

Tetrahedron 55 (1999) 3191-3208

TETRAHEDRON

Asymmetric Electrophilic Methoxyselenenylations and Cyclizations with 3-Camphorseleno Derivatives

Thomas G. Back,* Brian P. Dyck and Siqiao Nan

Department of Chemistry, University of Calgary, Calgary, Alberta, Canada, T2N 1N4

Received 3 September 1998; revised 6 October 1998; accepted 7 October 1998

Abstract: A series of novel 3-camphor-based diselenides, differing in substitution at C-2, was prepared. The corresponding allyl selenides were used as protecting groups for the diselenide moieties in several subsequent transformations. The diastereoselective methoxyselenenylation of alkenes was achieved with methanolic selenenyl triflates derived from the camphor diselenides, of which the 2-keto analogue proved the most effective. Diastereoselective electrophilic cyclizations of unsaturated alcohols, carboxylic acids and amides were most effectively performed with the corresponding selenenyl chloride, containing a *spiro*-oxazolidinone moiety at C-2 of the camphor residue. The absolute configurations of several products were determined by reductive deselenization. © 1999 Elsevier Science Ltd. All rights reserved.

Dedicated to the memory of Professor Sir Derek H.R. Barton

Selenenyl chlorides and certain other electrophiles of general structure RSeX undergo 1,2-additions to olefins and related unsaturated substrates.^{1,2} Typically, these reactions proceed *via* bridged seleniranium ion intermediates, resulting in the stereospecific *anti* incorporation of the moieties RSe and X. When the addition is performed in the presence of an external nucleophile, the latter can react with the seleniranium ion, resulting in its incorporation into the product instead of the original leaving group X (Scheme 1).² The regiochemistry of such processes with unsymmetrical olefins generally favours formation of the corresponding Markovnikov adduct (where X or the external nucleophile attack the more substituted olefinic



carbon atom).^{2,3} Furthermore, when a nucleophile is tethered to the alkene substrate, intramolecular attack upon the seleniranium ion takes place, leading to a cyclized product^{2c,4} (Scheme 2). The term cyclofunctionalization has been employed to denote such processes.⁵ Removal of the selenium residue in the



final step can be accomplished reductively, or oxidatively by selenoxide *syn*-elimination, affording saturated or unsaturated products. The synthetic usefulness of these processes is well-established.^{2,4,5}

A recent variation of this chemistry consists of using a chiral moiety R^* instead of R in the original selenium electrophile to control the stereochemistry of new chiral centers developed during the process. This results in diastereoselective additions or cyclizations, ultimately leading to the enantioselective formation of deselenized products. Thus, asymmetric methoxyselenenylations,⁶ where the external nucleophile is methanol, and asymmetric cyclofunctionalizations^{6a,6g,6o,7} have attracted considerable recent interest, using a variety of chiral selenium electrophiles. We considered that the camphorseleno moiety might be particularly suitable for these types of reactions for several reasons. Both antipodes of camphor are commercially available and we recently reported the efficient preparation of diselenide 1a in one step from (*R*)-(+)-camphor and elemental selenium.⁸ The 2-keto group of 1a also provides the opportunity to modify the structure by, for example, introducing bulky substituents, groups capable of coordinating with the selenium atom at the adjacent site, or groups that can preorganize the reactants by hydrogen-bonding with the nucleophile. Moreover, the diselenide functionality can be used for conveniently generating a series of more powerful electrophiles. We now report the preparation of several modified camphorseleno diselenides, their conversion into selenenic electrophiles and an evaluation of their efficacy in methoxyselenenylations,^{9a,10} and cyclofunctionalizations.^{9b}

Preparation of Camphor Diselenides

Diselenide 1a was prepared on a scale of 50-100 g and was used as the starting material for diselenides 1b-1g. The vigorous conditions required for the reduction of ketone and nitrile functions at the C-2 position in subsequent transformations (*vide infra*) resulted in simultaneous cleavage of the C-Se bond when the diselenide moiety was present. To prevent this, an effective method for protecting the diselenide moiety¹¹ as the corresponding allyl selenide was devised and is shown in Scheme 3. Deprotection was achieved by oxidation, spontaneous [2,3]sigmatropic rearrangement of the resulting selenoxide¹² and reductive workup. Thus, diselenide 1a was protected as the allyl selenide 2, followed by cyanohydrin formation and reduction with lithium aluminum hydride (Scheme 4). The resulting amino alcohol 3 was then N-acetylated to 4 or cyclized to the corresponding *spiro*-oxazolidinone 5 with N,N'-carbonylbis(imidazole) (CBI). Deprotection was achieved by oxidation with *m*-chloroperbenzoic acid (MCPBA), followed by a [2,3]shift and workup with hydrazine to afford the desired modified diselenides 1b and 1c. The modified diselenide 1b contains an *endo* nucleophilic amido group in close proximity to the *endo* selenium atom. Coordination between electrophilic selenium centers and nucleophilic heteroatoms such as N or O have been shown to play a key role in the stereoselectivity manifested by other chiral auxiliary groups used in selenium chemistry.^{6a,6k,6n} On the other hand, the rigid *spiro*-oxazolidinone moiety at C-2 of 1c blocks access to one



Scheme 3

side of the selenium substituent at C-3. Thus, selenenic electrophiles derived from diselenides **1b** and **1c** might be expected to provide improved stereoselectivity compared to **1a**. Similarly, reduction of **2** with lithium aluminum hydride furnished a mixture of *exo* and *endo* alcohols (**6** and **8**, respectively), which afforded acetates **7** and **9**, respectively.

Deprotection of the allyl selenide group in the usual manner provided diselenides 1d and 1f, which afforded 1e and 1g after saponification (Scheme 4). Comparison of the stereoselectivities afforded by *exo* and *endo* alcohol isomers (or their acetates) was expected to reveal the effects of O-Se coordination, since the *endo* isomers are more suitably oriented for such interactions.



Methoxyselenenylations

A comparison of the different camphorseleno groups shown in Scheme 4 in asymmetric methoxyselenenylations was performed under a standard set of conditions in order to determine the best candidate for further optimization. Diselenides 1a-1g were converted *in situ* into the corresponding selenenyl triflates 10a-10g in dichloromethane-methanol at -78°C, followed by the addition of *trans*-5-decene (Scheme 5). The results are shown in Table 1. Under these conditions, the triflate 10b failed to react with the alkene to afford the adduct 11, but underwent cyclization to the corresponding selenenamide 12, which is a stable, isolable compound that has been reported previously.¹³ The *endo*-acetoxy and -hydroxy triflates 10f and 10g, respectively, also failed to afford 11, with substantial amounts of the parent diselenides being recovered after hydrolytic workup. A possible explanation for the failure of the latter to effect the methoxyselenenylation of the alkene is that cyclic species 13 and 14 were formed analogously to 12, but in this case underwent subsequent hydrolysis and disproportionation¹⁴ to produce the recovered diselenides 1f and 1g. Thus, strongly nucleophilic groups suitably positioned for forming intramolecular covalent bonds with the selenium atom of the camphorseleno triflates are incompatible with methoxyselenenylation. In contrast, the remaining selenenyl triflates 10a, 10c, 10d and 10e afforded the corresponding adducts 11a, 11c, 11d and 11e, respectively. Moreover, Table 1 indicates that triflate 10a provided both the highest yield of the correspon-



Scheme 5

ding adduct, as well as the highest diastereomeric ratio (d.r.). Since the parent diselenide 1a was produced in just one step from camphor and selenium, its superior effectiveness in this process is especially fortunate.

Attempts at optimization of the diastereoselectivity of the reaction with electrophiles derived from 1a with *cis*- and *trans*-5-decene are shown in Table 2. An increase in the temperature to -42° C lowered the d.r. significantly compared to -78° C, while lowering it further to -95° C had little effect. Ether and toluene as cosolvents gave comparable d.r.'s to those obtained in dichloromethane. The selenenyl chloride and bromide derived from 1a produced more complex product mixtures and the reaction with the relatively sluggish chloride had to be carried out at room temperature. The corresponding selenenyl tetrafluoroborate and hexafluorophosphate (generated *in situ* by use of AgBF₄ and AgPF₆ instead of AgOTf in Scheme 5) were comparable to the triflate 10a. Based on these results, we chose the conditions of entry 1 in Table 2 for further experiments with other alkenes.

decene with different selenenyl triflates					
entry R*SeOTf		isolated yield of 11 (%)	d.r. ^{b,c}		
1	10a	88	94:6		
2	10b	d			
3	10c	65	66:34		
4	10d	63	82:18		
5	10e	51	85:15		
6	10f	e			
7	10g	е			

Table 1.ª Methoxyselenenylation of trans-5-

(a) All reactions were performed in dichloromethane at -78°C. (b) d.r.=diastereomeric ratio. (c) Measured by NMR integration. (d) Triflate **10b** cyclized to **12**. (e) No methoxyselenenylation occurred under these conditions.

	\mathbf{Y}
Table 2. Methoxyselenenylation	A H
of cis- and trans-5-decene with	Sex

				<u> </u>	
entry	х	geometry	solvent	temp. °C	d.r. ^{a,b}
1	OTf	trans	CH ₂ Cl ₂	-78	94:6
2	OTf	trans	CH ₂ Cl ₂	-95	95:5
3	OTf	trans	CH ₂ Cl ₂	-42	83:17
4	OTf	trans	Et ₂ O	-78	92:8
5	OTf	trans	PhMe	-78	93:7
6	BF₄	trans	CH ₂ Cl ₂	-78	92:8
. 7	OTf	cis	CH ₂ Cl ₂	-78	75:25
8	BF₄	cis		-78	77:23
9	PF ₆	cis	CH ₂ Cl ₂	-78	78:22
10	Br	trans	CH ₂ Cl ₂	-78	С
11	CI	trans	CH ₂ Cl ₂	23	с

(a) d.r.=diastereomeric ratio. (b) Measured by NMR integration. (c) A complex mixture was obtained.

Table 3 shows that the procedure provides moderate to high d.r.'s with a series of alkyl-, aryl-, mono-, di- and trisubstituted alkenes. As observed previously with other chiral selenenic electrophiles,^{6a,6b,6h,6i} trans-olefins gave superior d.r.'s compared to *cis* olefins (see entry 1 vs. 2 and entry 3 vs. 4). It has been pointed out that it is the facial selectivity during the initial formation of the seleniranium ion intermediate that determines the diastereoselectivity of addition in the case of a *trans*-olefin. On the other hand, identical seleniranium ions are formed from attack of the electrophile upon the two faces of a

Table 3.ª Methoxyselenenylations of olefins with 10a

entry	substrate	product	isolated yield (%)	d.r. ^{b,c}
1	Bu	Bu SeR*	88	94:6
2	Bu Bu	Bu MeO SeR*	88	75:25
3	Ph	^{MeO} → ^{Ph} Ph SeR*	65 ^d	84:16
4	Ph_Ph	Ph → Ph MeO SeR*	66	69:31
5	Ph	OMe Ph SeR*	77	74:26
6	Ph	Ph SeR*	88	83:17
7	∕ ₀ ∕		71	81:19
8	\sim	MeO SeR*	69	87:13
9	\bigcirc		71	75:25
10	\bigcirc		9 0	84:16
11	Ph		73	86:14

(a) All reactions were performed in dichloromethane at -78°C.
(b) d.r. = diastereomeric ratio. (c) Measured by ¹H- or ⁷⁷Se-NMR integration. (d) The product contained a small amount of diselenide 1a after chromatography. The yield is based on NMR integration of the isolated product mixture.

symmetrical *cis*-olefin, and the diastereoselectivity is thus determined by the site of attack by the nucleophile upon the seleniranium ion in the productforming step.^{6f}

In each example in Table 3, the mixture of diastereomers was isolated by chromatography and the d.r. was determined by ¹H or ⁷⁷Se NMR integration. In the case of *cis*-stilbene (entry 4), the product could not be separated from a small amount of diselenide 1a that was formed as a byproduct and the reported yield is based on NMR integration of the isolated mixture.

The absolute configuration of the new stereocenter in the adduct derived from styrene (entry 5) was determined by reductive deselenization to 15 with triphenvltin hydride¹⁵ (Scheme 6). Comparison of the product by GC analysis on a chiral Cyclodex B column with authentic (R)-methyl ether 15, derived from the O-methylation of (R)-1-phenylethanol, indicated that the major enantiomer from the deselenization also had the R-configuration. Therefore, the corresponding stereocenter in the major diastereomer of the adduct had the S configuration. There was an excellent correlation between the d.r of the adduct (74:26) and the enantiomeric ratio (e.r.) of the deselenized product (72:28). The absolute configurations of new stereocenters in the other products in Table 3 are not known with certainty at this time.



Cyclofunctionalizations

The cyclofunctionalization of unsaturated alcohols and carboxylic acids was also investigated. These reactions can be performed with selenenyl chlorides 16, derived from the corresponding diselenides 1 with sulfuryl chloride, and generation of the more reactive triflates proved unnecessary. In order to evaluate the efficacy of various camphorseleno moieties, we performed cyclizations of two test substrates under identical conditions, in dichloromethane at -78° C. The results with 4-penten-1-ol and 4-pentenoic acid are shown in Table 4. It is interesting to note that the camphor auxiliary containing the 2-keto group that had provided the best results in methoxyselenenylations afforded very poor diastereoselectivity in cyclofunctionalizations (entry 1 and 2), whereas the *spiro*-oxazolidinone analogue proved highly effective in the latter processes (entry 5 and 6), but not in the former. Additional experiments revealed that again higher temperatures

Table 4.ª Cyclization of 4-penten-1-ol and 4pentenoic acid with selenenyl chlorides 16 D*CaCl

\sim	~∩н.	16	_ ×⇒⊂	
	X			
entry	R*SeCl	х	isolated yield (%)	d.r. ^{b,c}
1	16a	H,H	57	58:42
2		0	87	53:47
3	16b	H,H	66	71:29
4		0	73	73:27
5	16C	H,H	89	90:10
6		0	85	93:7
7	1 6e	H,H	99	52:48
8		0	81	51:49
9	16g	H,H	82	65:35
10		0	100	64:36

(a) All reactions were performed in dichloromethane at -78°C. (b) d.r. = diastereomeric ratio. (c) Measured by NMR integration.

resulted in lower d.r.'s while further cooling to -95°C gave comparable, or in some cases improved, diastereoselectivity. The use of ether, toluene or methanol as the solvent gave inferior results and the inclusion of triethylamine resulted in more complex product mixtures. With this information in hand, we proceeded to investigate the cyclization of other unsaturated alcohols and carboxylic acids in dichloromethane at -95 °C, using the selenenyl chloride 16c. The results are shown in Table 5.

Table 5 shows that d.r.'s ranging from modest to excellent are available with a wide variety of substrates. In general, mono- and 1,2-disubstituted alkenes gave the best results. In contrast to the methoxyselenenylations effected with 10a, and to cyclofunctionalizations reported with other chiral selenium electrophiles, 6a,7b cis-alkenes gave comparable or better d.r.'s than trans-alkenes.

In general, the reactions were performed at -95°C for 45 min, after which time the colour of the selenenvl chloride had disappeared. The mixtures were then warmed to room temperature and subjected to chromatography over silica-gel. Longer

reaction times were required for the consumption of the selenenyl chloride in entry 7 (4 h at -95°C) and 13 (8 h at -95°C and 12 h at room temperature). In several examples, NMR analysis of the crude mixture prior to chromatography indicated the presence of different products from the ones listed in Table 5. Thus, in entry 10, the corresponding 1,2-addition product (see Scheme 2) was tentatively identified, but it reacted further during chromatography to form the expected lactone shown in the Table. In entries 3 and 11, NMR spectra of the initial crude materials indicated mixtures of exo and endo cyclization products (see Scheme 2). In entry 11, equilibration to the exo-lactone shown in the Table again occurred during chromatography, while in entry 3, treatment with a catalytic amount of p-toluenesulfonic acid was required in order to complete the transformation to the corresponding exo cyclic ether.¹⁶ These observations are consistent with the following scenario. The overall stereochemical outcome of the process is determined by the facial selectivity in the initial step, leading to the formation of diastereomeric seleniranium ions, regardless of which of the three products in Scheme 2 is/are ultimately formed. This step requires low temperatures for optimum diastereoselectivity. Subsequent product formation via either the 1,2-addition pathway or via endo or exo cyclization is stereospecific (anti attack upon the seleniranium ion) and reversible. Thus, equilibration between the three products proceeds via the same seleniranium ion diastereomers, whose ratio remains unchanged. The diastereoselectivity is therefore established in the first step at -95°C, while the nature of the final product (1,2-, exo or endo) is determined subsequently and under thermodynamic control in the above protocol. Only the major products were isolated, characterized and shown in the Table.

The absolute configurations of two representative products in Table 5 from entries 2 and 10 were determined by tin hydride deselenization to afford products 17 and 18, which have known specific rotations.



Thus, it was established by polarimetry that the major enantiomer of 17 and 18 in each case had the S- configuration, and therefore the corresponding stereocenters in both selenides were R. (Scheme 7). There was again excellent agreement between the e.r.'s of the products and the d.r.'s of their selenide precursors. As with methoxyselenenylations, the extrapolation of these results to obtain the absolute configurations of new stereocenters in other products in Table 5 cannot be made with certainty.

entry	substrate	product	isolated yield (%)	d.r. ^{b,c}
1	<i>М</i> он	O SeR⁺	96	87:13
2	≁	{ ^O } SeR*	87	84:16
3	~~~он		92	85:15
4	∽∽он	 SeR* 	80	9 5:5
5	Сн		93	71:29
6	∙∕∕ он	∑ ⁰ ∫ SeR*	61	84:16
7	ООН		73	57:43
8	C CH		93	92:8
9	CO ₂ H	0_0_SeR*	87	91:9
10	CO ₂ H	0 ₹ ⁰ SeR*	81	>95:5
11	∽∽ ^{CO} 2 ^H	° ₹ ⁰ ↓ SeR•	80	89:11
12	<u> </u>	° ₹°,	78	91:9
13	С0⁵н	SeR*	66	67:33

Table 5.ª Cyclizations of alkenols and alkenoic acids with 16c

(a) All reactions were performed in dichloromethane at -95°C. (b) d.r. = diastereomeric ratio. (c) Measured by NMR integration, except in entry 7 where diastereomers were separated.

0

Ĥ

corresponding selenenyl chlorides, although equilibration of the initial product mixture is sometimes required to obtain optimum results. Both types of reaction give considerably higher diastereoselectivity at low temperatures. Furthermore, these mechanistically related processes place surprisingly different demands upon the C-2 substituent of the camphor moiety. Thus, while the 2-keto moiety of **10a** gave the best results in methoxyselenenylations and the *spiro*-oxazolidinone group of **16c** proved ineffective, the converse was

We also investigated the cyclofunctionalization of amide 19 and urethane 24 with selenenyl chloride 16c. Surprisingly, amide 19 did not furnish the corresponding lactam, but instead afforded other products dependent upon the conditions. Thus, under neutral conditions, the unstable 1.2-addition product 20 was obtained. When the reaction was performed in the presence of p-toluenesulfonic acid, or when 20 was exposed to silica-gel, the product was the lactone 22, identical to the product in entry 10 in Table 5. Finally, when the reaction was repeated in the presence of potassium t-butoxide, the hydroxy nitrile 23 was isolated. Evidently, the ambident amide nucleophile cyclizes through the carbonyl oxygen atom and generates the iminium ion 21, which undergoes hydrolysis or elimination to afford 22 and 23, respectively. It is noteworthy that all three products were obtained with very high d.r.'s (Scheme 8). Urethane 24, on the other hand, cyclized to the corresponding lactam 25 as expected. Unforunately, the d.r. could not be determined accurately by NMR integration because of overlapping signals. Consequently, the product was subjected to deselenization and the e.r. of the lactam 26 was determined by GC with a Cyclodex B column (Scheme 8).

Conclusions

In conclusion, these experiments show that camphor-based selenium electrophiles are useful reagents for asymmetric transformations. They afford modest to excellent diastereoselectivity in both methoxyselenenylations and cyclofunctionalizations, depending on the nature of the substrate. While methoxyselenenylations require selenium reagents with nonnucleophilic counterions (e.g. triflate), cyclofunctionalizations proceed efficiently with the true for cyclofunctionalizations. Further work is in progress to ascertain more precisely the role played by the C-2 substituent, which may include steric, coordination and/or hydrogen-bonding effects, in determining the stereoselectivity, and to extend this work to other types of asymmetric selenium chemistry.



Experimental Section

NMR spectra were recorded on a Bruker ACE 200 or AM 400 spectrometer in CDCl₃ solution unless otherwise indicated. Chemical shifts of ⁷⁷Se NMR spectra are reported relative to dimethyl selenide as the standard. Chromatography was performed on flash grade silica-gel. GC was performed on a 30 m Cyclodex B column (J & W Scientific Co.). Diselenide 1a was prepared as described previously.⁸ Ether (R)-15 was prepared by treating (R)-1-phenylethanol (Aldrich Chemical Co.) with NaH and methyl iodide in THF. It had an e.r. >98:2 when analyzed by GC on a chiral column. Other reagents were purchased and purified as required. Organic solutions were dried over anhydrous Na₂SO₄ or MgSO₄.

Allyl endo-3-camphoryl selenide (2). Sodium borohydride (4.14 g, 110 mmol) was added in portions to an ice-cooled solution of diselenide 1a (10.0 g, 21.7 mmol) in 200 mL of ethanol. The reaction mixture was stirred for an additional 1 h at room temperature. Allyl iodide (8.0 mL, 88 mmol) was added and stirring was continued for 45 min. The mixture was poured into 500 mL of ether, washed with 5% HCl solution, three times with water and brine, and was dried and concentrated *in vacuo*. The residue was chromatographed (elution with 10% ethyl acetate-hexanes) to afford 10.9 g (92%) of 2 as a pale yellow oil: IR (film) 1735, 1630 cm⁻¹; ¹H NMR δ 6.04-5.83 (m, 1 H), 5.13-5.01 (m, 2 H), 3.64-3.61 (m, 1 H), 3.57 (dd, J = 12.0, 8.6 Hz, 1 H), 3.30 (ddd, J = 11.4, 7.5, 0.7 Hz, 1 H), 2.17-2.13 (m, 1 H), 1.94-1.40 (m, 4 H), 1.02 (s, 3 H), 0.93 (s, 3 H), 0.90 (s, 3 H); mass spectrum, *m/z* (relative intensity) 272 (42, M⁺), 231 (3), 152 (82), 41 (100). Anal. calc'd. for C₁₃H₂₀OSe: C, 57.56; H, 7.43. Found: C, 57.59; H, 7.39.

Amino alcohol 3. A mixture of selenide 2 (18.9 g, 69.8 mmol), trimethylsilyl cyanide (10.2 mL, 76.5 mmol) and ZnI₂ (2.23 g, 6.99 mmol) was stirred for 2 days. The mixture was diluted with 300 mL of ether, washed twice with water and brine, dried, filtered through Celite and concentrated *in vacuo* to afford 24.8 g (96%) of the corresponding cyanohydrin trimethylsilyl ether, which solidified on standing: mp 49-53°C; IR (film) 2228, 1630 cm⁻¹; ¹H NMR δ 5.94-5.85 (m, 1 H), 5.08-5.04 (m, 1 H), 5.00-4.98 (m, 1 H), 3.45 (dd, *J*= 3.7, 1.9 Hz, 1 H), 3.22 (d, *J*= 7.5 Hz, 1 H), 3.20 (d, *J*= 8.1 Hz, 1 H), 1.84-1.81 (m, 1 H), 1.77-1.53 (m, 4 H), 1.07 (s, 3 H), 0.96 (s, 3 H), 0.95 (s, 3 H), 0.27 (s, 9 H); mass spectrum, *m/z* (relative intensity) 371 (8, M⁺),

330 (2), 250 (62), 151 (13), 95 (84), 83 (100). Anal. calc'd. for $C_{17}H_{29}NOSeSi$: C, 55.12; H, 7.89; N, 3.78. Found: C, 55.39; H, 7.54; N, 3.90.

The above cyanohydrin (24.0 g, 64.8 mmol) in 100 mL of anhydrous ether was added over 1 h to an ice-cooled suspension of 12.3 g (325 mmol) of LiAlH₄ in 100 mL of ether. The mixture was refluxed for 9 h and cooled to room temperature. Water (13 mL), 4 N NaOH solution (13 mL) and water (39 mL) were added cautiously with vigorous stirring. The mixture was filtered, the aqueous layer was removed, and the ether layer was dried and concentrated *in vacuo* to afford 20.1 g (100%) of 3 as a colourless oil: IR (film) 3395, 3305, 1630 cm⁻¹; ¹H NMR δ 5.97-5.84 (m, 1 H), 5.11-4.99 (m, 2 H), 3.39-3.36 (m, 1 H), 3.23-3.17 (m, 2 H), 2.96 (d, *J*= 12.4 Hz, 1 H), 2.53 (d, *J*= 12.4 Hz, 1 H), 1.80-1.75 (m, 1 H), 1.69-1.27 (m, 4 H); 1.21 (s, 3 H), 0.90 (s, 3 H), 0.83 (s, 3 H). The crude product was employed without further purification in subsequent procedures.

Acetamide 4. Amino alcohol 3 (5.20 g, 17.1 mmol) was stirred in 30 mL of a 2:1 mixture of of pyridine and acetic anhydride at room temperature for 16 h. The mixture was poured into 100 mL of ether, washed twice with 5% HCl solution and K₂CO₃ solution, dried and concentrated *in vacuo*. The residue was chromatographed (elution with 60% ethyl acetate-hexanes) to afford 4.98 g (84%) of 4 as a yellow oil: IR (film) 3309, 1649 cm⁻¹; ¹H NMR δ 6.22 (br s, 1 H), 6.05-5.84 (m, 1 H), 5.15-5.01 (m, 2 H), 3.81 (dd, *J*= 14.3, 7.8 Hz, 1 H), 3.43-3.39 (m, 1 H), 3.28-3.10 (m, 4 H), 2.04 (s, 3 H), 1.84-1.80 (m, 1 H), 1.66-1.22 (m, 4 H), 1.14 (s, 3 H), 0.95 (s, 3 H), 0.89 (s, 3 H); mass spectrum, *m/z* (relative intensity) 345 (3, M⁺), 304 (7), 224 (41), 109 (63), 72 (68), 43 (100). Anal. calc'd. for C₁₆H₂₇NO₂Se: C, 55.81; H, 7.90; N, 4.07. Found: C, 56.15; H, 7.98; N, 4.02.

Diselenide 1b. A suspension of 2.17 g (7.2 mmol) of 57% MCPBA in 10 mL of dichloromethane was added to a stirred solution of acetamide 4 (1.42 g, 4.13 mmol) in 50 mL of dichloromethane at -78° C. The mixture was warmed to -40° C over 25 min, and diethylamine was added until the mixture became homogeneous (ca. 4 mL). Ethyl vinyl ether (3 mL) was added and the mixture was maintained at -28° C for 4 h with occasional swirling. Hydrazine (0.65 mL, 20.7 mmol) was added and the mixture was stirred at room temperature for 30 min. The solution was diluted with 50 mL of dichloromethane, washed twice with 1.5 N NaOH solution, water and brine, dried and concentrated *in vacuo*. The product was chromatographed (elution with 10% methanol-ethyl acetate) to afford 1.13 g (90%) of **1b** as a yellow foam: IR (Nujol) 3291, 1635 cm⁻¹; ¹H NMR δ 6.18-6.07 (m, 2 H), 4.03-4.00 (m, 2 H), 3.70 (dd, *J*= 14.4, 7.2 Hz, 2 H), 3.55 (s, 2 H), 3.34 (dd, J= 14.4, 4.7 Hz, 2 H), 2.04 (s, 6 H), 2.08-2.03 (m, 2 H), 1.67-1.26 (m, 8 H), 1.17 (s, 6 H), 0.94 (s, 6 H), 0.90 (s, 6 H); mass spectrum, *m/z* (relative intensity) 608 (1, M⁺), 305 (10), 287 (16), 206 (64), 109 (65), 43 (100). Anal. calc'd. for C₂₆H₄₄N₂O₄Se₂: C, 51.48; H, 7.31; N, 4.62. Found: C, 51.22; H, 7.23; N, 4.55.

Oxazolidinone 5. Amino alcohol **3** (980 mg, 3.24 mmol) and N,N'-carbonylbis(imidazole) (579 mg, 3.57 mmol) were stirred in 5 mL of dry THF for 7 h at room temperature. The solution was poured into 50 mL of ether, washed with 5% HCl solution and brine, dried and concentrated *in vacuo*. The residue was chromatographed (elution with 60% ethyl acetate-hexanes) to afford 849 mg (80%) of **5** as a white powder: mp 112-113°C (from ethyl acetate-hexanes); IR (film) 3381, 1714, 1631 cm⁻¹; ¹H NMR δ 5.91 (br s, 1 H), 5.95-5.73 (m, 1 H), 5.09-5.00 (m, 2 H), 4.07 (d, *J*= 9.2 Hz, 1 H), 3.67 (dd, *J*= 3.8, 2.5 Hz, 1 H), 3.55 (d, *J*= 9.2 Hz, 1 H), 3.26-3.16 (m, 2 H), 1.96-1.92 (m, 1 H), 1.82-1.18 (m, 4 H), 1.14 (s, 3 H), 0.93 (s, 3 H), 0.91 (s, 3 H); mass spectrum, *m/z* (relative intensity) 329 (100, M⁺), 288 (16), 228 (21), 164 (23), 126 (27), 41 (36). Anal. calc'd. for C₁₅H₂₃NO₂Se: C, 54.88; H, 7.06; N, 4.27. Found: C, 54.58; H, 6.96; N, 4.25.

Diselenide 1c. The product1c was prepared in 75% yield from 5 by the same procedure as employed in the preparation of 1b: mp 278-282 °C (from ethanol); IR (Nujol) 3262, 1748 cm⁻¹; ¹H NMR δ 5.59 (br s, 2 H), 4.15 (dd, J= 3.9, 2.2 Hz, 2 H), 3.85 (d, J= 9.5 Hz, 2 H), 3.57 (d, J= 9.5 Hz, 2 H), 2.12-2.08 (m, 2 H), 1.64-1.25 (m, 6 H), 1.17 (s, 6 H), 1.11-1.04 (m, 2 H), 0.94 (s, 12 H); mass spectrum, m/z (relative intensity) 576 (11, M⁺), 369 (3), 208 (100), 164 (48), 147 (42), 41 (56). Anal. calc'd. for C₂₄H₃₆N₂O₄Se₂: C, 50.18; H, 6.32; N, 4.88. Found: C, 50.34; H, 6.25; N, 4.90.

exo-Alcohol 6 and endo-alcohol 8. Selenide 2 (5.01 g, 18.5 mmol) in 40 mL of dry ether was added over 5 min to an ice-cooled suspension of LiAlH₄ (2.11 g, 55.7 mmol) in 20 mL of dry ether. The mixture

was stirred for 4 h at room temperature. Water (2 mL), 4 N NaOH solution (2 mL) and water (6 mL) were cautiously added with vigorous stirring. The mixture was filtered, dried and concentrated *in vacuo*. The residue was chromatographed (elution with 20% ethyl acetate-hexanes) to afford 1.54 g (30%) of the *endo*-alcohol **8**, followed by 3.00 g (59%) of the *exo*-alcohol **6**, each obtained as a colourless oil.

exo-Alcohol **6**: IR (film) 3457, 1632 cm⁻¹; ¹H NMR δ 6.10-5.89 (m, 1 H), 5.15-4.98 (m, 2 H), 3.54 (d, J= 3.9 Hz, 1 H), 3.39-3.37 (m, 1 H), 3.26 (br d, J= 6.7 Hz, 2 H), 1.82-1.80 (m, 1 H), 1.80 (br s, 1 H), 1.69-1.51 (m, 4 H), 1.08 (s, 3 H), 0.89 (s, 6 H); mass spectrum, m/z (relative intensity) 274 (14, M⁺), 233 (5), 153 (9), 95 (34), 83 (90), 41 (100). Anal. calc'd for C₁₃H₂₂OSe: C, 57.14; H, 8.11. Found: C, 56.79; H, 7.63.

endo-Alcohol 8: IR (film) 3448, 1631 cm⁻¹; ¹H NMR δ 6.00-5.79 (m, 1 H), 5.10-4.99 (m, 2 H), 3.73-3.71 (m, 2 H), 3.13 (d, *J*=7.7 Hz, 2 H), 1.93-1.89 (m, 1 H), 1.83-1.55 (m, 2 H), 1.36-1.13 (m, 2 H), 0.95 (s, 3 H), 0.91 (s, 3 H), 0.89 (s, 3 H); mass spectrum, *m/z* (relative intensity) 274 (21, M⁺), 233 (8), 153 (15), 95 (41), 83 (100), 41 (71). Anal. calc'd. for C₁₃H₂₂OSe: C, 57.14; H, 8.11. Found: C, 57.34; H, 7.91.

exo-Acetate 7. Alcohol 6 (3.70 g, 13.6 mmol) was heated at 105°C in 50 mL of a 2:1 solution of pyridine and acetic anhydride for 14 h. The solution was cooled, poured into 100 mL of ether, washed three times with 5% HCl solution, water and brine, dried and concentrated *in vacuo* to afford 4.24 g (99%) of 7 as a yellow oil: IR (film) 1732, 1670 cm⁻¹; ¹H NMR δ 6.01-5.80 (m, 1 H), 5.04-4.96 (m, 1 H), 4.96-4.93 (m, 1 H), 4.82 (d, *J*= 4.0 Hz, 1 H), 3.44-3.42 (m, 1 H), 3.17 (d, *J*= 7.7 Hz, 2 H), 2.06 (s, 3 H), 1.86-1.84 (m, 1 H), 1.72-1.53 (m, 3 H), 1.38-1.21 (m, 1 H), 1.04 (s, 3 H), 0.90 (s, 3 H), 0.79 (s, 3 H). The crude product was employed without further purification in subsequent procedures.

endo-Acetate 9. Product 9 was obtained in 99% yield as a colourless oil from alcohol 8 via the same procedure used in the preparation of 7. IR (film) 1740, 1631 cm⁻¹; ¹H NMR δ 5.91-5.74 (m, 1 H), 5.06-4.94 (m, 3 H), 3.66 (ddd, J= 9.6, 4.2, 2.3 Hz, 1 H), 3.08 (d, J=7.8 Hz, 1 H), 3.06 (d, J= 7.5 Hz, 1 H), 2.14 (s, 3 H), 1.89-1.62 (m, 3 H), 1.35-1.22 (m, 1 H), 0.99 (s, 3 H), 0.95 (s, 3 H), 0.82 (s, 3 H). The crude product was employed without further purification in subsequent procedures.

Diselenide 1d. Product1d was prepared in 68% yield from 7 by the same procedure as employed in the preparation of 1b: yellow solid, mp 114-116°C (from ethanol); IR (Nujol) 1730 cm⁻¹; ¹H NMR δ 4.70 (d, J= 4.2 Hz, 2 H), 3.87 (ddd, J= 4.1, 4.1, 1.4 Hz, 2 H), 2.07 (s, 6 H), 1.99-1.95 (m, 2 H), 1.78-1.53 (m, 6 H), 1.28-1.19 (m, 2 H), 1.06 (s, 6 H), 0.91 (s, 6 H), 0.79 (s, 6 H); mass spectrum, m/z (relative intensity) 550 (12, M⁺), 135 (94), 43 (100). Anal. calc'd. for C₂₄H₃₈O₄Se₂: C, 52.56; H, 6.98. Found: C, 52.39; H, 6.76.

Diselenide 1e. Compound 1d (1.68 g, 3.06 mmol) was heated at 70°C for 6 h in 35 mL of dioxane and 20 mL of 1 N aqueous NaOH solution. The mixture was concentrated *in vacuo*, the residue was taken up in 100 mL of ether, washed with water and brine, dried and evaporated to afford 1.31 g (92%) of 1e as a yellow solid: mp 125-129°C (from ethanol); IR (Nujol) 3341 cm⁻¹; ¹H NMR δ 3.83 (ddd, *J*= 3.9, 3.9, 2.3 Hz, 2 H), 3.73-3.71 (m, 2 H), 3.03 (s, 2 H), 2.03-1.99 (m, 2 H), 1.67-1.47 (m, 6 H), 1.10 (s, 6 H), 1.40-1.00 (m, 2 H), 0.89 (s, 6 H), 0.88 (s, 6 H); mass spectrum, *m/z* (relative intensity) 466 (10, M⁺), 296 (8), 135 (90), 83 (100). Anal. calc'd. for C₂₀H₃₄O₂Se₂: C, 51.73; H, 7.38. Found: C, 51.66; H, 7.11.

Diselenide 1f. Product1f was prepared in 50% yield from 7 by the same procedure as employed in the preparation of 1b: yellow solid, mp 124-125°C (from ethanol); IR (Nujol) 1731 cm⁻¹; ¹H NMR δ 5.16 (dd, J= 9.8, 2.0 Hz, 2 H), 4.10 (ddd, J= 9.7, 4.1, 2.6 Hz, 2 H), 2.10 (s, 6 H), 1.97-1.93 (m, 2 H), 1.87-1.74 (m, 4 H), 1.70-1.64 (m, 2 H), 1.35-1.20 (m, 2 H), 1.01 (s, 6 H), 0.97 (s, 6 H), 0.81 (s, 6 H); mass spectrum, m/z (relative intensity) 550 (1, M⁺), 135 (67), 43 (100). Anal. calc'd. for C₂₄H₃₈O₄Se₂: C, 52.56; H, 6.98. Found: C, 52.27; H, 6.71.

Diselenide 1g. Product **1g** was prepared in 92% yield from **1f** by the same procedure as employed in the preparation of **1e**: yellow solid, mp 126-130°C (from ethanol); IR (Nujol) 3487 cm⁻¹; ¹H NMR δ 4.25 (ddd, J= 9.2, 4.2, 2.5 Hz, 2 H), 3.96 (d, J= 8.9 Hz, 2 H), 2.71 (br s, 2 H), 2.03-1.99 (m, 2 H), 1.87-1.74 (m, 2 H), 1.66-1.40 (m, 4 H), 1.29-1.14 (m, 2 H), 0.95 (s, 6 H), 0.92 (s, 6 H), 0.88 (s, 6 H); mass spectrum, m/z (relative intensity) 466 (17, M⁺), 296 (3), 135 (69), 95 (100). Anal. calc'd. for C₂₀H₃₄O₂Se₂: C, 51.73; H, 7.38. Found: C, 51.55; H, 7.07.

Methoxyselenenylations in Tables 1-3. The same general procedure as given for entry 1 of Table 3 below was employed in Tables 1 and 2, using *cis*- or *trans*-5-decene, with the variations indicated in the Tables. D.r.'s were measured by integration of ¹H NMR signals from protons at C-3 or C-4 of the camphor moiety, which were generally well-separated for the two diastereomers, or by integration of the methoxy or camphor methyl signals. In entry 7 of Table 3, the respective ⁷⁷Se NMR signals were integrated. Spectroscopic properties for the other adducts in Table 3 are given below. Assignments of ¹³C NMR signals are tentative because of frequent coincidence between signals from the two stereoisomers and the low intensity of peaks from the minor products.

Methoxyselenenylation of *trans*-5-decene (Typical procedure, Table 3, entry 1). Diselenide 1a (50 mg, 0.11 mmol) and 100 mg of 4 Å molecular sieves were stirred in 3 mL of dry dichloromethane. A 1 M solution of bromine (0.11 mL, 0.11 mmol) in tetrachloromethane was added dropwise at -78°C under nitrogen, with stirring. After 15 min, a 0.70 M methanol solution of silver triflate (0.45 mL, 0.30 mmol) was added, followed after another 15 min by *trans*-5-decene (0.10 mL, 0.53 mmol). Stirring was continued for 1 h at -78°C. The reaction was quenched with aqueous NaHCO₃ solution, diluted with 10 mL of dichloromethane, washed with water and brine, dried, filtered, and concentrated *in vacuo*. The residue was chromatographed (elution with 5% ethyl acetate-hexanes) to afford 78 mg (88%) of the addition product as a pale yellow oil: IR (film), 1738 (C=O) cm⁻¹; ¹H NMR major diastereomer: δ 3.78 (d, *J*= 4.7 Hz, 1 H), 3.42 (s, 3 H), 3.49-3.32 (m, 2 H), 2.21-2.19 (m, 1 H), 1.86-1.25 (m, 16 H), 1.02 (s, 3 H), 0.93 (s, 3 H), 0.92 (s, 3 H), 0.92-0.89 (m, 6 H); minor diastereomer: δ 3.99 (d, *J*= 4.8 Hz, 1 H), 3.39 (s, 3 H); ¹³C NMR major diastereomer: δ 218.5, 85.4, 58.4, 58.2, 48.9, 47.0, 46.6, 46.0, 31.7, 31.4, 30.9, 30.6, 28.5, 23.7, 23.1, 22.8, 19.8, 14.3 (two signals), 14.2, 10.0; minor diastereomer: δ 85.8, 57.9, 30.7 (two signals), 23.5, 19.8; mass spectrum, *m/z* (relative intensity) 402 (21, M⁺), 370 (19), 230 (50), 151 (65), 101 (100), 69 (99). Exact mass calc'd for C₂₁H₃₈O₂Se: 402.2040. Found: 402.2059.

Methoxyselenenylation of *cis*-5-decene (Table 3, entry 2). IR (film) 1738 cm⁻¹; ¹H NMR, major diastereomer: δ 3.65 (d, J= 4.6 Hz, 1 H), 3.40 (s, 3 H), 3.48-3.25 (m, 2 H), 2.25-2.21 (m, 1 H), 1.91-1.01 (m, 16 H), 1.02 (s, 3 H), 0.93 (s, 3 H), 0.91 (s, 3 H), 0.99-0.61 (m, 6 H); minor diastereomer: δ 3.75 (d, J= 3.4 Hz, 1 H), 3.38 (s, 3 H), 2.18-2.17 (m, 1 H); ¹³C NMR, major diastereomer: δ 218.6, 84.9, 58.4, 57.9, 49.0, 48.9, 46.7, 45.6, 32.0, 31.1, 30.9, 30.6, 28.9, 28.8, 23.7, 22.8, 19.8 (two signals), 14.3 (two signals), 10.0; minor diastereomer: δ 84.8, 58.3, 58.0, 47.0, 45.5, 31.7, 31.1, 30.6, 29.9, 23.6, 23.0, 19.9, 14.2; mass spectrum, m/z (relative intensity) 402 (10, M⁺), 370 (5), 230 (14), 171 (29), 151 (17), 101 (100). Exact mass calc'd for C₂₁H₃₈O₂Se: 402.2040. Found: 402.2055.

Methoxyselenenylation of *trans-stilbene* (Table 3, entry 3). The adduct could not be separated from a small amount of diselenide 1a, and the yield as well as the d.r. given in Table 3 is based on ¹H NMR integration: ¹H NMR, major diastereomer: δ 7.55-7.13 (m, 10 H), 4.71 (d, *J*= 9.3 Hz, 1 H), 4.55 (d, *J*= 9.2 Hz, 1 H), 3.12 (s, 3 H), 2.72-2.69 (m, 1 H), 2.04-1.26 (m, 5 H,), 0.88 (s, 3 H), 0.83 (s, 3 H), 0.51 (s, 3 H); minor diastereomer: δ 3.11-2.99 (m, 3 H), 0.60 (s, 3 H).

Methoxyselenenylation of *cis*-stilbene (Table 3, entry 4). IR (film) 1735 cm⁻¹; ¹H-NMR, major diastereomer: δ 7.23-7.09 (m, 10 H), 4.87 (d, J= 9.4 Hz, 1 H), 4.55 (d, J= 9.4 Hz, 1 H), 3.27 (s, 3 H), 3.05-3.00 (m, 1 H), 2.00-0.93 (m, 5 H), 0.88 (s, 3 H), 0.84 (s, 3 H), 0.54 (s, 3 H); minor diastereomer: δ 3.29 (s, 3 H), 0.92 (s, 3 H); ¹³C NMR, major diastereomer: δ 139.5, 129.6, 128.3 (two signals), 128.0, 127.6, 127.5, 127.3, 88.2, 57.3, 56.7, 49.0, 48.4, 46.3, 30.8, 24.1, 23.3, 20.0, 19.4, 9.9; minor diastereomer: δ 129.2, 128.6, 51.5, 47.0, 46.9, 19.8, 19.6, 10.0; mass spectrum, *m/z* (relative intensity) 442 (5, M⁺), 410 (10), 321 (100), 211 (41), 121 (60). Exact mass calc'd for C₂₅H₃₀O₂Se 442.1415. Found: 442.1423.

Methoxyselenenylation and deselenization of styrene (Table 3, entry 5). IR (film) 1735 cm⁻¹; ¹H NMR, major diastereomer: δ 7.37-7.26 (m, 5 H), 4.48 (dd, J= 8.6, 4.5 Hz, 1 H), 3.56-3.54 (m, 1 H), 3.27 (s, 3 H), 3.26-2.96 (m, 2 H), 2.14-2.10 (m, 1 H), 1.82-1.38 (m, 4 H), 0.99 (s, 3 H), 0.91 (s, 3 H), 0.81 (s, 3 H); minor diastereomer: δ 4.39-4.42 (t, J= 7.1 Hz, 1 H), 3.25 (s, 3 H), 2.06-2.04 (m, 1 H), 0.98 (s, 3 H), 0.89 (s, 3 H), 0.79 (s, 3 H); ¹³C NMR, major diastereomer: δ 218.7, 141.4, 128.7, 128.2, 126.8, 84.4, 57.2, 48.6, 48.5, 47.3, 46.9, 32.0, 30.7, 29.9, 23.5, 19.8 (two signals), 9.9; minor diastereomer: δ 128.3, 127.2, 84.6, 31.2,

30.7, 23.5, 19.7; mass spectrum, m/z (relative intensity) 366 (9, M⁺), 334 (16), 230 (11), 121 (100). Exact mass calc'd for C₁₉H₂₆O₂Se: 366.1100. Found: 366.1063.

A mixture of AIBN (10 mg) and triphenyltin hydride (192 mg, 0.55 mmol) was added dropwise to a refluxing solution of the above product (100 mg, 0.27 mmol) in 2 mL of toluene under nitrogen. After 2 h, additional triphenyltin hydride (96 mg, 0.27 mmol) and AIBN (5 mg) were added, and heating was continued for 1 h. The reaction mixture was separated by chromatography (elution with hexanes followed by 10% ether-hexanes). The solvent was removed by distillation, followed by Kugelrohr distillation of the residue (bp 70-90 °C, 130 mmHg) to afford the methyl ether 15 as a colourless oil, the e.r. of which was determined to be 74:26 by GC on a Cyclodex B column. The absolute configuration of the major enantiomer was assigned by comparison with an authentic sample of the (R)-enantiomer. The NMR spectrum of the product was identical to that of the authentic sample.

Methoxyselenenylation of α -methylstyrene (Table 3, entry 6). IR (film) 1740 cm⁻¹; ¹H NMR, major diastereomer: δ 7.39-7.14 (m, 5 H), 3.31-3.05 (m, 3 H), 3.06 (s, 3 H), 1.95-1.93 (m, 1 H), 1.65 (s, 3 H), 1.72-1.26 (m, 4 H), 0.89 (s, 3 H), 0.79 (s, 3 H), 0.66 (s, 3 H); minor diastereomer: δ 3.04 (s, 3 H), 1.89-1.85 (m, 1 H), 1.63 (s, 3 H), 0.87 (s, 3 H); ¹³C NMR, major diastereomer: δ 218.6, 144.0, 128.4, 127.5, 126.5, 79.6, 79.2, 58.3, 51.1, 48.3, 46.8, 46.6, 38.2, 30.7, 23.4, 23.2, 19.8, 9.8; minor diastereomer: δ 127.6, 126.7, 58.2, 51.1, 48.4, 46.8, 38.0, 30.6, 23.5, 19.7; mass spectrum, *m/z* (relative intensity) 380 (6, M⁺), 348 (5), 135 (100), 43 (47). Exact mass calc'd for C₂₀H₂₈O₂Se: 380.1257. Found: 380.1271.

Methoxyselenenylation of ethyl vinyl ether (Table 3, entry 7). IR (film) 1746 cm⁻¹; ¹H NMR, major diastereomer: δ 4.70 (t, J= 5.5 Hz, 1 H), 3.89 (dd, J= 4.4, 1.9 Hz, 1 H), 3.76-3.71 (m, 1 H), 3.59-3.54 (m, 1 H), 3.37 (s, 3 H), 3.01 (dd, J= 12.8, 5.8 Hz, 1 H), 2.91 (dd, J= 12.8, 5.2 Hz, 1H), 2.21-2.20 (m, 1 H), 1.80-1.40 (m, 4 H), 1.21 (t, J= 7.1 Hz, 3 H), 1.01 (s, 3 H), 0.92 (s, 3 H), 0.90 (s, 3 H); minor diastereomer: δ 3.36 (s, 3 H), 0.93 (s, 3 H); ¹³C NMR, major diastereomer: δ 218.5, 104.6, 62.5, 58.4, 53.8, 48.5, 47.2, 47.0, 30.7, 26.8, 23.5, 19.8 (two signals), 15.5, 9.9; minor diastereomer: δ 62.7, 53.5, 29.9. ⁷⁷Se NMR, major diastereomer: δ 191.6; minor diastereomer: δ 193.7; mass spectrum: m/z (relative intensity) 334 (1, M⁺), 302 (4), 89 (100), 61 (53). Exact mass calculated for C₁₅H₂₆O₃Se: 334.1049. Found: 334. 1053.

Methoxyselenenylation of *trans*-2-butene (Table 3, entry 8). IR (film): 1729 cm⁻¹; ¹H NMR, major diastereomer: δ 3.77 (d, J= 4.8 Hz, 1 H), 3.38-3.72 (m, 2 H), 3.37 (s, 3 H), 2.21-2.20 (m, 1 H), 2.05-1.50 (m, 4 H), 1.46 (d, J=7.0 Hz, 3 H), 1.21 (d, J= 6.2 Hz, 3 H), 1.03 (s, 3 H), 0.93 (s, 3 H), 0.92 (s, 3 H); minor diastereomer: δ 3.95 (d, J= 4.6 Hz, 1 H), 3.36 (s, 3 H), 1.02 (s, 3 H), 0.91 (s, 3 H); ¹³C NMR, 218.7, 80.9, 58.3, 57.0, 49.0, 47.1, 45.7, 41.0, 30.7, 23.8, 19.9, 19.8, 17.4, 16.8, 9.9; minor diastereomer: δ 81.5, 56.9, 49.0, 46.2, 41.1, 41.0, 23.6, 19.8, 18.4, 16.8, 16.4; mass spectrum, *m/z* (relative intensity) 318 (5, M⁺), 230 (8), 152 (33), 87 (46), 41 (100). Exact mass calc'd for C₁₅H₂₆O₂Se: 318.1100. Found: 318.1078.

Methoxyselenenylation of cyclohexene (Table 3 , entry 9). IR (film) 1739 cm⁻¹; ¹H NMR, major diastereomer: δ 4.09-4.07 (m, 1 H), 3.38 (s, 3 H), 3.36-3.18 (m, 2 H), 2.21-1.25 (m, 13 H), 1.02 (s, 3 H), 0.92 (s, 6 H); minor diastereomer: δ 3.99-3.40 (m, 1 H), 1.01 (s, 3 H), 0.90 (s, 6 H); ¹³C NMR, major diastereomer: δ 218.2, 83.6, 58.3, 56.5, 48.8, 47.1 (two signals), 43.0, 31.4, 30.8, 30.1, 25.5, 23.6, 23.3, 20.0, 19.9, 9.9; minor diastereomer: δ 85.0, 56.8, 49.2, 47.3, 44.5, 32.6, 31.0, 26.3, 24.0, 23.7, 20.0, 19.8; mass spectrum, *m/z* (relative intensity) 344 (8, M⁺), 312 (11), 230 (12), 151 (11), 113 (78), 81 (100), 45 (53). Exact Mass calc'd for C₁₇H₂₈O₂Se: 344.1257. Found: 344.1242.

Methoxyselenenylation of 1-methylcyclohexene (Table 3 , entry 10). IR (film) 1734 cm⁻¹; ¹H NMR, major diastereomer: δ 3.91 (d, J= 4.7 Hz, 1 H), 3.57 (dd, J= 9.1, 3.9 Hz, 1 H), 3.26 (s, 3 H), 2.23-2.17 (m, 1 H), 1.89-1.40 (m, 12 H), 1.31 (s, 3 H), 1.02 (s, 3 H), 0.92 (s, 6 H); minor diastereomer: δ 3.42 (dd, J= 10.1, 3.8 Hz, 1 H) 3.22 (s, 3 H), 1.27 (s, 3 H) 0.90 (s, 6 H); ¹³C NMR, major diastereomer: δ 218.5, 68.0, 58.3, 48.7, 48.6, 47.1, 47.0, 46.5, 34.9, 30.7, 29.9, 25.1, 23.7, 22.6, 21.6, 19.9, 10.0, 9.9; minor diastereomer: δ 48.9, 23.6, 22.8, 19.8; mass spectrum, m/z (relative intensity) 358 (14, M⁺), 326 (12), 207 (45), 95 (100), 41 (61). Exact mass calc'd for C₁₈H₃₀O₂Se: 358.1413. Found: 358.1403.

Methoxyselenenylation of 1-phenylcyclohexene (Table 3 , entry 11). IR (film) 1737 cm⁻¹; ¹H NMR, major diastereomer: δ 7.50-7.21 (m, 5 H), 3.14-3.01 (m, 1 H), 2.99 (s, 3 H), 2.69-2.36 (m, 2 H), 2.32 (dd, J= 4.5, 1.4 Hz, 1 H), 2.10-1.00 (m, 11 H), 0.93 (s, 3 H), 0.77 (s, 3 H), 0.48 (s, 3 H); minor diastereomer:

δ 3.76-3.57 (m, 1 H), 2.96 (s, 3 H), 2.29-2.19 (m, 1 H); ¹³C NMR, major diastereomer: δ 216.9, 143.8, 128.2, 128.0, 127.5, 80.8, 58.2, 50.6, 49.1, 48.7, 47.4, 46.5, 30.8, 30.2, 25.4, 23.0, 22.2, 21.1, 20.4, 19.8, 9.7; minor diastereomer: δ 144.1, 128.1, 127.4, 80.6, 58.1, 51.0, 50.5, 48.5, 46.8, 46.7, 30.6, 30.0, 25.4, 25.3, 23.4, 22.2, 19.5, 9.8; mass spectrum, *m/z* (relative intensity) 420 (28, M⁺), 388 (30), 269 (100), 189 (56), 91 (97). Exact mass calc'd for C₂₃H₃₂O₂Se: 420.1570. Found: 420.1552.

Cyclizations in Tables 4-5. The same general procedure as given for entry 1 of Table 5 (vide infra) was employed in Table 4, using 4-penten-1-ol and 4-pentenoic acid as substrates, with the variations indicated in the Table. The same procedure was also used for the other examples in Table 5, with variations as indicated below. D.r.'s were measured by integration of ¹H NMR signals from protons at C-3 of the camphor moiety, which were generally well-separated for the two diastereomers, or of signals from protons attached to oxygen-substituted carbon atoms. Assignments of ¹³C NMR signals are tentative because of frequent coincidence between signals from the two stereoisomers and the low intensity of peaks from the minor products.

Cyclization of 5-hexen-1-ol (Table 5, entry 1). Sulfuryl chloride (14 μ L, 0.17 mmol) was added to a mixture of diselenide 1c (99.5 mg, 0.17 mmol) and ca. 20 mg of 4 Å molecular sieves in 5 mL of dichloromethane, and stirring was continued for 15 min. The resulting orange mixture was cooled to -95°C, 46 μ L (0.38 mmol) of 5-hexen-1-ol was added and the orange colour was immediately discharged. The mixture was stirred for an additional 45 min at -95°C and was then filtered through Celite and concentrated *in vacuo*. The residue was chromatographed (elution with ethyl acetate) to afford 129 mg (96%) of the corresponding cyclic ether diastereomers as a colourless oil: IR (film) 3285, 1756 cm⁻¹; ¹H NMR, major diastereomer: δ 5.41 (s, 1 H), 4.08 (d, *J*= 9.2 Hz, 1 H), 3.99 (dt, *J*= 11.2, 1.9 Hz, 1 H), 3.77-3.76 (m, 1 H), 3.54 (d, *J*= 9.2 Hz, 1 H), 3.47-3.40 (m, 2 H), 2.79 (dd, *J*= 12.0, 7.7 Hz, 1 H), 2.64 (dd, *J*= 12.0, 4.6 Hz, 1 H), 2.03-2.01 (m, 1 H), 1.87-1.79 (m, 1 H), 1.71-1.68 (m, 1 H), 1.67-1.26 (m, 7 H), 1.15 (s, 3 H), 1.06 (ddd, *J*= 13.3, 9.1, 4.1 Hz, 1 H), 0.93 (s, 3 H), 0.92 (s, 3 H); minor diastereomer: δ 5.46 (s, 1 H), 2.74-2.70 (m, 1 H); ¹³C NMR, major diastereomer: δ 159.1, 93.1, 68.7, 68.6, 55.5, 52.9, 52.1, 48.1, 46.6, 32.0 (two signals) 28.8, 25.8, 23.3, 22.5, 20.4, 20.1, 10.9; minor diastereomer: δ 48.1, 31.0; mass spectrum, *m/z* (relative intensity) 387 (13, M⁺), 343 (12), 288 (61), 208 (62), 85 (100). Exact mass calc'd for C₁₈H₂₉NO₃Se: 387.1313. Found: 387.1305.

Cyclization and deselenization of 4-penten-1-ol (Table 5, entry 2). IR (film) 3273, 1768 cm⁻¹; ¹H NMR (C₆D₆), major diastereomer: δ 6.78 (br s, 1 H), 4.05-3.99 (m, 1 H), 3.93-3.92 (m, 1 H), 3.86-3.76 (m, 2 H), 3.63-3.57 (m, 1 H), 3.10 (d, *J*= 9.4 Hz, 1 H), 2.80 (dd, *J*= 12.1, 5.8 Hz, 1 H), 2.69 (dd, *J*= 12.2, 5.8 Hz, 1 H), 1.85-1.83 (m, 1 H), 1.81-1.24 (m, 7 H), 1.15 (s, 3 H), 1.10-1.00 (m, 1 H), 0.74 (s, 3 H), 0.65 (s, 3 H); minor diastereomer: δ 4.08-4.07 (m, 1 H), 1.89-1.87 (m, 1 H), 1.17 (s, 3 H). ¹³C NMR (C₆D₆), major diastereomer: δ 160.2, 92.8, 79.4, 68.6, 56.4, 53.3, 52.8, 48.5, 47.1, 32.2, 30.9, 29.2, 26.6, 23.0, 20.8, 20.6, 11.1; minor diastereomer: δ 92.8, 80.1, 68.5, 56.2, 52.7, 48.5, 32.4, 30.6, 30.5, 27.3, 24.1; mass spectrum, *m/z* (relative intensity) 373 (16, M⁺), 288 (63), 208 (89), 71 (100). Exact mass calc'd for C₁₇H₂₇NO₃Se: 373.1156. Found: 373.1175.

A mixture of AIBN (10 mg) and tri-*n*-butyltin hydride (0.39 mL, 1.45 mmol) was added to a refluxing solution of the above product (240 mg, 0.643 mmol) in 1.5 mL of C_6D_6 under nitrogen. After 2 h, additional AIBN (5 mg) and tri-*n*-butyltin hydride (0.19 mL) were added and heating was continued for 1 h. The mixture was distilled and only the fraction with bp 75-79°C was collected. A second distillation afforded a C_6D_6 solution of 17 with no contaminating camphor or tin residues (NMR). Trichloroethylene was added to serve as an internal standard and the concentration of 17 was determined by NMR integration. $[\alpha]_D + 22.1^\circ$ (c 1.7); lit.¹⁷ $[\alpha]_D + 27.01$ for the S-enantiomer. This corresponds to an e.r. of 91:9 (cf. d.r.= 84:16 in entry 2 of Table 5 and 90:10 in entry 5 of Table 4.

Cyclization of (E)-4-hexen-1-ol (Table 5, entry 3). The procedure of entry 1 was followed, except that the crude product was dissolved in 5 mL of dichloromethane and stirred with 14 mg of *p*-toluenesulfonic acid for 14 h prior to chromatography to afford the product as a colourless oil: IR (film) 3283, 1747 cm⁻¹; ¹H NMR, major diastereomer: δ 5.85 (br s, 1 H), 3.95 (d, J= 9.1 Hz, 1 H), 3.96-3.89 (m, 1 H), 3.74 (dd, J= 3.8,

2.7 Hz, 1 H), 3.57 (d, J= 9.2 Hz, 1 H), 3.46-3.31 (m, 2 H), 2.67-2.60 (m, 1 H), 2.24-2.19 (m, 1 H), 1.97-1.95 (m, 1 H), 1.74-1.57 (m, 3 H), 1.36 (d, J= 6.1 Hz, 3 H), 1.49-1.24 (m, 3 H), 1.16 (s, 3 H), 1.07 (ddd, J= 13.5, 9.2, 4.2 Hz, 1 H), 0.93 (s, 6 H); minor diastereomer: δ 5.80 (br s, 1 H), 3.82 (dd, J= 3.9, 2.5 Hz, 1 H), 3.57 (d, J= 9.3 Hz, 1 H), 2.75-2.67 (m, 1 H), 1.37 (d, J= 6.0 Hz, 3 H), 1.18 (s, 3 H); ¹³C NMR, major diastereomer: δ 159.5, 92.7, 78.6, 68.0, 54.5, 52.9, 52.4, 47.9, 46.7, 44.8, 33.1, 28.6, 27.9, 22.4, 20.9, 20.3, 19.9, 10.8; minor diastereomer: δ 159.4, 92.6, 77.8, 52.6, 52.1, 48.1, 46.4, 43.6, 33.0, 22.5, 21.0, 20.4, 10.8; mass spectrum, m/z (relative intensity) 387 (20, M⁺), 288 (30), 208 (46), 99 (96), 41 (100). Exact mass calc'd for C₁₈H₂₉NO₃Se: 387.1313. Found: 387.1329.

Cyclization of (Z)-4-hexen-1-ol (Table 5, entry 4). IR (film) 3282, 1754 cm⁻¹; ¹H NMR (C₆D₆), major diastereomer: δ 6.37 (br s, 1 H), 3.98-3.97 (m, 1 H), 3.85-3.74 (m, 2 H), 3.77 (d, J= 9.2 Hz, 1 H), 3.65 (m, 1 H), 3.13-3.07 (m, 1 H), 3.03 (d, J= 9.3 Hz, 1 H), 1.85-1.83 (m, 1 H), 1.80-1.51 (m, 4 H), 1.49 (d, J= 7.1 Hz, 3 H), 1.37-1.31 (m, 2 H), 1.17 (s, 3 H), 1.13-1.00 (m, 1 H), 0.74 (s, 3 H), 0.74-0.68 (m, 1 H), 0.66 (s, 3 H); minor diastereomer: δ 6.28 (br s, 1 H), 4.20-4.19 (m, 1 H), 3.69 (d, J= 9.3 Hz, 1 H), 1.92-1.90 (m, 1 H), 1.43 (d, J= 7.1 Hz, 3 H); ¹³C NMR, major diastereomer: δ 158.9, 93.1, 83.2, 68.6, 53.0, 52.9, 52.7, 46.6, 40.6, 30.2, 29.7, 28.8, 26.1, 22.7, 20.4, 20.1, 19.5, 10.9; mass spectrum, *m/z* (relative intensity) 387 (13, M⁺), 288 (39), 208 (65), 148 (74), 41 (100). Exact mass calc'd for C₁₈H₂₉NO₃Se: 387.1313. Found: 387.1318.

Cyclization of 4-methyl-4-penten-1-ol (Table 5, entry 5). IR (film) 3297, 1755 cm⁻¹; ¹H NMR (C₆D₆), major diastereomer: δ 6.46 (br s, 1 H), 4.14-4.12 (m, 1 H), 3.79 (d, J= 9.3 Hz, 1 H), 3.88-3.69 (m, 2 H), 3.05 (d, J= 9.3 Hz, 1 H), 2.82 (d, J= 11.8 Hz, 1 H), 2.74 (d, J= 12.3 Hz, 1 H), 1.92-1.90 (m, 1 H), 1.85-1.60 (m, 4 H), 1.52-1.47 (m, 1 H), 1.38-1.37 (m, 1 H), 1.32 (s, 3 H), 1.18 (s, 3 H), 1.08-1.00 (m, 1 H), 0.73 (s, 3 H), 0.71-0.69 (m, 1 H), 0.65 (s, 3 H); minor diastereomer: δ 6.53 (br s, 1 H), 3.92-3.90 (m, 1 H), 2.85 (d, J= 11.3 Hz, 1 H), 1.29 (s, 3 H), 1.16 (s, 3 H); ¹³C NMR, major diastereomer: δ 159.2, 93.1, 82.4, 67.8, 55.9, 55.6, 52.9, 52.0, 48.0, 46.6, 37.2, 36.9, 28.8, 26.3, 22.4, 20.4, 20.0, 10.8; minor diastereomer: δ 28.8; mass spectrum, m/z (relative intensity) 387 (5, M⁺), 288 (6), 208 (8), 149 (25), 129 (33), 85 (100). Exact mass calc'd for C₁₈H₂₉NO₃Se: 387.1313. Found: 387.1315.

Cyclization of 2,2-dimethyl-4-penten-1-ol (Table 5, entry 6). IR (film) 3281, 1758 cm⁻¹; ¹H NMR, major diastereomer: δ 5.32 (br s, 1 H), 4.18-4.12 (m, 1 H), 4.03 (d, J= 9.1 Hz, 1 H), 3.83-3.81 (m, 1 H), 3.54 (d, J= 9.1 Hz, 1 H), 2.82-2.71 (m, 2 H), 2.14-2.03 (m, 1 H), 2.02-1.99 (m, 1 H), 1.78-1.70 (m, 3 H), 1.68-1.54 (m, 1 H), 1.48-1.30 (m, 2 H), 1.26 (s, 3 H), 1.22 (s, 3 H), 1.15 (s, 3 H), 1.09-1.04 (m, 1 H), 0.93 (s, 3 H), 0.92 (s, 3 H); minor diastereomer: δ 5.29 (br s, 1 H), 3.90-3.88 (m, 1 H), 1.27 (s, 3 H); ¹³C NMR, major diastereomer: δ 159.3, 92.9, 81.4, 78.4, 77.9, 55.1, 52.8, 51.8, 46.5, 38.5, 32.0, 30.7, 29.1, 28.7, 27.9, 22.3, 20.4, 20.0, 10.8; minor diastereomer: δ 81.4, 55.5, 52.8, 51.9, 48.0, 38.4, 32.1, 31.0, 29.1, 27.9; mass spectrum, m/z (relative intensity) 401 (17, M⁺), 288 (43), 208 (70), 99 (79), 43 (100). Exact mass calc'd for C₁₉H₃₁NO₃Se: 401.1473. Found: 401.1450.

Cyclization of 2-(1-cyclohexenyl)ethanol (Table 5, entry 7). The procedure of entry 1 was followed, except that 4 h at -95° C was required to discharge the colour of the selenenyl chloride. Chromatography (elution with 60% ethyl acetate-hexanes) afforded the separated diastereomers.

Minor diastereomer (less polar): IR (film) 3284, 1756 cm⁻¹; ¹H NMR: δ 5.08 (br s, 1 H), 3.98-3.87 (m, 3 H), 3.76-3.74 (m, 1 H), 3.66 (dd, J= 3.8, 2.8 Hz, 1 H), 3.60 (d, J= 9.2 Hz, 1 H), 2.34-2.21 (m, 1 H), 2.15 (ddd, J= 12.2, 7.8, 4.2 Hz, 1 H), 1.92-1.90 (m, 1 H), 1.90-1.81 (m, 1 H), 1.75-1.33 (m, 10 H), 1.18 (s, 3 H), 1.10-1.06 (m, 1 H), 0.94 (s, 6 H); ¹³C NMR: δ 159.0, 92.6, 80.7, 65.0, 53.8, 53.1, 49.9, 48.1, 46.8, 41.5, 33.9, 28.7, 26.2, 22.9, 22.3, 20.4, 20.1 (two signals), 10.9; mass spectrum, m/z (relative intensity) 413 (5, M⁺), 228 (10), 208 (8), 125 (100). Exact mass calc'd for C₂₀H₃₁NO₃Se: 413.1473. Found: 413.1479.

Major diastereomer (more polar): IR (film) 3232, 1761 cm⁻¹; ¹H NMR: δ 5.07 (br s, 1 H), 3.97-3.86 (m, 3 H), 3.76-3.74 (m, 1 H), 3.66 (dd, *J*= 3.8, 2.9 Hz, 1 H), 3.61 (d, *J*= 9.0 Hz, 1 H), 2.31-2.24 (m, 1 H), 2.16 (ddd, *J*= 12.4, 7.8, 4.4 Hz, 1 H), 1.91-1.89 (m, 1 H), 1.85-1.81 (m, 1 H), 1.75-1.33 (m, 10 H), 1.18 (s, 3 H), 1.07 (ddd, *J*= 13.5, 9.3, 4.0 Hz, 1 H), 0.94 (s, 6 H); ¹³C NMR: δ 159.0, 92.6, 80.9, 65.1, 53.8, 53.1, 52.9, 50.1, 46.8, 41.4, 33.3, 29.7, 28.7, 26.3, 22.8, 22.2, 20.4, 20.3, 20.1, 10.9; mass spectrum, *m/z* (relative

intensity) 413 (6, M^+), 228 (16), 208 (10), 125 (100). Exact mass calc'd for $C_{20}H_{31}NO_3Se$: 413.1473. Found: 413.1477.

Cyclization of 2-(3-propenyl)phenol (Table 5, entry 8). IR (film) 3298, 1747 cm⁻¹; ¹H NMR, major diastereomer: δ 7.14-7.05 (m, 2 H), 6.88-6.76 (m, 2 H), 5.84 (br s, 1 H), 4.46 (quintet, J= 6.6 Hz, 1 H), 4.02 (d, J= 9.5 Hz, 1 H), 3.75-3.73 (m, 1 H), 3.53 (d, J= 9.6 Hz, 1 H), 3.36 (dd, J= 13.8, 6.1 Hz, 1 H), 3.07-2.98 (m, 2 H), 2.93 (dd, J= 13.9, 7.3 Hz, 1 H), 2.00-1.98 (m, 1 H), 1.61-1.55 (m, 1 H), 1.43 (ddd, J= 12.7, 12.7, 4.3 Hz, 1 H), 1.32 (ddd, J= 13.0, 8.9, 4.2 Hz, 1 H), 1.10 (s, 3 H), 1.03 (ddd, J= 13.4, 9.2, 4.0 Hz, 1 H), 0.91 (s, 3 H), 0.90 (s, 3 H); minor diastereomer: δ 5.80 (br s, 1 H), 4.40-4.38 (m, 1 H), 4.11 (d, J= 9.4 Hz, 1 H), 1.95-1.93 (m, 1 H), 1.11 (s, 3 H), 0.92 (s, 3 H), 0.88 (s, 3 H); ¹³C NMR, major diastereomer: δ 154.4, 131.8, 128.3, 123.9, 120.1, 115.7, 109.4, 93.6, 61.8, 56.2, 52.8, 51.7, 48.1, 46.7, 39.3, 32.8, 28.7, 22.4, 20.3, 19.9, 10.7; minor diastereomer: δ 131.6, 126.3, 120.2, 116.0, 35.5, 20.2, 20.0, 10.8; mass spectrum, m/z (relative intensity) 421 (32, M⁺), 377 (19), 288 (27), 244 (77), 208 (27), 131 (94), 91 (94), 44 (100). Exact mass calc'd for C₂₁H₂₇NO₃Se: 421.1127. Found: 421.1159.

Cyclization of 5-hexenoic acid (Table 5, entry 9). IR (film) 3277, 1756 cm⁻¹; ¹H NMR, major diastereomer: δ 6.28 (br s, 1 H), 4.04 (d, J= 9.1 Hz, 1 H), 4.05-4.02 (m, 1 H), 3.69-3.68 (m, 1 H), 3.60 (d, J= 9.4 Hz, 1 H), 3.07 (dd, J= 12.7, 5.6 Hz, 1 H), 2.95 (dd, J= 12.8, 7.8 Hz, 1 H), 2.47-2.33 (m, 2 H), 2.15-2.10 (m, 1 H), 2.05-2.03 (m, 1 H), 1.94-1.77 (m, 1 H), 1.75-1.60 (m, 3 H), 1.47 (ddd, J= 12.9, 12.9, 4.3 Hz, 1 H), 1.29 (ddd, J= 13.3, 8.9, 4.4 Hz, 1 H), 1.15 (s, 3 H), 1.07 (ddd, J= 13.5, 9.3, 4.1 Hz, 1 H), 0.94 (s, 3 H), 0.93 (s, 3 H); minor diastereomer: δ 4.12 (d, J= 9.8 Hz, 1 H), 3.77-3.76 (m, 1 H); ¹³C NMR, major diastereomer: δ 171.0, 159.1, 92.8, 79.7, 56.5, 52.9, 52.0, 48.1, 46.6, 29.5, 29.3, 28.7, 27.6, 22.4, 20.3, 19.9, 18.2, 10.7; minor diastereomer: δ 79.6, 56.8, 52.8, 52.2, 46.6, 29.8, 29.4, 27.8, 18.3 (two signals), 18.2, 10.7; mass spectrum, m/z (relative intensity) 401 (8, M⁺), 287 (19), 208 (44), 113 (45), 55 (69), 41 (100). Exact mass calc'd for C₁₈H₂₇NO₄Se: 401.1124. Found: 401.1108.

Cyclization and deselenization of 4-pentenoic acid (Table 5, entry 10). IR (film) 3321, 1732 cm⁻¹; ¹H NMR (CDCl₃-C₆D₆ 1:1), major diastereomer: δ 4.72 (br s, 1 H), 4.27-4.21 (m, 1 H), 3.68 (dd, *J*= 3.6, 2.7 Hz, 1 H), 3.62 (d, *J*= 9.3 Hz, 1 H), 3.07 (d, *J*= 9.3 Hz, 1 H), 2.61-2.53 (m, 2 H), 2.21 (ddd, *J*= 17.8, 9.8, 4.7 Hz, 1 H), 2.11-2.02 (m, 1 H), 1.89-1.87 (m, 1 H), 1.84-1.76 (m, 1 H), 1.51-1.38 (m, 2 H), 1.29-1.14 (m, 3 H), 1.12 (s, 3 H), 0.78 (s, 3 H), 0.76 (s, 3 H); ¹³C NMR, major diastereomer: δ 176.5, 159.2, 92.9, 79.3, 56.6, 52.9, 52.0, 48.2, 46.7, 42.9, 29.3, 28.8, 27.7, 22.4, 20.3, 19.9, 10.8; mass spectrum, *m/z* (relative intensity) 387 (19, M⁺), 288 (15), 208 (100), 83 (98). Exact mass calc'd for C₁₇H₂₅NO₄Se: 387.0951. Found: 387.0951. No signals that could be attributed to the minor diastereomer were observed in either the ¹H or ¹³C NMR spectra.

A mixture of AIBN (10 mg) and tri-*n*-butyltin hydride (0.40 mL, 1.49 mmol) was added to a refluxing solution of the above product (257 mg, 0.66 mmol) in 2 mL of toluene under nitrogen. After 2 h, additional AIBN (5 mg) and tri-*n*-butyltin hydride (0.20 mL) were added and heating was continued for 1 h. The mixture was concentrated and chromatographed (elution with 10%-50% ether-hexanes, followed by pure ether). The solvent was removed by distillation from the fraction eluting with 50% ether-hexanes and the residue was subjected to Kugelrohr distillation to afford 27 mg (40%) of **18**, bp 105-115°C, 39 mmHg; $[\alpha]_D$ - 27.9° (c 2.0); lit.¹⁸ $[\alpha]_D$ -29.6 (c 1.29 CH₂Cl₂) for the S-enantiomer. This represents an e.r. of 97:3. The product had IR and NMR spectra in close agreement with the literature. The fraction eluting with ether afforded 122 mg (88%) of *spiro*-oxazolidinone **27** (*vide infra*).

Cyclization of (E)-4-hexenoic acid (Table 5, entry 11). IR (film) 3263, 1767 cm⁻¹; ¹H NMR, major diastereomer: δ 5.69 (br s, 1 H), 4.53 (m, 1 H), 3.98 (d, J= 9.2 Hz, 1 H), 3.87-3.86 (m, 1 H), 3.59 (d, J= 9.3 Hz, 1 H), 3.28-3.11 (m, 1 H), 2.67-2.50 (m, 2 H), 2.39-2.30 (m, 1 H), 2.12-2.01 (m, 1 H), 2.00-1.98 (m, 1 H), 1.64-1.55 (m, 1 H), 1.55-1.49 (m, 1 H), 1.45 (d, J= 7.3 Hz, 3 H), 1.25 (ddd, J= 13.2, 9.1, 4.5 Hz, 1 H), 1.17 (s, 3 H), 1.06 (ddd, J= 13.6, 9.3, 3.8 Hz, 1 H), 0.93 (s, 3 H), 0.92 (s, 3 H); irradiation of the m at δ 3.28-3.11 collapsed the d at δ 1.45 into a s; minor diastereomer: δ 3.81-3.80 (m, 1 H), 3.58 (d, J= 9.1 Hz, 1 H); ¹³C NMR, major diastereomer: δ 176.6, 159.6, 92.8, 83.2, 55.5, 52.7, 52.4, 48.0, 46.8, 40.5, 28.8, 28.6, 25.3, 22.4, 20.1, 19.8, 18.5, 10.7; minor diastereomer: δ 176.7, 159.4, 92.6, 83.4, 54.2, 52.8, 52.5, 46.6, 46.5, 39.8,

28.5, 24.8, 22.5, 20.2, 19.8, 18.1, 10.7; mass spectrum, m/z (relative intensity) 401 (11, M⁺), 288 (11), 208 (48), 55 (100). Exact mass calc'd for C₁₈H₂₇NO₄Se: 401.1108. Found: 401.1115.

Cyclization of (Z)-4-hexenoic acid (Table 5, entry 12). IR (film) 3300, 1768, 1755 cm⁻¹; ¹H NMR (C₆D₆), major diastereomer: δ 6.47 (br s, 1 H), 4.19 (ddd, *J*= 7.4, 4.0, 4.0 Hz, 1 H), 3.89-3.88 (m, 1 H), 3.63 (d, *J*= 9.4 Hz, 1 H), 3.06 (d, *J*= 9.4 Hz, 1 H), 2.94 (dq, *J*= 7.0, 4.6 Hz, 1 H), 2.29-2.07 (m, 2 H), 1.84-1.82 (m, 1 H), 1.78-1.61 (m, 2 H), 1.34 (d, *J*= 7.1 Hz, 3 H), 1.32-1.21 (m, 2 H), 1.20 (s, 3 H), 1.03 (ddd, *J*= 12.9, 12.9, 4.8 Hz, 1 H), 0.73 (s, 3 H), 0.70-0.68 (m, 1 H), 0.65 (s, 3 H); irradiation of the dq at δ 2.94 collapsed the d at δ 1.34 to a s; minor diastereomer: δ 6.34 (br s, 1 H), 4.09-4.04 (m, 1 H), 3.67 (d, *J*= 9.4 Hz, 1 H), 2.88-2.85 (m, 1 H), 1.88-1.86 (m, 1 H); ¹³C NMR, major diastereomer: δ 176.7, 159.2, 92.8, 83.2, 54.4, 53.0, 52.5, 48.2, 46.7, 39.2, 28.9, 28.7, 25.1, 22.6, 20.3, 20.0, 18.4, 10.8; minor diastereomer: δ 83.7, 29.0, 22.5; mass spectrum, *m/z* (relative intensity) 401 (9, M⁺), 288 (5), 208 (39), 83 (53), 41 (100). Exact mass calc'd for C₁₈H₂₇NO₄Se: 401.1108. Found: 401.1120.

Cyclization of (1-cyclohexenyl)acetic acid (Table 5, entry 13). The procedure of entry 1 was followed, except that 8 h at -95°C, followed by 12 h at room temperature, was required to discharge the colour of the selenenyl chloride. IR (film) 3318, 1772, 1760 cm⁻¹; ¹H NMR, major diastereomer: δ 5.75 (br, s, 1 H), 4.45-4.41 (m, 1 H), 3.83 (d, *J*= 9.3 Hz, 1 H), 3.63 (d, *J*= 9.3 Hz, 1 H), 3.60-3.58 (m, 1 H), 2.81-2.67 (m, 2 H), 2.04-1.45 (m, 11 H), 1.35-1.21 (m, 1 H), 1.18 (s, 3 H), 1.07 (ddd, *J*= 13.7, 9.4, 4.1 Hz, 1 H), 0.94 (s, 6 H); minor diastereomer: δ 5.68 (br s, 1 H), 3.78 (d, *J*= 9.4 Hz, 1 H), 3.56-3.55 (m, 1 H), 0.95 (s, 3 H); ¹³C NMR, major diastereomer: δ 174.8, 165.7, 92.3, 82.7, 53.5, 53.4, 53.0, 48.2, 46.9, 46.8, 45.3, 33.8, 28.6, 25.7, 22.8, 21.4, 20.3, 20.0, 19.7, 10.8; minor diastereomer: δ 174.7, 82.6, 53.7, 53.5, 47.1, 46.1, 45.7, 45.5, 34.3, 26.2, 22.8, 21.3, 20.4, 19.8, 10.7; mass spectrum, *m/z* (relative intensity) 427 (8, M⁺), 228 (32), 208 (20), 148 (72), 41 (100). Exact mass calc'd for C₂₀H₂₉NO₄Se: 427.1266. Found: 427.1299.

Reactions of 4-pentenamide (19) with selenenyl chloride 16c. Diselenide 1c (50 mg, 0.087 mmol) was dissolved in 3 mL of dichloromethane at 0°C. Sulfuryl chloride (6.9 μ L, 0.087 mmol) was added and stirring was continued for 10 min. The resulting solution of 16c was cooled to -78°C, amide 19 (21 mg, 0.21 mmol) was added, and the orange colour was discharged immediately. The mixture was stirred for an additional 1 h, and was then concentrated *in vacuo* and rapidly chromatographed (elution with ethyl acetate) to afford 37 mg (ca. 50%) of the crude chloride 20 as a colourless oil with d.r. 95:5 (NMR integration), which was converted into lactone 22 upon prolonged standing or slow chromatography; IR (film) 3228, 1752, 1668, 751 cm⁻¹; ¹H NMR, major diastereomer: δ 6.25 (br s, 1 H), 6.01 (br s, 2 H), 4.14-4.05 (m, 1 H), 4.02 (d, *J*= 8.9 Hz, 1 H), 3.58 (m, 2 H), 3.13 (dd, *J*= 13.1, 5.1 Hz, 1 H), 2.93 (m, 1 H), 2.50-2.43 (m, 2 H), 2.18-1.23 (m, 7 H), 1.15 (s, 3 H), 0.94 (s, 3 H), 0.93 (s, 3 H); minor diastereomer: δ 6.18 (br s, 1 H).

Diselenide 1c (100 mg, 0.17 mmol) was converted into the selenenyl chloride 16c as in the preceding procedure. The resulting solution was cooled to -95° C, amide 19 (41 mg, 0.41 mmol) was added, and the orange colour was discharged immediately. After 1 h, the mixture was warmed to room temperature and *p*-toluenesulfonic acid (10 mg) was added. After 10 h, the solution was concentrated *in vacuo*, and the residue was chromatographed (elution with ethyl acetate) to afford 118 mg (88%) of lactone 22, obtained as a colourless oil, which had ¹H and ¹³C NMR spectra identical to those of the sample from entry 10 in Table 5. Only one diastereomer was detected.

The reaction of amide 19 and selenenyl chloride 16c (generated from 0.17 mmol of 1c) was performed as in the above procedure. After 1 h, the mixture was warmed to room temperature and potassium *t*-butoxide (117 mg, 1.05 mmol) was added. After 4 h, the solution was concentrated *in vacuo*, and was chromatographed (elution with ethyl acetate) to afford 90 mg (67%) of 23 as a colourless oil: IR (film) 3360, 2247, 1749 cm⁻¹; ¹H NMR δ 5.71 (br s, 1 H), 4.06 (d, *J*= 9.3 Hz, 1 H), 3.85 (br s, 1 H), 3.77 (dd, *J*= 3.9, 2.4 Hz, 1 H), 3.59 (d, *J*= 9.4 Hz, 1 H), 3.09-3.07 (m, 1 H), 2.84 (dd, *J*= 12.6, 5.1 Hz, 1 H), 2.70 (dd, *J*= 12.6, 7.4 Hz, 1 H), 2.54 (dd, *J*= 7.7, 6.7 Hz, 2 H), 2.07-2.00 (m, 1 H), 1.97-1.21 (m, 6 H), 1.16 (s, 3 H), 0.94 (s, 3 H), 0.93 (s, 3 H); ¹³C NMR (C₆D₆) δ 160.2, 120.5, 93.2, 70.0, 57.2, 53.2, 53.0, 48.6, 47.2, 33.2, 32.6, 29.2, 23.0, 20.6, 20.5, 14.1, 11.1; mass spectrum, *m/z* (relative intensity) 386 (16, M⁺), 288 (34), 208 (77), 83 (100). Exact mass calc'd for C₁₇H₂₆N₂O₃Se: 386.1102. Found: 386.1102. Only one diastereomer was detected.

Cyclization and deselenization of methyl N-(5-pentenyl)carbamate (24). Diselenide 1c (100 mg, 0.17 mmol) was converted into the selenenyl chloride 16c as in the preceding procedure. The resulting solution was cooled to -78° C, carbamate 24 (60 mg, 0.42 mmol) was added, and the orange colour was discharged immediately. After 1 h, the mixture was warmed to room temperature and silica-gel (100 mg) was added to the mixture. Stirring was continued overnight, the mixture was filtered, washed with brine, dried and chromatographed (elution with 80% ethyl acetate-hexanes) to afford 110 mg (73%) of lactam 25 as a colourless oil: IR (film) 3377, 1774, 1701 cm⁻¹; ¹H NMR, major diastereomer: δ 5.50 (br s, 1 H); 4.09-3.95 (m, 3 H), 3.71-3.65 (m, 3 H), 3.55 (d, *J*= 5.1 Hz, 1 H,), 2.00-1.20 (m, 13 H), 1.15 (s, 3 H), 0.92 (s, 6 H); minor diastereomer: 5.72 (br s, 1 H); ¹³C NMR (C₆D₆), major diastereomer: δ 170.0, 155.5, 88.0, 59.1, 51.6, 51.3, 50.8, 48.5, 47.9, 47.2, 34.2, 30.7, 30.6, 27.8, 24.0, 23.9, 21.3, 20.1, 11.8; minor diastereomer: δ 58.8, 58.3, 52.1, 51.1, 49.3, 48.2, 47.4, 31.5, 29.3, 24.1, 23.8, 23.2, 20.9, 20.1; mass spectrum, *m/z* (relative intensity) 430 (5, M⁺), 288 (15), 208 (10), 128 (100). Exact mass calc'd for C₁₉H₃₀N₂O₄Se: 430.1374. Found: 430.1366.

A mixture of AIBN (10 mg) and tri-*n*-butyltin hydride (138 μ L, 0.52 mmol) was added to a refluxing solution of **25** (110 mg, 0.26 mmol) in 2 mL of toluene under nitrogen. After 2 h, additional tri-*n*-butyltin hydride (69 μ L, 0.26 mmol) and AIBN (5 mg) were added, and heating was continued for 1 h. The reaction mixture was separated by chromatography (elution with hexanes followed by 10-50% diethyl ether-hexanes) to afford 8 mg (20%) of carbamate **26**¹⁹ as a yellow oil, followed by 49 mg (91%) of *spiro*-oxazolidinone **27**. The e.r. of **26** was determined to be 72:28 by GC on a chiral Cyclodex B column. Compound **27**: mp 148°C (from benzene-hexanes); IR (Nujol) 3246, 1744 cm⁻¹; ¹H NMR 5.75 (br s, 1 H), 3.70 (d, *J*= 8.2 Hz, 1 H), 3.25 (d, *J*= 8.6 Hz, 1 H), 2.40 (ddd, *J*= 13.9, 4.4, 3.2 Hz, 1 H), 1.85-1.81 (m, 1 H), 1.77-1.37 (m, 3 H), 1.07 (s, 3 H), 1.23-0.99 (m, 2 H), 0.90 (s, 3 H), 0.89 (s, 3 H); mass spectrum, *m/z* (relative intensity) **209** (8, M⁺), 194 (10), 148 (29), 95 (100). Anal. calc'd. for C₁₂H₁₉NO₂: C, 68.87; H, 9.15; N, 6.69. Found: C, 69.12; H, 9.26; N, 6.65.

Acknowledgements

We thank the Natural Sciences and Engineering Research Council of Canada for financial support and for a Postgraduate Scholarship to B.P.D. We thank Dr. R. Yamdagni, Ms. Q. Wu and Ms. D. Fox for mass spectra and elemental analyses.

References

- 1. Schmid, G.H.; Garratt, D.G. In The Chemistry of Double-bonded Functional Groups. Supplement A, Part 2; Patai S., Ed.; Wiley: New York, 1977; Chapter 9.
- For reviews of electrophilic selenium reactions, see: (a) Paulmier, C. Selenium Reagents and Intermediates in Organic Synthesis; Pergamon Press: Oxford, 1986; Chapter 7. (b) Back T.G. In Organoselenium Chemistry; Liotta, D., Ed.; Wiley: New York, 1987; Chapter 1. (c) Back, T.G. In The Chemistry of Organic Selenium and Tellurium Compounds; Patai, S., Ed.; Wiley: Chichester, 1987; Volume 2, Chapter 3.
- 3. For examples of anti-Markovnikov additions of selenenyl chlorides under kinetic conditions, see: (a) Raucher, S. J. Org. Chem. 1977, 42, 2950. (b) Ho, P.-T.; Kolt, R.J. Can. J. Chem. 1982, 60, 663.
- For reviews, see: (a) Reference 2a; Chapter 8. (b) Nicolaou, K.C.; Petasis, N.A.; Claremon, D.A. In Organoselenium Chemistry; Liotta, D., Ed.; Wiley: New York, 1987; Chapter 2. (c) Nicolaou K.C.; Petasis, N.A. In Selenium in Natural Products Synthesis; CIS: Philadelphia, 1984; Chapter 7.
- (a) Clive, D.L.J.; Chittattu, G.; Curtis, N.J.; Kiel, W.A.; Wong, C.K. J. Chem. Soc., Chem. Commun. 1977, 725. (b) Clive, D.L.J.; Russell, C.G.; Chittattu, G.; Singh, A. Tetrahedron 1980, 36, 1399.
- (a) Fujita, K.; Murata, K.; Iwaoka, M.; Tomoda, S. Tetrahedron 1997, 53, 2029. (b) Fujita, K.; Murata, K.; Iwaoka, M.; Tomoda, S. Tetrahedron Lett. 1995, 36, 5219. (c) Fujita, K.; Iwaoka, M.; Tomoda, S.

Chem. Lett. 1994, 923. (d) Fujita, K.; Iwaoka, M.; Tomoda, S. Chem. Lett. 1992, 1123. (e) Tomoda, S.; Fujita, K.; Iwaoka, M. J. Chem. Soc., Chem. Commun. 1990, 129. (f) Tomoda, S.; Iwaoka, M. Chem. Lett. 1988, 1895. (g) Déziel, R.; Malenfant, E.; Thibault, C.; Fréchette, S.; Gravel, M. Tetrahedron Lett. 1997, 38, 4753. (h) Déziel, R.; Goulet, S.; Grenier, L.; Bordeleau, J.; Bernier, J. J. Org. Chem. 1993, 58, 3619. (i) Fukuzawa, S.; Takahashi, K.; Kato, H.; Yamazaki, H. J. Org. Chem. 1997, 62, 7711. (j) Fukuzawa, S.; Kasugahara, Y.; Uemura, S. Tetrahedron Lett. 1994, 35, 9403. (k) Wirth, T.; Fragale, G.; Spichty, M. J. Am. Chem. Soc. 1998, 120, 3376. (l) Wirth, T.; Häuptli, S.; Leuenberger, M. Tetrahedron Asymmetry 1998, 9, 547. (m) Wirth, T.; Fragale, G. Synthesis 1998, 162. (n) Wirth, T.; Fragale, G. Chem. Eur. J. 1997, 3, 1894. (o) Wirth, T.; Angew. Chem. Int. Ed. Engl. 1995, 34, 1726.

- (a) Nishibayashi, Y.; Srivastava, S.K.; Takada, H.; Fukuzawa, S.; Uemura, S. J. Chem. Soc., Chem. Commun. 1995, 2321. (b) Fujita, K.; Murata, K.; Iwaoka, M.; Tomoda, S. J. Chem. Soc., Chem. Commun. 1995, 1641. (c) Déziel, R.; Malenfant, E. J. Org. Chem. 1995, 60, 4660.
- 8. Back, T.G.; Dyck, B.P.; Parvez, M. J. Org. Chem. 1995, 60, 703.
- 9. (a) Preliminary communication: Back, T.G.; Nan, S. J. Chem. Soc., Perkin Trans. 1 (in press). (b) Preliminary communication: Back, T.G.; Dyck, B.P. J. Chem. Soc., Chem. Commun. 1996, 2567.
- 10. Subsequently to our report of the preparation of diselenide 1a (ref. 8) and its use in asymmetric cyclizations (ref. 9b), an independent report appeared on the use of a selenenyl sulfate derived from 1a in asymmetric methoxyselenenylations: Tiecco, M.; Testaferri, L.; Santi, C.; Marini, F.; Bagnoli, L.; Temperini, A. Tetrahedron Lett. 1998, 39, 2809.
- 11. Few protecting groups have been reported for selenols and diselenides; for recent examples, see: Reinerth, W.A.; Tour, J.M. J. Org. Chem. 1998, 63, 2397.
- 12. For a review of [2,3]sigmatropic rearrangements of allylic selenoxides, see: Reich, H.J. In Organoselenium Chemistry; Liotta, D., Ed.; Wiley: New York, 1987; Chapter 8.
- (a) Back, T.G.; Dyck, B.P. J. Am. Chem. Soc. 1997, 119, 2079. (b) Back, T.G.; Dyck, B.P.; Nan, S.; Parvez, M. Acta Cryst. 1998, C54, 425.
- Selenenic acids (RSeOH) are unstable and disproportionate to seleninic acids (RSeO₂H) and diselenides (RSeSeR): (a) Reich, H.J.; Wollowitz, S.; Trend, J.E.; Chow, F.; Wendelborn, D.F. J. Org. Chem. 1978, 43, 1697. (b) Hori, T.; Sharpless, K.B. J. Org. Chem. 1978, 43, 1689.
- Clive, D.L.J.; Chittattu, G.J.; Farina, V.; Kiel, W.A.; Menchen, S.M.; Russell, C.G.; Singh, A.; Wong, C.K.; Curtis, N.J. J. Am. Chem. Soc. 1980, 102, 4438.
- 16. The cyclization of trans- and cis-4-hexen-1-ols with PhSeCl results in endo- and exo-cyclization, respectively, in the absence of p-toluenesulfonic acid: Konstantinovic, S.; Bugarcic, Z.; Milosavljevic, S.; Schroth, G.; Mihailovic, M.L. Liebigs Ann. Chem. 1992, 261.
- Dictionary of Organic Compounds, 6th edition; Cadogan, J.I.G.; Ley, S.V.; Pattenden, G., Eds.; Chapman and Hall: London, 1996, Volume 6, p. 5835-5836, entry T001299.
- 18. Mori, K. Tetrahedron 1975, 31, 3011.
- 19. Dicks, P.F.; Glover, S.A.; Goosen, A.; McCleland, C.W. Tetrahedron 1987, 43, 923.