. Calcd for $C_{18}H_{34}O_2S_2$: C, 62.38; H, 9.89. Found: C, 62.52; H, 10.02.

2,2,4,4,7,7,9,9-Octamethyldecane-3,8-dione (26). A solution of the crude diimine **22** (532 mg, 1.90 mmol) in methanol (15 mL) and 6 M HCl (5 mL) was heated under reflux for 3 h. The mixture was diluted with aqueous $NaHCO_3$. The organic layer separated was washed with water, dried, and evaporated to dryness. The residue was purified by column chromatography (CH_2Cl_2) to give **26** (441 mg, 82%): colorless crystals, mp 40−41 °C (hexane). ^{1}H NMR (400 MHz) δ 1.23 (s, 18H), 1.24 (s, 12H), 1.40 (s, 4H); ^{13}C NMR (100.6 MHz) δ 26.4, 28.3, 36.8, 45.70, 49.1, 218.4; IR (KBr, cm^{-1}) 1682. Anal. Calcd for $C_{18}H_{34}O_2$: C, 76.54; H, 12.13. Found: C, 76.58; H, 12.23.

Reaction of the Dihydrazone 24 with Se_2Cl_2. To a solution of the dihydrazone **23** (409 mg, 1.32 mmol) and tributylamine (1.48 g, 8.0 mmol) in benzene (15 mL) under argon was added a benzene solution of Se_2Cl_2 (0.87 M, 4.6 mL, 4.0 mmol) dropwise at 0 °C in the dark. After stirring for 2.5 h at room temperature and then for 1 h under reflux, the mixture was diluted with aqueous NH_4Cl. The organic layer separated was washed with water, dried, and evaporated to dryness. The residue was subjected to column chromatography (hexane−CH_2Cl_2 2:1) to elute the crude 1,3-diselenetane **35** (184 mg), the crude 1,3,4-selenadiazoline **34** (185 mg) and the monoselenodiketone **36** (130 mg, 41%) in this order. The crude compounds **34** and **35** were purified by recrystallization from EtOH to give pure **34** (99 mg, 21%) and **35** (20 mg, 9%), respectively. The light-sensitive compounds **34** and **35** were protected from light as far as possible.

7,8-Diaza-1,6-di-*tert*-butyl-2,2,5,5-tetramethyl-9-selenabicyclo[4.2.1]nonan-7-ene (34): pale yellow crystals, mp 105−106.5 °C decomp (CH_3CN). ^{1}H NMR (400 MHz) at 298 K δ 0.72 (br s, 1H, CH_2), 0.93 (br s, 1H, CH_2), 1.1−1.5 (m, 31H), 2.22 (br s, 1H, CH_2); at 273 K δ 0.71 (dd, J = 15.2, 9.4 Hz, 1H, CH_2), 0.92 (dd, J = 14.8, 9.2 Hz, 1H, CH_2), 1.18 (s, 3H, Me), 1.25 (br s, 9H, *t*-Bu), 1.33 (s, 9H, *t*-Bu), 1.36 (s, 3H, Me), 1.38 (s, 3H, Me), 1.43 (s, 3H, Me), 2.20 (pseudo t, J = 13.7 Hz, 1H, CH_2); at 273 K one of the four CH_2 protons was not observed, but at 243 K, a part of an AB quartet due to the proton appeared at δ 1.21 owing to broadening of the singlet at δ 1.25; ^{13}C NMR (100.6 MHz, 263 K) δ 23.0 (Me), 30.3 (Me), 30.7 (Me), 31.1 (br s, *t*-Bu), 31.5 (Me), 32.5 (*t*-Bu), 40.9 (CH_2), 42.4 (C), 43.1 (C), 45.1 (CH_2), 46.8 (C), 124.9 (C), 127.2 (C), at this temperature the ring inversion is slow compared to the NMR time scale. One of the quaternary carbons was not observed. ^{77}Se NMR (76.3 MHz) δ 228; IR (KBr, cm^{-1}) 3000, 2924, 1472, 1368, 1034; MS *m*/*z* (rel intensity) 328 (M$^+$ − N_2 − 2, 10, ^{80}Se), 57 (100). Anal. Calcd for $C_{18}H_{34}N_2Se$: C, 60.49; H, 9.59; N, 7.84. Found: C, 60.31; H, 9.71; N, 7.65.

1,6-Di-*tert*-butyl-2,2,5,5-tetramethyl-7,8-diselenabicyclo-[4.1.1]octane (35): pale yellow needles, mp 145 °C (CH_3CN). ^{1}H NMR (400 MHz) δ 1.11 (s, 6H), 1.24 (s, 18H), 1.32 (br d, J = 12.3 Hz, 2H), 1.40 (s, 6H), 3.02 (br d, J = 13.4 Hz, 2H); ^{13}C NMR (50 MHz) δ 24.6, 28.5, 30.2, 42.7, 44.9, 46.8, 47.7; MS *m*/*z* (rel intensity) 410 (M$^+$, 10, $^{80}Se_2$), 57 (100). Anal. Calcd for $C_{18}H_{34}Se_2$: C, 52.94; H, 8.39. Found: C, 53.00; H, 8.52.

2,2,4,4,7,7,9,9-Octamethyl-8-selenoxodecan-3-one (36): green oil. ^{1}H NMR (400 MHz) δ 1.203 (s, 6H), 1.208 (s, 9H), 1.44−1.49 (m, 2H), 1.50 (s, 9H), 1.52 (s, 6H), 1.76−1.80 (m, 2H); ^{13}C NMR (100.6 MHz) δ 26.4, 28.3, 31.3, 32.5, 36.7, 39.7, 45.7, 49.2, 60.4, 63.3, 218.4, 291.3; IR (neat, cm^{-1}) 1684; UV−vis (cyclohexane, $c = 3.95 \times 10^{-2}$ or 3.16×10^{-5} M, nm) λ_{max} (log ϵ) 274 (3.78), 707 (1.29); MS *m*/*z* (rel intensity) 348 (M$^+$, 26, ^{80}Se), 54 (100); HRMS calcd for $[C_{18}H_{34}O^{80}Se]^+$ 346.1775, found 346.1780.

Thermolysis of the Selenadiazoline 34. The selenadiazoline **34** (267 mg, 0.747 mmol) in a bottom-round flask was heated on an oil bath warmed at 100 °C for 2.5 h. The pentane-soluble ingredients in the thermolysate were subjected to column chromatography (pentane). The fraction containing the cyclohexene **10** was concentrated on a hot-water bath for evaporation of the solvent to give **10** (80 mg, 43%) as a colorless solid.

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1,6-Di-*t*-butyl-2,2,5,5-tetramethylcyclohexene (10): colorless crystals; mp 138−139 °C (CH_3CN). ^1H NMR (400 MHz) δ 1.28 (s, 12H), 1.37 (s, 18H), 1.44 (s, 4H); ^{13}C NMR (100.6 MHz) δ 34.6, 35.4, 40.0, 43.1, 43.4, 153.7; IR (KBr, cm^{-1}) 2922, 1456, 1397, 1384, 1362, 1188; UV−vis (cyclohexane, $c = 6.0 \times 10^{-4}$ M, nm) λ_{max} (log ϵ) 245 (3.72); MS *m*/*z* (rel intensity) 250 (M^+, 24), 137 (100). Anal. Calcd for $C_{18}H_{34}$: C, 86.32; H, 13.68. Found: C, 86.09; H, 13.82.

1,6-Di-*tert*-butyl-2,2,5,5-tetramethyl-7,8-diselenabicyclo-[4.1.1]octane 7-*endo*,8-*endo*-Dioxide (39). To a solution of the diselenetane **35** (65 mg, 0.16 mmol) in dichloromethane (10 mL) was added DMD (0.082 M, 5.0 mL, 0.41 mmol) in three portions at 0 °C. The mixture was warmed to room temperature and stirred for 30 min. The solvent was evaporated to dryness to give spectroscopically pure **39** (70 mg, 100%): colorless powder, decomp above 80 °C (CH_2Cl_2−hexane). ^1H NMR (400 MHz) δ 1.23−1.30 (m, 2H), 1.47 (s, 6H), 1.51 (s, 18H), 1.73 (s, 6H), 4.30−4.37 (m); ^{13}C NMR (100.6 MHz) δ 28.4, 31.6, 35.4, 38.8, 43.9, 49.0, 97.3; IR (KBr, cm^{-1}) 824. Anal. Calcd for $C_{18}H_{34}Se_2O_2$: C, 49.09; H, 7.78. Found: C, 48.63; H, 7.74.

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Supporting Information Available: Structure determination summaries and tables of X-ray structure data for **9**, **14**, and **34**. ^1H and ^{13}C NMR data with assignment and full lists of infrared and mass spectral data for all new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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