Efficient Synthesis of Selenocarbonyl Compounds by Treating Carbonyl Compounds with Bis(1,5-cyclooctanediylboryl) Selenide

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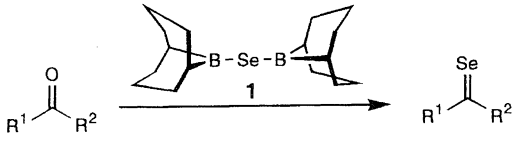
Selenoaldehydes and selenoketones were generated in situ, by treating aldehydes or ketones, respectively, with bis(1,5-cyclooctanediylboryl) selenide; the resulting selenocarbonyl compounds were trapped with 2,3-dimethyl-1,3-butadiene to give the corresponding [4+2] cycloadducts. The treatment of amides, an ester, and ketones possessing bulky substituents with the reagent also afforded the corresponding selenoamides, a selenoester, and sterically protected selones, respectively, in modest yields. On the other hand, a similar treatment of cinnamaldehyde with the reagent gave the 2, 3-dihydroselenophene derivative, which originated from a [4+2]-type self-dimerization of in situ generated 3-phenyl-2-propeneselenal.

The one-step conversion of carbonyl compounds to the corresponding selenocarbonyl compounds using selenium-containing reagents is one of the most important concerns in organic heteroatom chemistry.[1—13] In most cases, such reagents include reactive selenium–metal or selenium–heteroatom bonds which behave as synthetic equivalents of H_2Se. However, among such types of reagents, the syntheses of boryl selenides and boryl metal selenides have been achieved mainly based on structural interest[14—22] in spite of their potential to promote oxygen–selenium exchange reactions caused by their affinity to oxygen functionalities, due to their Lewis-acid character. Exactly, some boryl selenides were thought to play some essential roles in the conversion of carbonyl compounds to the corresponding selenocarbonyl compounds by a combined treatment with $[(c\text{-}C_6H_{11})_3Sn]_2Se$–$BCl_3$[5] or $[(CH_3)_3Si]_2Se$–$BF_3{\cdot}OEt_2$.[9] It was naturally expected that a structural modification of such alkylboryl selenides using relatively sterically crowded dialkylboranes would be sufficiently effective to reduce their air-lability of the reagents based on so-called steric protection, as is commonly known to be the case with general dialkylboranes and alkylhaloboranes. During our studies concerning the syntheses of selenocarbonyl compounds using reagents which possess the ability to introduce selenium functionalities to organic compounds, we previously reported on the efficient one-step conversion of various carbonyl compounds to the corresponding selenocarbonyl compounds by treating with bis(1,5-cyclooctanediylboryl) selenide (**1**), as shown in Scheme 1.[22,23] Herein, we describe the details concerning the reactions using **1**.

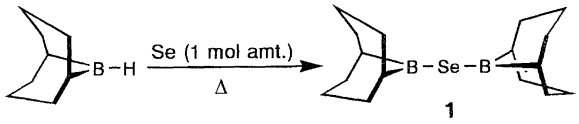
Results and Discussion

Preparation of Bis[1,5-cyclooctanediylboryl] Selenide (1). Bis(1,5-cyclooctanediylboryl) selenide (**1**) was prepared by treating 9-borabicyclo[3.3.1]nonane (9-BBN) with 1 molar amount of elemental selenium in benzene, toluene, or mesitylene at about 150 °C for 2 h in a sealed tube based on the Köster's method (Scheme 2).[22] However, the isolation of **1** was rather difficult due to the lability of **1** toward exposure to air. Thus, the resulting yellow-colored solution of the reaction mixture of 9-BBN and elemental selenium was used for subsequent reactions with carbonyl compounds without the isolation of **1**. The contents of **1** in the reaction mixture were also estimated on the basis of the amount of the starting 9-BBN in all cases.

Treatment of Aldehydes or Ketones with Bis(1,5-cyclooctanediylboryl) Selenide (1). A dichloromethane, a benzene, or a toluene solution of aldehydes or ketones (**2**) was treated with a yellow-colored solution containing 1.2—



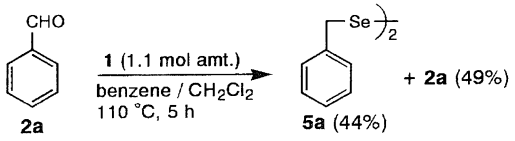
Scheme 1.



Scheme 2.

2.0 molar amount of bis(1,5-cyclooctanediylboryl) selenide (**1**), resulting from the reaction of 9-BBN with elemental selenium, and an excess amount of 2,3-dimethyl-1,3-butadiene under an Ar atmosphere at 80—110 °C for several hours in a sealed tube. After cooling to room temperature, the reaction was quenched with an aqueous sodium bicarbonate solution, and subjected to the usual workup. In all cases, the subsequent chromatographic separation of the crude products on silica gel gave [4+2] cycloadducts (**4**) of the in situ generated selones with the diene in modest to high yields besides the starting ketones and diselenides **5**. All of the physical data concerning the products, including the MS, IR, ^{1}H NMR, and ^{13}C NMR spectra, were fully consistent with the structures of 5,6-dihydro-2*H*-selenins **4**;[9,24—26] the data concerning **4a** and **4f** were also identical with those of the reported data. The elemental-analysis data of these products also satisfied the structures of **4**. All of the results concerning the reactions are given in Table 1. However, the [4+2] cycloadducts **4** were labile toward exposure to the air, and caused a gradual decomposition to give a complex mixture during storage in most cases, except for **4g**.

On the other hand, when benzaldehyde (**2a**) was treated with a solution of **1** in a similar way to that described above in the absence of a diene, dibenzyl diselenide (**5a**, 44% yield) was mainly afforded[27] and 2,4,6-triphenyl-1,3,5-triselenane, the trimer of selenobenzaldehyde (**3a**), was not found at all in the crude reaction mixture (Scheme 3).[9] This result indicated that reagent **1** possesses a strong reducing ability toward selenocarbonyl compounds. We have already found that the treatment of benzaldehyde (**2a**) with $(Me_3Si)_2Se$[9] or $(Me_2SnSe)_3$[12] and a Lewis acid gave dibenzyl diselenide (**5a**). In those cases, Lewis acids behaved not only as an activator of the reagents, probably by weakening the Si–Se and Sn–Se bonds of the reagents to generate some reactive



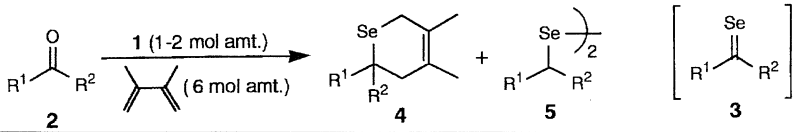
Scheme 3.

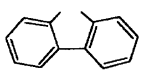
species related to the selenide ion, but also as a catalyst for the acid-induced ring fission of 1,3,5-triselenanes.[9] It was thus assumed that **1**, possessing an inherent Lewis acid character, might cause similar reactions under the conditions mentioned above without adding a Lewis acid. In any case, reagent **1** caused a further reduction of in situ generated selenobenzaldehyde (**3a**) to give diselenide **5a**, even if only a 1.1 molar amount of **1** was treated with **2a**.

Treatment of Amides or Ethyl Benzoate with Bis(1,5-cyclooctanediylboryl) Selenide (1). When *N,N*-dimethylformamide (**6a**), *N,N*-diisopropylformamide (**6b**), or *N,N*-dimethylacetamide (**6c**) was treated with a benzene, a toluene, or a mesitylene solution of **1** in a sealed tube at room temperature or at a higher temperature under an Ar atmosphere, the corresponding selenoamides **8a–c** were obtained in modest-to-low yields in all cases.[10,11] All of the physical properties of **8a–c**, including the MS, IR, and ^{1}H NMR spectra, were fully consistent with the structures of selenoamides **8a–c**, and were identical with those of the reported physical data. The structures of selenoamides **8a–c** were also confirmed based on the conversion to the corresponding amides by treating a dichloromethane solution of the selenoamides with mCPBA (1.2 mol amt.) at 0 °C.[28,29]

Interestingly, the conversion of **6a** to **8a** was carried out even at room temperature, and the yield of **8a** was lowered by a treatment of **6a** with **1** at a higher temperature. On the other hand, the treatment of **6b**, **6c**, or **6d** with **1** at room temperature only gave the recovery of the substrates, and a

Table 1. Reaction of Bis(1,5-cyclooctanediylboryl) Selenide (**1**) with Aldehydes and Ketones (**2**) in the Presence of an Excess Amount of 2,3-Dimethyl-1,3-butadiene[a]



Substrate			1	Solvent[b]	Temp	Time	Yield/%[c]		
R^1	R^2	2	mol amt.		°C	h	4	5	2
C_6H_5	H	**2a**	1.2	Benzene/CH_2Cl_2	110	18	79 (**4a**)	Trace (**5a**)	0
C_6H_5	H	**2a**	1.2	Benzene	110	3	64 (**4a**)	0	19
C_6H_5	H	**2a**	1.2	Toluene	Reflux[d]	18	30 (**4a**)	0	16
$p-ClC_6H_4$	H	**2b**	2.0	Benzene/CH_2Cl_2	110	18	70 (**4b**)	Trace (**5b**)	—[e]
$p-CH_3OC_6H_4$	H	**2c**	1.2	Benzene/CH_2Cl_2	110	8	51 (**4c**)	Trace (**5c**)	—[e]
C_6H_5	CH_3	**2d**	2.0	Benzene/CH_2Cl_2	80	15	54 (**4d**)	—[e]	—[e]
C_6H_5	C_2H_5	**2e**	2.0	Benzene/CH_2Cl_2	80	24	81 (**4e**)	—[e]	—[e]
C_6H_5	C_6H_5	**2f**	2.0	Benzene/CH_2Cl_2	110	24	96 (**4f**)	—[e]	—[e]
		**2g**	2.0	Benzene/CH_2Cl_2	110	48	84 (**4g**)	—[e]	—[e]

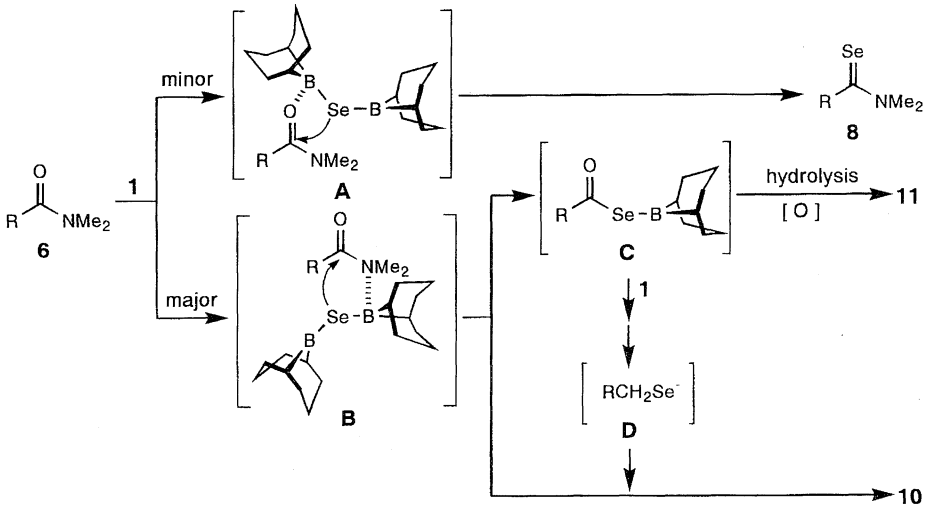
a) All reactions were carried out in a sealed tube. b) Benzene : dichloromethane (v/v) = 1 : 1. c) Isolated yields. d) The reaction mixture was heated at refluxing temperature under an Ar atmosphere. e) Not determined.

higher temperature was needed to convert **6b** or **6c** to the corresponding selenoamides. It was supposed that the steric bulkiness around the amide moiety of the substrates might affect the reactivity with **1**, which possesses a bulky dialkylboryl substituent. In contrast, the treatment of *N,N*-dimethylbenzamide (**6d**) with **1** at a higher temperature only gave a complex mixture containing *Se*-benzyl benzenecarboselenoate (**10d**, 28%) along with the recovery of **6d**. Dibenzoyl diselenide (**11d**) was also obtained from the aqueous layer in 6% yield after acidification with an excess amount of aqueous hydrochloric acid and a subsequent extraction.

It was naturally assumed that amides **6** reacted with **1** during the primary stage to give complexes **A** and **B**. Complex **A**, bearing a B–O interaction, was thought to be converted into selenoamides **8** through the usual oxygen–selenium exchange reaction. On the other hand, complex **B**, possessing a strong interaction of the nitrogen atoms of the substrates with the trivalent boron atoms of **1**, was assumed to cause a facile elimination of the dialkylamino groups to generate benzenecarboselenoic acid derivatives **C** (R = Ph), which caused a hydrolytic cleavage and subsequent aerobic oxidation during the workup to give dibenzoyl diselenide (**11d** (R^1 = Ph)). Furthermore, the formation of *Se*-benzyl benzenecarboselenoate (**10d** (R^1 = Ph)) also suggested that reagent **1** caused a further reduction of **C** at an elevated temperature to give the phenylmethaneselenolate anion (**D** (R = Ph)), which caused a nucleophilic attack toward the carbonyl carbon atoms of the amide-boron complex **B**. In any case, it was supposed that the strong coordinating interaction of the boron atom of **1** with the nitrogen atom of the amide group accelerated the formation of **C**, rather than an oxygen-selenium exchange reaction, and that the former reaction course might lower the yields of the expected selenoamides **8** in all cases starting from the amides (Scheme 4). A similar treatment of a dichloromethane solution of ethyl benzoate (**7**) with a benzene solution of **1** also gave the corresponding selenoester **9** in low yield along with the recovery of the substrate.[11] It was also supposed that the lower reactivity of ester **7** than that of amides **6** could also be attributed to the lower coordinating ability of the oxygen atoms of the ester with the boron atom of **1**. All of the results concerning the conversion of amides **6** and ethyl benzoate (**7**) to the corresponding selenoamides **8** and ester **9** using **1** are given in Table 2.

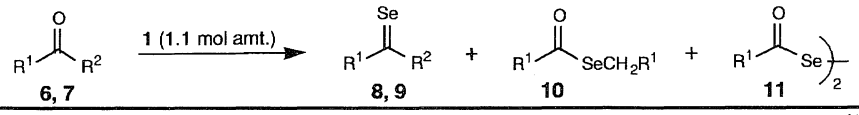
One-Step Preparation of Sterically Hindered Selones. The treatment of a dichloromethane solution of sterically hindered chiral ketones (1,3,3-trimethylbicyclo[2.2.1]heptan-2-one (*d*-fenchone, **12**), 4,7,7-trimethylspiro[bicyclo[2.2.1]-heptane-2,1′-cyclopentan]-3-one (**13**),[30,31] and 1′,3′-dihydro-4,7,7-trimethylspiro[bicyclo[2.2.1]heptane-2,2′-indan]-3-one (**14**)[30,32]) with a benzene solution of **1** at 110—130 °C for 3—4 d under an Ar atmosphere gave the corresponding selones, **15**,[8,33—37] **17**,[23] and **19** in 35, 33, and 38% yields, respectively, as deep blue oil (**17**) or deep blue crystals (**15**, **19**), as given in Table 3. In each case, an inseparable mixture of stereoisomers of diselenides, **16**, **18**, or **20**, was also afforded in 5—41% combined yields along with the selones and the recovery of the starting ketones (about 20—30% yields); the isomeric ratios of diselenides **16**, **18**, or **20** were about 2 : 1, which were estimated from integrating the ^{1}H NMR signals of the methine protons adjacent to the selenium atoms. The physical data concerning **15** were identical in all respects with those of the reported data, and the physical data of **17** and **19**, including MS, IR, ^{1}H NMR, and ^{13}C NMR spectra, were also fully consistent with the structures of the selones. Especially the ^{13}C NMR spectra of **17** and **19** showed significant singlet signals of the selenocarbonyl carbons at the δ = 290—300 ppm region.[35—37]

In contrast to the case for the conversion of ketone **13** to the corresponding selone **17** using **1**, all attempts to convert **13** to **17** using our previously reported methods, in which $[(CH_3)_3Si]_2Se$–BF_3·OEt_2[9] or $[(CH_3)_2SnSe]_3$-BF_3·OEt_2-$AlCl_3$[12] was treated with a ketone, were unsuccessful. These results clearly demonstrated that reagent **1** possesses a strong ability to undergo oxygen–selenium exchange reactions toward sterically hindered ketones. It was assumed that the Lewis-acid character of **1** caused an elec-



Scheme 4.

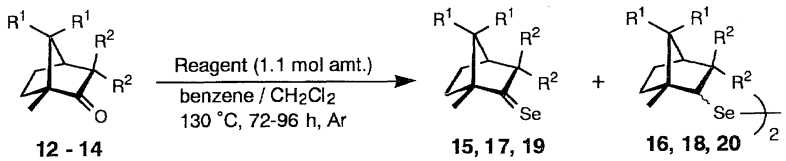
Table 2. Synthesis of Selenocarbonyl Compounds by Treating Carboxylic Acid Derivatives with Bis(1,5-cyclooctanediylboryl) Selenide (**1**)[a]



Substrate			Solvent	Temp	Time	Yield/%[b]			
R^1	R^2	6,7		°C	h	8,9	10	11	6,7
H	$N(CH_3)_2$	**6a**	Toluene	R.T.	24	39 (**8a**)	—[c]	—[c]	0
H	$N[CH(CH_3)_2]_2$	**6b**	Benzene/CH_2Cl_2[d]	110	1	16 (**8b**)	—[c]	—[c]	0
CH_3	$N(CH_3)_2$	**6c**	Mesitylene/$CHCl_3$[e]	63	5	34 (**8c**)	—[c]	—[c]	0
C_6H_5	$N(CH_3)_2$	**6d**	Benzene/CH_2Cl_2[d]	Reflux[f]	18	0 (**8d**)	28 (**10d**)	6 (**11d**)	28[g]
C_6H_5	$N(CH_3)_2$	**6d**	Mesitylene	60	5	0 (**8d**)	25 (**10d**)	—[c]	67[g]
C_6H_5	OC_2H_5	**7**[h]	Benzene/CH_2Cl_2[d]	130	10	14 (**9**)	—[c]	—[c]	81[g]

a) All reactions were carried out in a sealed tube. b) Isolated yields. c) Not isolated. d) Benzene : dichloromethane (v/v) = 1 : 1. e) Mesitylene : chloroform (v/v) = 1 : 1. f) The reaction mixture was heated at refluxing temperature under an Ar atmosphere. g) A trace amount of dibenzyl diselenide (**5d**) was obtained. h) The reaction was performed in the presence of 24 molar amount of 2,3-dimethyl-1,3-butadiene.

Table 3. Synthesis of Selones by Treating Sterically Hindered Ketones (**12**—**14**) with Bis(1,5-cyclooctanediylboryl) Selenide (**1**)[a]



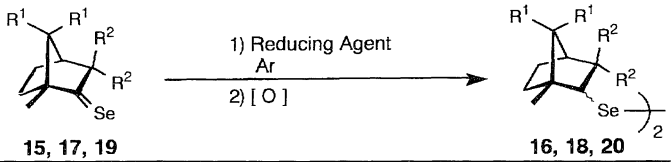
Substrate			Reagent	Yield/%[b]		
R^1	R^2			Selone	Diselenide[c] (ratio)[d]	Recovery
H	CH_3	**12**	**1**	5 (**15**)	41 (**16**)[e]	10
CH_3	$-(CH_2)_4-$	**13**	**1**	3 (**17**)	16 (**18**, 2 : 1 : 1)	25
CH_3	*o*-$C_6H_4(CH_2-)_2$	**14**	**1**	8 (**19**)	5 (**20**)[e]	20
CH_3	$-(CH_2)_4-$	**13**	$(Me_3Si)_2Se-BF_3\cdot OEt_2$	0 (**17**)	0 (**18**)	Quant.
CH_3	$-(CH_2)_4-$	**13**	$(Me_2SnSe)_3-BF_3\cdot OEt_2-AlCl_3$	0 (**17**)	0 (**18**)	Quant.

a) All reactions were carried out in a sealed tube. b) Isolated yields. c) Combined yields of the distereomeric mixture of diselenides. d) The ratios of *exo,exo* : *exo,endo* : *endo,endo*-diselenides were estimated from the integration of the ^1H NMR spectra of the crude mixtures. e) The ratio of the isomers was not determined.

tronic interaction between the alkylboryl moiety of **1** with the carbonyl oxygen atoms, and that the B–O interaction might overcome the steric interaction between the reagent and the substrates, even if the carbonyl groups of the substrates were highly hindered.[8] It is also noteworthy that the conversion of **13** and **14** into the corresponding hydrazones was completely unsuccessful based on a treatment with hydrazine monohydrate, in contrast to the case of *d*-fenchone (**12**), due to the steric hindrance of the carbonyl moiety of **13** and **14**. Thus, the methods of Barton[34] and Guziec,[35] in which the treatment of ketone hydazones with diselenium dihalides, such as Se_2Br_2 or Se_2Cl_2, was included in the procedure, were unable to be applied to the synthesis of selones **17** and **19**. In addition, **17** and **19** were very stable toward exposure to air and the irradiation of sunlight, in contrast to **15**, which gradually decomposed to *d*-fenchone (**12**) with the extrusion of elemental selenium during storage under aerobic conditions. Treating these ketones with reagent **1** in the presence of an excess amount of 2,3-dimethyl-1,3-butadiene gave only the same selones, **15**, **17**, or **19**, respectively, and no [4+2] cycloadducts originating from the selones were found in the reaction mixture in all cases. These results indicated that the steric protection was much effective for stabilizing these selones toward various reagents.

Treating a THF solution of selones, **15**, **17**, or **19**, with an excess amount of lithium aluminum hydride at room temperature, followed by exposing the reaction mixture to air, gave an inseparable mixture of the stereoisomers of diselenides **16**, **18**, or **20**, respectively (Table 4); also the ^1H NMR spectra of these diselenides were identical to those of the major stereoisomers of the diselenides afforded as by-products of the reactions of **12**—**14** with **1**. Especially, the treatment of a THF solution of **17** or **19** with super hydride ($LiEt_3BH$, 2.2 mol amt.) in place of lithium aluminum hydride predominantly afforded *exo*-diselenides, **18** or **20**, respectively. The ^1H NMR spectra of **18** and **20** revealed sharp singlet signals

Table 4. Reduction of Selones **15**, **17**, and **19** with Various Reducing Agents[a)]



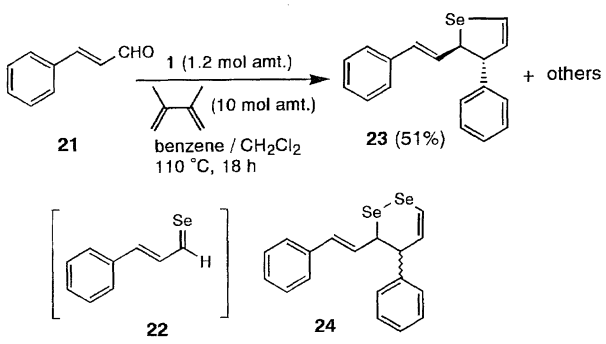
15, 17, 19 **16, 18, 20**

Selone			Reducing agent		Solvent	Temp	Time	Yield/%[b)]		
R^1	R^2		(mol amt.)			°C	h	Diselenide (ratio)[c,d)]		Recovery
H	CH_3	**15**	$LiAlH_4$	(20)	THF	R.T.	7	Quant.	(**16**)[e)]	0
CH_3	$-(CH_2)_4-$	**17**	$LiAlH_4$	(20)	THF	R.T.	4	73	(**18**, 2 : 1 : 1)	0
CH_3	$-(CH_2)_4-$	**17**	$LiEt_3BH$	(2.2)	THF	Reflux	7	70	(**18**, 50 : 1 : 1)[f)]	0
CH_3	$-(CH_2)_4-$	**17**	9-BBN	(2.2)	THF	R.T.	21	15	(**18**, 2 : 1 : 1)	78
CH_3	$-(CH_2)_4-$	**17**	NaTeH	(2.2)[g)]	CH_3OH	50	4	20	(**18**, 2 : 1 : 1)	68
CH_3	$-(CH_2)_4-$	**17**	Et_3SiH	(2.2)[h)]	Hexane	Reflux	22	7	(**18**, 2 : 1 : 1)	84
CH_3	$o-C_6H_4(CH_2-)_2$	**19**	$LiEt_3BH$	(2.2)	THF	Reflux	3	76	(**20**)[i)]	0

a) All reactions were performed by treating selones with a reducing agent under the condition shown in the table, and the resulting reaction mixtures were exposed to air with vigorous stirring. b) Isolated yields. c) Combined yields of the stereoisomers. d) The ratios of *exo,exo* : *exo,endo* : *endo,endo*-diselenides were estimated from the integration of the ^{1}H NMR spectra of the crude mixtures. e) **16** was afforded as a single isomer, and the stereochemistry of **16** was assumed to be *endo,endo* by the method as mentioned in the text. f) *Exo,exo*-**18** was obtained in 64% yield after recrystallization. g) Prepared by treating elemental tellurium with $NaBH_4$ in water under an Ar atmosphere, and then a methanolic solution of **17** was added to the reaction mixture. h) A hexane solution of **17** was treated with Et_3SiH (2.2 mol. amt.) and AIBN (0.22 mol amt.) at refluxing temperature. i) The isomeric ratio of **20** was not determined. However, *exo,exo*-**20** was obtained in 64% yield after recrystallization of the crude product.

at $\delta = 3.29$ and 2.70, respectively, and both signals were assigned to the *endo* protons at the C-3 position, lacking the W-type long-range coupling. An NOE experiment of **18** also revealed the signal of an *endo* proton at the C-3 position located near to the *endo* proton at the C-5 or C-6 position. On the other hand, the ^{1}H NMR spectrum of **16** revealed a sharp doublet at $\delta = 3.10$; the J value of the signal, probably due to the W-coupling of the *exo* proton at the C-3 position, was 3.0 Hz. However, the stereochemistry of **16** was not finally determined based on the physical data. In any case, it was indicated that the nucleophilic attack of super hydride from the less hindered side of the selone moiety of **15**, **17**, and **19** afforded *endo, endo*-**16**, *exo,exo*-**18**, and *exo,exo*-**20**, respectively, with excellent stereoselectivity.[32,38,39)] On the other hand, the treatment of selone **17** with other reducing agents, such as NaTeH, 9-BBN, or Et_3SiH–AIBN, only gave a mixture of stereoisomers of **18** with low stereoselectivity, and the isomeric ratios of **18** were similar to those of the diselenides **18** given as the by-products of the reaction of **14** with **1**. From these results (as shown above), it has become apparent that selones **15**, **17**, and **19** were easily reduced to give selenolate ions by a further reduction of selones with reagent **1** and by the treatment of selones with various reducing agents. The lower stereoselectivity of the reduction of selones with **1**, in contrast to the case of using a super hydride reduction, suggested that the reduction might proceed through either a selenophilic attack of **1** to the selenium atoms of the selones or through a non-ionic, electron-transfer process.

Treatment of Cinnamaldehyde with Bis(1,5-cyclooctanediylboryl) Selenide (1). The treatment of a dichloromethane solution of cinnamaldehyde (**21**) with a benzene solution of **1** at 110 °C for 18 h in a sealed tube under an Ar atmosphere afforded an unexpected heterocyclic compound, 3-phenyl-2-styryl-2,3-dihydroselenophene (**23**), in 44% yield along with a trace amount of the isomeric compound of **23** (Scheme 5). The treatment of **21** with **1** in the presence of an excess amount of 2,3-dimethyl-1,3-butadiene in a similar manner also afforded the same product **23** in 51% yield. All of the physical data, including the MS, IR, ^{1}H NMR, and ^{13}C NMR spectra, were fully consistent with the structure of **23**. The relative stereochemistry of the substituents at the C-2 and C-3 positions was also determined to be *trans* by an NOE experiment, in which no NOE was observed between two protons at the C-2 and C-3 positions. Segi has already reported on the conversion of cinnamaldehyde into a mixture of stereoisomers of 1,2-diselenin derivative **24** (major : minor = 82 : 18, however, the relative configurations of the isomers were not determined),[40)] the [4+2]-type self-condensed dimer of 3-phenyl-2-propeneselenal (**22**), by treating with $(Me_2Al)_2Se$. Actually, the extrusion of elemental selenium from the reaction mixture and the crude product resulting from the reaction of **21** with **1** was observed dur-



Scheme 5.

ing the steps of the workup and chromatographic purification. Based on the results, it was suggested that **23** could be formed by the selenium extrusion of the initially formed **24**, and that the stereoisomeric mixture of in situ formed **24** might afford a mixture of *trans*-**23** and *cis*-**23**, from which *trans*-**23** was finally isolated, probably due to the easily crystallizing nature of *trans*-**23**. It was assumed that the minor isomer of **23** might be excluded out during the usual chromatographic purification and recrystallization steps. However, the treatment of **21** with **1** under milder reaction conditions only gave the recovery of **21**, and attempts to isolate **24** from **21** and **1** were not successful at all in our case.

Conclusion. In conclusion, various selenocarbonyl compounds were efficiently synthesized by treating carbonyl compounds with a solution of bis(1,5-cyclooctanediylboryl) selenide (**1**), prepared from 9-borabicyclo[3.3.1]nonane (9-BBN) with elemental selenium. Further applications of the sterically hindered selones, **17** and **19**, for the chiral auxiliary of asymmetric syntheses are now in progress in our laboratory.

Experimental

Instruments. The melting points were determined with a Büchi 535 micro-melting-point apparatus. ^{1}H NMR spectra were recorded on a Hitachi R-22 (90 MHz) or a Bruker AC-400P (400 MHz) spectrometer, and the chemical shifts of the ^{1}H NMR spectra are given in δ relative to internal tetramethylsilane (TMS). ^{13}C NMR spectra were recorded on a Bruker AC-400P (100 MHz). Mass spectra were recorded on a Hitachi M-2000 mass spectrometer with electron-impact ionization at 20 or 70 eV using a direct inlet system. IR spectra were recorded for thin-film (neat) or KBr disks on a JASCO FT/IR-7300 spectrometer. The optical rotations were recorded on a JASCO DIP-1000 digital polarimeter. Elemental analyses were performed using a Yanagimoto MT-3 CHN analyzer.

Materials. Column chromatography was performed using silica gel (Merck, Cat. No. 7734 or 9385) without a pretreatment. Dichloromethane and chloroform were dried over P_4O_{10}, and were freshly distilled before use. Benzene, toluene, hexane, and mesitylene were dried over CaH_2 and freshly distilled before use. All of the substrates and reagents (including elemental selenium, elemental tellurium, 9-borabicyclo[3.3.1]nonane dimer (9-BBN), 2,3-dimethyl-1,3-butadiene, benzaldehyde, *p*-chlorobenzaldehyde, *p*-anisaldehyde, acetophenone, propiophenone, benzophenone, fluorenone, cinnamaldehyde, *d*-fenchone, *d*-camphor, 1,4-dibromobutane, *o*-phenylenebis(methylene) dichloride, *N,N*-dimethylformamide, *N,N*-diisopropylformamide, *N,N*-dimethylacetamide, *N,N*-dimethylbenzamide, ethyl benzoate, sodium amide, lithium aluminum hydride, super hydride ($LiEt_3BH$), sodium borohydride, triethylsilane, 2,2′-azobis(isobutyronitrile) (AIBN), and hydrazine monohydrate) were commercially available reagent grade, and were used without any pretreatment.

Preparation of Bis(1,5-cyclooctanediylboryl) Selenide (1). A benzene, toluene, or mesitylene solution (50 ml) of 9-borabicyclo[3.3.1]nonane (805 mg, 3.30 mmol) was treated with selenium powder (261 mg, 3.30 mmol) under an Ar atmosphere, and the reaction mixture was sealed in an autoclave and then heated at 150 °C for 2 h. After cooling the reaction mixture to room temperature, the resulting yellow solution was subjected to a direct treatment with various substrates without the isolation of **1**.

General Procedure for the Treatment of Aldehydes and Ketones with Bis(1,5-cyclooctanediylboryl) Selenide (1) in the Presence of an Excess Amount of 2,3-Dimethyl-1,3-butadiene. A dichloromethane, a benzene, or a toluene solution of aldehydes or ketones (**2**, 3.00 mmol) was treated with a benzene or toluene solution (15 ml) of bis(1,5-cyclooctanediylboryl) selenide (**1**, 3.30 mmol) and an excess amount of 2,3-dimethyl-1,3-butadiene (1.478 g, 18.0 mmol); the reaction mixture was heated at 80—110 °C for several hours in a sealed tube. After cooling the reaction mixture to room temperature and treating with an aqueous $NaHCO_3$ solution, the reaction mixture was extracted with dichloromethane. The organic layer was washed with brine and dried over anhydrous Na_2SO_4. A crude yellow oil was obtained upon removing the solvent in vacuo. The resulting products were purified using column chromatography on silica gel to obtain 5,6-dihydro-2*H*-selenins **4** in high-to-modest yields along with a trace amount of the corresponding diselenides **5**.

4a (R^1=C_6H_5, R^2=H):[24,25] Yellow oil; MS *m/z* 252 (M^+; bp, ^{80}Se); IR (neat) 3027, 2915, 1600, 1493, 1451, 1160, 764, 697 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ = 1.74 (3H, s), 1.83 (3H, s), 2.48–2.75 (2H, m), 3.09 (1H, d, *J* = 14.7 Hz), 3.41 (1H, d, *J* = 14.7 Hz), 4.18 (1H, dd, *J* = 10.4, 4.0 Hz), 7.19—7.35 (5H, m); ^{13}C NMR ($CDCl_3$) δ = 19.8 (q), 20.7 (q), 24.1 (t), 38.5 (d), 40.8 (t), 124.7 (s), 126.8 (d), 127.4 (d), 128.5 (d), 129.3 (s), 143.5 (s). Found: C, 61.85; H, 6.38 %. Calcd for $C_{13}H_{16}Se$: C, 62.15; H, 6.42 %.

4b (R^1=*p*-ClC_6H_4, R^2=H): Yellow oil; MS *m/z* 286 (M^+; bp, ^{80}Se); IR (neat) 2988, 2915, 1490, 1407, 1089, 1014, 829, 738, 528 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ = 1.73 (3H, s), 1.82 (3H, s), 2.48 (1H, dd, *J* = 16.6, 3.1 Hz), 2.65 (1H, dd, *J* = 18.2, 9.5 Hz), 3.07 (1H, d, *J* = 14.8 Hz), 3.37 (1H, d, *J* = 14.8 Hz), 4.15 (1H, dd, *J* = 10.0, 4.1 Hz), 7.21—7.30 (5H, m); ^{13}C NMR ($CDCl_3$) δ = 19.7 (q), 20.7 (q), 23.9 (dd), 37.6 (d), 40.5 (dd), 124.9 (s), 128.5 (d), 128.7 (d), 129.0 (s), 132.3 (s), 142.1 (s). Found: C, 54.42; H, 5.20 %. Calcd for $C_{13}H_{15}ClSe$: C, 54.66; H, 5.29 %.

4c (R^1=*p*-$CH_3OC_6H_4$, R^2=H): Yellow oil; MS *m/z* 282 (M^+; bp, ^{80}Se); IR (neat) 2995, 2921, 1610, 1511, 1463, 1251, 831 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ = 1.76 (3H, s), 1.81 (3H, s), 2.47 (1H, dd, *J* = 16.8, 2.9 Hz), 2.68 (1H, dd, *J* = 13.6, 10.7 Hz), 3.06 (1H, d, *J* = 15.0 Hz), 3.75 (3H, s), 4.15 (1H, dd, J = 10.5, 3.9 Hz), 6.82 (2H, m), 7.26 (2H, m); ^{13}C NMR ($CDCl_3$) δ = 19.7 (q), 20.7 (q), 24.0 (t), 37.7 (d), 40.9 (t), 55.1 (q), 113.7 (d), 129.2 (d), 135.4 (s), 158.3 (s). Found: C, 59.65; H, 6.32 %. Calcd for $C_{14}H_{18}OSe$: C, 59.79; H, 6.45 %.

4d (R^1=C_6H_5, R^2=CH_3): Yellow oil; MS *m/z* 266 (M^+; 96%, ^{80}Se), 184 (M^+−Se; bp); IR (neat) 2890, 1590, 1490, 1440, 1370, 1150, 1100, 1030, 690 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ = 1.75 (3H, s), 1.78 (6H, br.s), 2.47 (1H, d, *J* = 17.0 Hz), 2.81 (1H, d, *J* = 17.0 Hz), 2.95 (1H, d, *J* = 15.2 Hz), 3.05 (1H, d, *J* = 15.2 Hz), 7.13—7.20 (1H, m), 7.21—7.30 (2H, m), 7.46—7.50 (2H, m); ^{13}C NMR ($CDCl_3$) δ = 19.8 (q), 21.1 (q), 23.8 (t), 30.7 (q), 42.3 (s), 47.0 (t), 123.8 (s), 126.2 (d), 126.4 (d), 127.9 (d), 128.2 (s), 147.4 (s). Found: C, 63.10; H, 6.72 %. Calcd for $C_{14}H_{18}Se$: C, 63.39; H, 6.84 %.

4e (R^1=C_6H_5, R^2=C_2H_5): Yellow oil; MS *m/z* 280 (M^+; 36%, ^{80}Se), 199 (M^+−Se; bp); IR (neat) 2900, 1590, 1480, 1440, 1370, 1150, 1070, 1030, 690 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ = 0.75 (3H, t, *J* = 7.5 Hz), 1.73 (3H, br.s), 1.77 (3H, br.s), 2.02 (1H, dq, *J* = 14.4, 7.5 Hz), 2.14 (1H, dq, *J* = 14.4, 7.5 Hz), 2.64 (1H, br.d, *J* = 17.0 Hz), 2.75 (1H, br.d, *J* = 17.0 Hz), 2.87 (1H, br.d, *J* = 15.0 Hz), 2.92 (1H, br.d, *J* = 15.0 Hz), 7.13—7.31 (3H, m), 7.40—7.44 (2H, m); ^{13}C NMR ($CDCl_3$) δ = 9.3 (q), 19.8 (q), 21.1 (q), 23.2 (t), 36.2 (t), 43.5 (t), 48.3 (s), 124.3 (s), 126.0 (d), 127.3 (d), 127.8 (d), 128.0 (s), 145.0 (s). Found: C, 64.17; H, 7.06 %. Calcd for $C_{15}H_{20}Se$: C, 64.51; H, 7.22 %.

4f (R^1=R^2=C_6H_5):[26] Yellow oil; MS *m/z* 328 (M^+; 23%, ^{80}Se), 247 (M^+−Se; bp); IR (neat) 3057, 2912, 1599, 1491, 1444, 1085, 1033, 747, 697 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ = 1.70 (6H, s), 2.84 (2H, br.s), 2.94 (2H, br.s), 7.15 (2H, d, *J* = 7.15 Hz), 7.21 (4H, dd, *J* = 7.7, 7.1 Hz), 7.32 (1H, d, *J* = 7.7 Hz); ^{13}C NMR ($CDCl_3$) δ = 20.0 (q), 20.7 (q), 24.6 (t), 47.6 (t), 51.8 (s), 124.5 (s), 126.4 (d), 127.9 (d), 128.2 (d), 128.8 (s), 147.0 (s). Found: C, 69.47; H, 6.02 %. Calcd for $C_{19}H_{20}Se$: C, 69.72; H, 6.16 %.

4g (R^1=R^2=–C_6H_4–C_6H_4–): Yellow columns, mp 108.5—109.0 °C; MS *m/z* 326 (M^+; bp, ^{80}Se), 245 (M^+−Se; 57%); IR (KBr) 2850, 1440, 1410, 1090, 740 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ = 1.78 (3H, br.s), 2.04 (3H, br.s), 2.67 (2H, br.s), 3.56 (2H, br.s), 7.23—7.39 (4H, m), 7.46—7.51 (2H, m), 7.70—7.74 (2H, m); ^{13}C NMR ($CDCl_3$) δ = 19.8 (q), 21.6 (q), 24.5 (t), 43.0 (t), 48.7 (s), 120.1 (d), 124.1 (d), 126.0 (s), 127.6 (d), 129.4 (s), 138.4 (s), 151.1 (s). Found: C, 70.04; H, 5.59 %. Calcd for $C_{19}H_{18}Se$: C, 70.15; H, 5.58 %.

Treatment of Benzaldehyde with Bis(1,5-cyclooctanediylboryl) Selenide (1) in the Absence of a Diene. To a dichloromethane solution of benzaldehyde (319 mg, 3.00 mmol) was added a benzene solution (15 ml) of bis(1,5-cyclooctanediylboryl) selenide (**1**, 3.30 mmol); the reaction mixture was then heated at 110 °C for 5 h in a sealed tube. After cooling to room temperature, and adding an excess amount of aqueous $NaHCO_3$ solution, the reaction mixture was subjected to the usual workup. The crude products were then purified using column chromatography on silica gel to obtain dibenzyl diselenide (**5a**, 225 mg, 44 %)[27] as yellow needles along with the recovered benzaldehyde (156 mg, 49 %).

General Procedure for the Treatment of Amides with Bis(1,5-cyclooctanediylboryl) Selenide (1). A dichloromethane or chloroform solution (15 ml) of amide (**6a**—**c**, 3.00 mmol) was treated with a benzene, a toluene, or a mesitylene solution (15 ml) of bis(1,5-cyclooctanediylboryl) selenide (**1**, 3.30 mmol); the reaction mixture was then stirred in a sealed tube at room temperature or higher temperature for several hours. After cooling to room temperature and quenching the reaction with an aqueous $NaHCO_3$ solution, the reaction mixture was subjected to the usual workup. The crude product was purified using column chromatography on silica gel to obtain the corresponding selenoamides (**8a**—**c**)[3,13,41] in modest yields as a yellow oil or solid. All of the physical data of the products were fully consistent with those of the reported data.

General Procedure of mCPBA Oxidation of Selenoamides 8. To a dichloromethane solution (20 ml) of a selenoamide (**8**, 1.00 mmol) was added a dichloromethane solution of mCPBA (259 mg (80%), 1.20 mmol); the reaction mixture was stirred at 0 °C for 3 h. The reaction mixture was quenched with an aqueous Na_2SO_3 solution, and extracted with dichloromethane. The organic layer was washed with an aqueous $NaHCO_3$ solution and with water, and then dried over anhydrous Na_2SO_4 powder. After removing the solvent in vacuo, the residue was separated by column chromatography on silica gel using chloroform as an eluent to give the corresponding amides **4** in almost quantitative yields.

Treatment of *N,N*-Dimethylbenzamide (6d) with Bis(1,5-cyclooctanediylboryl) Selenide (1). A dichloromethane or a mesitylene solution (15 ml) of *N,N*-dimethylbenzamide (**6d**, 746 mg, 5.00 mmol) was treated with a benzene or a mesitylene solution (15 ml) of bis(1,5-cyclooctanediylboryl) selenide (**1**, 5.50 mmol); the reaction mixture was then heated at refluxing temperature for 18 h under an Ar atmosphere. After quenching the reaction with a 10% aqueous NaOH solution, the reaction mixture was subjected to the usual workup. The crude product was purified using column chromatography on silica gel to obtain *Se*-benzyl benzenecarboselenoate (**10d**, 196 mg, 28%) as a yellow oil, besides the recovery of amide **6d** (174 mg, 23 %) and a trace amount of dibenzyl diselenide (**5a**). The aqueous layer of the extract was then acidified using an excess amount of aqueous HCl solution, and extracted with chloroform; the organic layer was then subjected to a workup (as described above) under aerobic conditions. The crude product was purified by using column chromatography on silica gel to obtain dibenzoyl diselenide (**11d**, 86 mg, 6%) as colorless needles.

11d: Colorless needles, mp 130.0 °C (lit,[42,43] mp 131.0—132.0 °C).

Treatment of Ethyl Benzoate with Bis(1,5-cyclooctanediylboryl) Selenide (1). A dichloromethane solution of ethyl benzoate (**7**, 1.096 g, 2.00 mmol) was treated with a benzene solution (15 ml) of bis(1,5-cyclooctanediylboryl) selenide (**1**, 2.40 mmol) and an excess amount of 2,3-dimethyl-1,3-butadiene (3.94 g, 48.0 mmol); the reaction mixture was then heated at 130 °C for 10 h in a sealed tube. After cooling to room temperature and quenching the reaction with a 10% aqueous NaOH solution, the reaction mixture was subjected to the usual workup. The crude product was purified by using column chromatography on silica gel to obtain *O*-ethyl benzeneselenoate (**9**, 58 mg, 14 %)[11] and the recovered ester (**7**, 888 mg, 81%).

Preparation of Sterically Hindered Ketones 13 and 14. A hexane solution (100 ml) of *d*-camphor (30.4 g, 20.0 mmol) was treated with sodium amide (19.1 g, 50.0 mmol) and 1,4-dibromobutane (54.0 g, 25.0 mmol) or *o*-phenylenebis(methylene) dichloride (43.8 g, 25.0 mmol) at refluxing temperature for 48 h under an Ar atmosphere according to the methods of Fujikura[31] or Helmchem.[32] The reaction was then quenched with an excess amount of water, and the reaction mixture was subjected to the usual workup. The crude product was purified by distillation in vacuo to give 4,7,7-trimethylspiro[bicyclo[2.2.1]heptane-2,1′-cyclopentan]-3-one (**13**, 28.9 g, 71%, colorless oil) or 1′,3′-dihydro-4,7,7-trimethylspiro[bicyclo[2.2.1]heptane-2,2′-indan]-3-one (**14**, 23.6 g, 47 %, colorless oil).

13: Colorless oil, bp 131.0 °C/7 mmHg (1 mmHg = 133.322 Pa) (lit,[31] 130 °C/10 mmHg)); $[\alpha]_D^{26}$ = +77.2° (*c* 0.1, $CHCl_3$); MS *m/z* 206 (M^+; 64%), 163 (M^+−C_3H_6; 94%), 96 (bp); IR (neat) 2961, 1732, 1448 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ = 0.86 (3H, s), 0.87 (3H, s), 0.98 (3H, s), 1.38—1.48 (2H, m), 1.52—1.68 (7H, m), 1.72—1.85 (4H, m); ^{13}C NMR ($CDCl_3$) δ = 9.8 (q), 20.4 (q), 22.4 (q), 23.1 (t), 26.7 (t), 27.0 (t), 30.7 (t), 38.2 (t), 39.3 (t), 46.7 (s), 54.2 (d), 56.4 (s), 58.9 (s), 190.4 (s). Found: C, 81.45; H, 10.72 %. Calcd for $C_{14}H_{22}O$: C, 81.50; H, 10.75 %.

14: Colorless prisms, mp 92.7—93.6 °C, bp 220.0—225.0 °C/17 mmHg; $[\alpha]_D^{24}$ = +64.7° (*c* 0.01, $CHCl_3$); MS *m/z* 254 (M^+; bp), 116 (C_9H_8; 48%); IR (neat) 2964, 1732, 1589, 1489, 1444, 935, 758, 559 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ = 0.93 (3H, s), 0.99 (3H, s), 1.03 (3H, s), 1.45(1H, ddd, *J* = 14.0, 9.0, 6.0 Hz), 1.66 (1H, ddd, *J* = 12.0, 9.0 3.0 Hz), 1.75—1.99 (2H, m), 1.99 (1H, d, *J* = 4.0 Hz), 2.98 (1H, d, *J* = 16.0 Hz), 3.09 (1H, d, *J* = 16.0 Hz), 3.20 (1H, d, *J* = 16.0 Hz), 3.30 (1H, d, *J* = 16.0 Hz), 7.07—7.17 (4H, m); ^{13}C NMR ($CDCl_3$) δ = 9.9 (q), 20.8 (q), 22.7 (q), 23.3 (t), 30.0 (t), 42.3 (t), 46.0 (t), 46.6 (s), 53.3 (d), 57.7 (s), 58.8 (s), 123.6 (d), 123.8 (d), 126.4 (d), 141.0 (s), 141.8 (s), 192.9 (s). Found: C, 85.23; H, 8.99 %. Calcd for $C_{18}H_{22}O$: C, 84.99; H, 8.72 %.

General Procedure for the Treatment of Sterically Hindered Ketones with Bis(1,5-cyclooctanediylboryl) Selenide (1). A dichloromethane solution (15 ml) of ketone (**12**—**14**, 3.0 mmol) was treated with a benzene solution (15 ml) of bis(1,5-cyclooctanediylboryl) selenide (**1**, 3.30 mmol); the reaction mixture was then heated at 110—130 °C for 3—4 d in a sealed tube. After cooling

to room temperature, adding an excess amount of dichloromethane (1000 ml), and quenching the reaction with an excess amount of 10% aqueous NaOH solution (500 ml), the reaction mixture was subjected to the usual workup. A crude green oil was obtained upon removal of the solvent in vacuo, and was subjected to distillation in vacuo to separate a fraction containing selones and the starting ketones from the diastereomeric mixture of diselenides. Subsequently, the mixture containing selones and ketones was subjected to separation using column chromatography on silica gel; the final purification of the products either by distillation in vacuo or by recrystallization gave 1,3,3-trimethylbicyclo[2.2.1]heptane-2-selone (**15**, 35%, deep blue solid), 4,7,7-trimethylspiro[bicyclo[2.2.1]heptane-2,1′-cyclopentane]-3-selone (**17**, 33%, deep blue oil), or 1′,3′-dihydro-4,7,7-trimethylspiro[bicyclo[2.2.1]heptane-2,2'-indane]-3-selone (**19**, 38%, deep blue solid). On the other hand, attempts to perform a chromatographic separation of a mixture of diselenides, **16**, **18**, or **20**, were not successful in all cases. However, in particular, the ratio of three isomers of diselenide **18** (*exo,exo*-**18** : *exo,endo*-**18** : *endo,endo*-**18**) was estimated to be about 3 : 1 : 1 by integrating the ^{1}H NMR spectrum of the mixture.

15: Deep-blue solid, mp 42.0—43.0 °C (lit,[33,34] mp 41—47 °C). Selone **15** was identical in all respects with the authentic 1,3,3-trimethylbicyclo[2.2.1]heptane-2-selone (**15**) prepared alternatively by the treatment of *d*-fenchone hydrazone with Se_2Br_2 according to Guziec's method.[35]

17: Deep-blue oil, bp 130 °C/7 mmHg; $[\alpha]_D^{24} = +147.2°$ (*c* 0.1, $CHCl_3$); MS *m/z* 270 (M^+; 15%, ^{80}Se); IR (neat) 2990, 1450, 1080, 800 cm^{-1}; ^{1}H NMR ($CDCl_3$) $\delta = 0.84$ (3H, s), 1.04 (3H, s), 1.21 (3H, s), 1.34—1.39 (2H, m), 1.55—1.67 (4H, m), 1.82—2.00 (5H, m), 2.09—2.20 (2H, m); ^{13}C NMR ($CDCl_3$) $\delta = 15.4$ (q), 21.7 (q), 23.0 (q), 26.7 (t), 27.2 (t), 31.6 (t), 43.0 (t), 45.9 (t), 48.7 (s), 56.2 (d), 73.0 (s), 76.3 (s), 299.0 (s). Found: C, 62.18; H, 8.33 %. Calcd for $C_{14}H_{22}Se$: C, 62.44; H, 8.23 %.

19: Deep-blue solid, mp 45.1—48.0 °C, bp 170.0—175.0 °C/17 mmHg; $[\alpha]_D^{24} = -8.35°$ (*c* 0.01, $CHCl_3$); MS *m/z* 318 (M^+; 22%, ^{80}Se), 142 (bp); IR (neat) 2959, 1488, 1459, 1389, 1072, 742 cm^{-1}; ^{1}H NMR ($CDCl_3$) $\delta = 0.99$ (3H, s), 1.09 (3H, s), 1.25 (3H, s), 1.34—1.41 (2H, m), 1.77 (1H, dt, $J = 14.0$, 6.0 Hz), 1.89 (1H, dtd, $J = 13.0$, 9.0, 4.0 Hz), 2.27 (1H, d, $J = 4.0$ Hz), 3.21 (1H, d, $J = 16.0$ Hz), 3.26 (1H, d, $J = 15.0$ Hz), 3.39 (1H, d, $J = 16.0$ Hz), 3.49 (1H, d, $J = 15.0$ Hz), 7.08—7.16 (4H, m); ^{13}C NMR ($CDCl_3$) $\delta = 16.0$ (q), 22.0 (q), 22.4 (q), 23.5 (t), 30.7 (t), 47.5 (t), 48.4 (s), 51.3 (t), 55.6 (d), 73.2 (s), 76.3 (s), 123.3 (d), 123.6 (d), 126.4 (d), 141.0 (s), 142.1 (s), 294.2 (s). Found: C, 68.03; H, 7.13 %. Calcd for $C_{18}H_{22}Se$: C, 68.13; H, 6.99 %.

Conversion of Sterically Hindered Selones to the Corresponding Diselenides by Treating with Lithium Aluminum Hydride. A THF solution (20 ml) of selone (**15** or **17**, 1.00 mmol) was treated with an excess amount of lithium aluminum hydride (189 mg, 5.00 mmol), and was then stirred for several hours at room temperature. The reaction mixture was exposed to air at room temperature with the vigorous stirring overnight. Then, the reaction was quenched with water, and the reaction mixture was subjected to the usual workup to give a yellow oil. The crude products were purified using column chromatography on silica gel to obtain the diastereomeric isomers of diselenides, **16** or **18**, respectively, in quantitative yields. A ^{1}H NMR measurement of the products showed that these diselenides were identical with those of the by-products afforded by the reactions of the starting ketones with bis(1,5-cyclooctanediylboryl) selenide (**1**). In particular, further recrystallization of a mixture of **16** from hexane-dichloromethane afforded *endo,endo*-**16** in quantitative yield as pale-yellow needles. On the other hand, the isomeric ratio of *exo,exo*-**18** : *exo,endo*-**18** : *endo,endo*-**18** was estimated to be about 2 : 1 : 1 in the case of starting from **17**.

Conversion of Sterically Hindered Selones to the Corresponding Diselenides by Treating with Super Hydride. A THF solution (20 ml) of selone (**17** or **19**, 1.00 mmol) was treated with a THF solution of super hydride ($LiEt_3BH$, 2.2 ml of 1 M solution of THF, 2.20 mmol, 1 M = 1 mol dm^{-3}) and was stirred for several hours at refluxing temperature. The reaction mixture was exposed to air at room temperature with the vigorous stirring overnight. Then, the reaction was quenched with water, and the reaction mixture was subjected to the usual workup to give a yellow oil as a mixture of three chromatographically inseparable isomers of **18** or **20**. The isomeric ratio of *exo,exo*-**18** : *exo,endo*-**18** : *endo,endo*-**18** was estimated to be about 50 : 1 : 1 by integrating the ^{1}H NMR spectrum of the crude reaction product. On the other hand, the ratio of *exo,exo*-**20** : *exo,endo*-**20** : *endo,endo*-**20** was not clarified by a similar procedure owing to an overlapping of the signals of the benzyl methylene groups at the region of $\delta = 2.0$—3.0. The crude products were purified using column chromatography on silica gel followed by recrystallization using hexane–ethanol to obtain diselenides, *exo,exo*-**18** and *exo,exo*-**20**, in modest yields as the major stereoisomers.

Treatment of Selone 17 with NaTeH. A methanolic solution (20 ml) of selone (**17**, 200 mg, 0.74 mmol) was treated with an aqueous solution of NaTeH, prepared by a treatment of elemental tellurium (213 mg, 1.63 mmol) with sodium borohydride (134 mg, 3.54 mmol) in water (10 ml) under an Ar atmosphere; the reaction mixture was stirred at 50 °C for 4 h. The reaction mixture was then exposed to air at room temperature with vigorous stirring overnight. Then, the reaction was quenched with water, and the reaction mixture was subjected to the usual workup to give a yellow oil as a mixture of chromatographically inseparable isomers of **18** (40 mg, 20% combined yield) along with the recovery of selone **17** (135 mg, 68%). The isomeric ratio of *exo,exo*-**18** : *exo,endo*-**18** : *endo, endo*-**18**, estimated from integrating the ^{1}H NMR spectrum of the mixture, was about 2 : 1 : 1.

Treatment of Selone 17 with 9-BBN Dimer. A THF solution (20 ml) of selone (**17**, 200 mg, 0.74 mmol) was treated with 9-BBN dimer (199 mg, 1.63 mmol) at room temperature for 21 h under an Ar atmosphere. The reaction mixture was then exposed to air at room temperature with vigorous stirring overnight. Then, the reaction was quenched with water, and the reaction mixture was subjected to the usual workup to give a yellow oil as a mixture of chromatographically inseparable isomers of **18** (30 mg, 15% combined yield) along with the recovery of selone **17** (156 mg, 78%). The isomeric ratio of *exo,exo*-**18** : *exo,endo*-**18** : *endo,endo*-**18** estimated from the integration of the ^{1}H NMR spectrum of the mixture was about 2 : 1 : 1.

Treatment of Selone 17 with Triethylsilane-AIBN. A hexane solution (20 ml) of selone (**17**, 200 mg, 0.74 mmol) was treated with triethylsilane (190 mg, 1.63 mmol) and a catalytic amount of AIBN (22 mg, 0.163 mmol) at refluxing temperature for 22 h under an Ar atmosphere. The reaction mixture was then exposed to air at room temperature with vigorous stirring overnight. Then, the reaction was quenched with water, and the reaction mixture was subjected to the usual workup to give a yellow oil as a mixture of chromatographically inseparable isomers of **18** (14 mg, 7% combined yield) along with the recovery of selone **17** (168 mg, 84%). The isomeric ratio of *exo,exo*-**18** : *exo,endo*-**18** : *endo,endo*-**18** estimated from the integration of the ^{1}H NMR spectrum of the mixture was about 2 : 1 : 1.

***endo,endo*-16 (Major Isomer):** Yellow needles, mp 51.0—

51.5 °C; $[\alpha]_D^{25} = -79.8°$ (*c* 0.1, $CHCl_3$); MS *m/z* 434 (M^+; 2%, ^{80}Se), 137 (bp); IR (KBr) 2860, 1440, 1360, 720 cm^{-1}; ^1H NMR ($CDCl_3$) δ = 1.02 (6H, s), 1.09 (6H, s), 1.20 (6H, s), 1.05—1.15 (2H, m), 1.26 (2H, dd, *J* = 9.8, 1.3 Hz), 1.35—1.42 (4H, m), 1.59 (2H, br.d, *J* = 9.8 Hz), 1.59—1.65 (2H, m), 1.73—1.76 (2H, m), 3.10 (2H, d, *J* = 3.0 Hz, *exo*-H at C-2); ^{13}C NMR ($CDCl_3$) δ = 21.4 (q), 26.2 (q), 26.2 (t), 29.6 (t), 31.8 (q), 40.7 (s), 43.6 (t), 48.3 (d), 51.0 (s), 73.2 (d). Found: C, 55.34; H, 7.97 %. Calcd for $C_{20}H_{34}Se_2$: C, 55.55; H, 7.93 %.

***exo,exo*-18 (Major Isomer):** Yellow needles, mp 121.5—122.0 °C; $[\alpha]_D^{26} = -93.4°$ (*c* 0.1, $CHCl_3$); MS *m/z* 542 (M^+; 21%, ^{80}Se), 271 ($M^+/2$; 28%, ^{80}Se), 160 (bp); IR (KBr) 2961, 1444, 1389, 1373, 1215, 760 cm^{-1}; ^1H NMR ($CDCl_3$) δ = 0.83 (6H, s), 0.94 (6H, s), 1.04 (6H, s), 1.28—1.33 (2H, m), 1.47 (2H, br.d, *J* = 2.1 Hz), 1.51—1.85 (20H, m), 2.15—2.23 (2H, m), 3.29 (2H, s, *endo*-H at C-3); The NOE (about 10%) was observed between the signal of *endo* proton at C-3 position (δ = 3.29) with the signal revealing at δ = 1.28—1.33 that were assigned to the *endo* proton of C-5 or C-6 position. ^{13}C NMR ($CDCl_3$) δ = 17.4 (q), 21.4 (q), 22.8 (q), 24.0 (t), 24.4 (t), 25.5 (t), 38.4 (t), 39.4 (dd), 42.7 (t), 49.3 (s), 52.4 (s), 55.7 (s), 57.5 (d), 78.2 (d). Found: C, 62.11; H, 8.60 %. Calcd for $C_{28}H_{46}Se_2$: C, 62.21; H, 8.58 %. The ^1H NMR measurement showed that a trace amount of the inseparable mixture of *exo,endo*-**18** and *endo,endo*-**18** was contained in the crude reaction mixture along with *exo,exo*-**18**. *Exo,endo*-**18** and *endo,endo*-**18**: ^1H NMR ($CDCl_3$) δ = 3.23 (2H, s, *endo*-H at C-3), 3.42 (2H, d, *J* = 2.0 Hz, *exo*-H at C-3), 3.48 (2H, d, J = 2.0 Hz, *exo*-H at C-3).

***exo,exo*-20 (Major Isomer):** Yellow prisms, mp 221.0—222.8 °C; $[\alpha]_D^{26} = +22.98°$ (*c* 0.01, $CHCl_3$); MS *m/z* 638 (M^+; 3%, ^{80}Se), 319 ($M^+/2$; 2%, ^{80}Se), 239 (bp; $C_{18}H_{23}$); IR (KBr) 2960, 1485, 1459, 1385, 1225, 747 cm^{-1}; ^1H NMR ($CDCl_3$) δ = 0.80 (6H, s), 0.83 (6H, s), 0.96 (6H, s), 0.88—1.02 (2H, m), 1.49—1.59 (6H, m), 1.62 (2H, br.s), 2.70 (2H, s, *endo*-H at C-3), 2.75 (2H, d, *J* = 15.5 Hz), 2.87 (2H, d, *J* = 16.1 Hz), 3.19 (2H, d, *J*=15.5 Hz), 3.35 (2H, d, *J*=16.1 Hz), 7.07—7.15 (6H, m), 7.23—7.25 (2H, m); ^{13}C NMR ($CDCl_3$) δ = 16.6 (q), 21.6 (q), 22.5 (q), 24.1 (t), 37.6 (t), 46.9 (dd), 48.3 (dd), 49.4 (s), 51.9 (s), 57.1 (d), 57.3 (s), 76.5 (d), 123.5 (d), 124.0 (d), 125.7 (d), 126.4 (d), 141.7 (s), 144.4 (s). Found: C, 67.87; H, 7.40 %. Calcd for $C_{36}H_{46}Se_2$: C, 67.91; H, 7.28 %.

Treatment of Cinnamaldehyde with Bis(1,5-cyclooctanediylboryl) Selenide (1). A dichloromethane solution of cinnamaldehyde (**21**, 397 mg, 3.00 mmol) was treated with a benzene solution (15 ml) of bis(1,5-cyclooctanediylboryl) selenide (**1**, 3.60 mmol) and an excess amount of 2,3-dimethyl-1,3-butadiene (2.47 g, 30.0 mmol); the reaction mixture was then heated at 110 °C for 18 h in a sealed tube. After cooling to room temperature and quenching the reaction with an aqueous $NaHCO_3$ solution, the reaction mixture was subjected to the usual workup. The crude product was purified by using column chromatography on silica gel to afford *trans*-3-phenyl-2-styryl-2,3-dihydroselenophene (**23**, 240 mg, 51 %) as colorless needles.

23: Colorless needles, mp 105.5—106.0 °C; MS *m/z* 312 (M^+; 68%, ^{80}Se), 231 (M^+−Se; bp); IR (KBr) 1570, 1470, 1440, 1270, 1240, 1140, 1100, 1070, 1010, 960, 730, 670, 580 cm^{-1}; ^1H NMR ($CDCl_3$) δ = 4.13 (1H, dt, *J* = 7.5, 2.5 Hz), 4.66 (1H, dd, *J* = 9.6, 7.7 Hz), 6.08 (1H, dd, *J* = 6.4, 2.5 Hz), 6.30 (1H, d, *J* = 15.6 Hz), 6.54 (1H, dd, *J* = 15.6, 9.6 Hz), 6.84 (1H, dd, *J* = 6.4, 2.5 Hz), 7.19—7.38 (10H, m), when the signals assigned to the proton at C-3 position (δ = 4.13) was irradiated, no NOE was observed with the signal of the proton at C-2 position (δ = 4.66) and a 4% NOE was observed with the signal of the proton at C-4 position (δ = 6.08); ^{13}C NMR ($CDCl_3$) δ = 56.4 (d), 62.0 (d), 122.7 (d), 126.4 (d), 127.1 (d), 127.6 (d), 127.7 (d), 129.8 (d), 130.4 (d), 130.6 (d), 136.5 (s), 141.3 (s). Found: C, 69.73; H, 5.14 %. Calcd for $C_{18}H_{16}Se$: C, 69.45; H, 5.18 %.

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References

1) C. Collard-Charon and M. Renson, *Bull. Soc. Chim. Belg.*, **72**, 304 (1963).
2) K. A. Jensen and P. H. Nielsen, *Acta Chem. Scand.*, **20**, 597 (1966).
3) I. D. Rae and M. J. Wade, *Int. J. Sulfur Chem.*, **8**, 519 (1976).
4) J. Voss and F. R. Bruhn, *Liebigs Ann. Chem.*, **1979**, 1931.
5) K. Steliou and M. Mrani, *J. Am. Chem. Soc.*, **104**, 3104 (1982).
6) M. Segi, T. Nakajima, S. Suga, S. Murai, I. Ryu, A. Ogawa, and N. Sonoda, *J. Am. Chem. Soc.*, **110**, 1976 (1988).
7) M. Segi, M. Takahashi, T. Nakajima, S. Suga, S. Murai, and N. Sonoda, *Tetrahedron Lett.*, **29**, 6965 (1988).
8) M. Segi, T. Koyama, T. Nakajima, S. Suga, S. Murai, and N. Sonoda, *Tetrahedron Lett.*, **30**, 2095 (1989).
9) Y. Takikawa, A. Uwano, H. Watanabe, M. Asanuma, and K. Shimada, *Tetrahedron Lett.*, **30**, 6047 (1989).
10) M. Segi, A. Kojima, T. Nakajima, and S. Suga, *Synlett*, **1991**, 105.
11) M. Segi, T. Takahashi, H. Ichinose, M. L. Guang, and T. Nakajima, *Tetrahedron Lett.*, **33**, 7865 (1992).
12) K. Shimada, S. Okuse, and Y. Takikawa, *Bull. Chem. Soc. Jpn.*, **65**, 2848 (1992).
13) Y. Takikawa, H. Watanabe, R. Sasaki, and K. Shimada, *Bull. Chem. Soc. Jpn.*, **67**, 876 (1994).
14) R. A. Zingaro, "The Chemistry of Organic Selenium and Tellurium Compounds," ed by S. Patai, John Wiley & Sons, New York (1986), Vol. 1, p. 343, and the references cited therein.
15) W. Siebert and F. Riegel, *Chem. Ber.*, **106**, 1012 (1973).
16) F. Riegel and W. Siebert, *Z. Naturforsch., B*, **29B**, 719 (1974).
17) W. Siebert, E. Gast, F. Riegel, and M. Schmidt, *J. Organomet. Chem.*, **90**, 13 (1975).
18) W. R. Leonald and T. Livinghouse, *J. Org. Chem.*, **50**, 730 (1985).
19) C. D. Habben, *Chem. Ber.*, **119**, 9 (1986).
20) R. Köster, G. Seidel, R. Boese, and B. Wrackmeyer, *Chem. Ber.*, **121**, 1955 (1988), and the references cited therein.
21) C. D. Habben, *Chem. Ber.*, **121**, 1967 (1988).
22) R. Köster, G. Seidel, and M. Yalpani, *Chem. Ber.*, **122,**1815 (1989), and the references cited therein.
23) K. Shimada, N. Jin, M. Fujimura, Y. Nagano, E. Kudoh, and Y. Takikawa, *Chem. Lett.*, **1992**, 1843.
24) G. Erker, R. Hock, and R. Nolte, *J. Am. Chem. Soc.*, **110**, 624 (1988).
25) G. Erker, R. Hock, C. Krüger, S. Werner, F. Klärner, and U. Artschwager-Perl, *Angew. Chem., Int. Ed. Engl.*, **29**, 1067 (1990).
26) K. Okuma, J. Sakata, Y. Tachibana, T. Honda, and H. Ohta, *Tetrahedron Lett.*, **28**, 6649 (1987).
27) a) V. I. Cohen, *J. Org. Chem.*, **42**, 2510 (1977); b) J. W. Lewicki, W. H. H. Gunther, and J. Y. C. Chu, *J. Org. Chem.*, **43**, 2672 (1978).
28) K. S. Kochhar, D. A. Cottrell, and H. W. Pinnick, *Tetrahedron Lett.*, **24**, 1323 (1983).

29) K. Shimada, S. Akimoto, H. Itoh, H. Nakamura, and Y. Takikawa, *Chem. Lett.*, **1994**, 1743.
30) A. P. Krapcho, *Synthesis*, **1974**, 383.
31) Y. Fujikura, T. Kitsuki, and M. Nakajima, Eur. Patent Appl. EP 208994 (1987). Jpn. Kokai Tokkyo Koho, JP 63 99028 (1988).
32) G. Helmchen, A. Selim, D. Dorsch, and I. Taufer, *Tetrahedron Lett.*, **31**, 3213 (1983).
33) T. G. Back, D. H. R. Barton, M. R. Britten-Kelly, and F. S. Guziec, Jr., *J. Chem. Soc., Chem. Commun.*, **1975**, 539.
34) T. G. Back, D. H. R. Barton, M. R. Britten-Kelly, and F. S. Guziec, Jr., *J. Chem. Soc., Perkin Trans. 1*, **1976**, 2079.
35) F. S. Guziec, Jr., and C. A. Moustakis, *J. Org. Chem.*, **49**, 189 (1984).
36) R. Okazaki, A. Ishii, and N. Inamoto, *J. Chem. Soc., Chem. Commun.*, **1983**, 1429.
37) A. Ishii, R. Okazaki, and N. Inamoto, *Bull. Chem. Soc. Jpn.*, **61**, 861 (1988).
38) H. C. Brown and H. R. Deck, *J. Am. Chem. Soc.*, **87**, 5620 (1965).
39) a) Y. Fujikura, T. Kitsuki, and M. Nakajima, Jpn. Kokai Tokkyo Koho, JP 63 99028 (1988); b) T. Kitsuki and Y. Fujikura, Jpn. Kokai Tokkyo Koho, JP 02 121938 (1990).
40) M. L. Guang, M. Segi, and T. Nakajima, *Tetrahedron Lett.*, **33**, 3515 (1992).
41) L. Henriksen, *Synthesis*, **1974**, 501.
42) L. Szperl and W. Wiorogorski, *Rocz. Chem.*, **12**, 71 (1932).
43) H. Ishihara, S. Sato, and Y. Hirabayashi, *Bull. Chem. Soc. Jpn.*, **50**, 3007 (1977).