Aminoselenenylation of Alkenes: Syntheses of β-Phenylseleno Carbamates and β-Phenylseleno Cyanamides

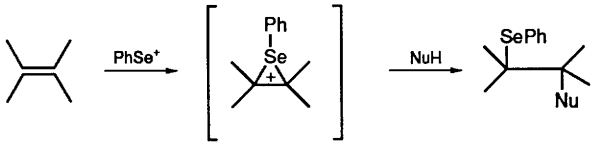
Cosme G. Francisco, Rosendo Hernández, Elisa I. León, José A. Salazar,* and Ernesto Suárez
Instituto de Productos Naturales Orgánicos, del CSIC, Carretera de La Esperanza 2, 38206 La Laguna, Tenerife, Spain

β-(Phenylseleno)alkylcarbamates and β-(phenylseleno)alkylcyanamides have been synthesized in good yields by reaction of alkenes with carbamates and cyanamide, respectively, in presence of benzeneselenenyl chloride–silver tetrafluoroborate or *N*-phenylselenophthalimide–H^+. The subsequent reductive or oxidative removal of the phenylseleno group affords alkylcarbamates and alkylcyanamides, and allylic carbamates, cyanamides, and cyanimides.

The alkene amination reaction is of current interest in organic synthesis due to the important role of nitrogen functional groups in biologically active compounds. Those methods which involve the introduction of a phenylseleno group (aminoselenenylation of alkenes) are specially interesting owing to the versatility and easy manipulation of organoselenium compounds.

The scarce use of nitrogen reagents in nucleophilic intermolecular addition to alkenes, in contrast with the widely used halogeno- and oxy-selenenylation,[1] may be explained in terms of the relatively poor nucleophilicity of the nitrogen atom. Several methods have been reported describing the synthesis of β-phenylselenocarboxamides,[2] sulphonamides,[3] azides,[4] nitrocompounds,[5] and isothiocyanates.[6]

In this paper we describe two new aminoselenenylation reactions, namely carbamato-[7] and cyanamido-selenenylation[8] of alkenes (Scheme 1). The first method allows an efficient preparation of β-phenylseleno and allylcarbamates, and the latter can be transformed eventually to the corresponding allylic primary amines. The second aminoselenenylation reaction reported affords β-phenylseleno cyanamides, which can be transformed into cyanamides, allylic cyanamides, and cyanimides.

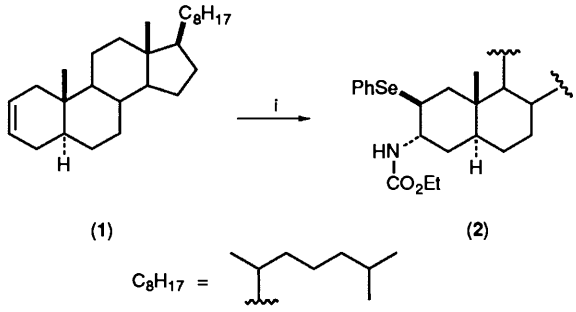


Scheme 1. NuH = H_2NCO_2R, H_2NCN.

Results and Discussion

Carbamatoselenenylation of Alkenes.—Initial attempts using ethyl carbamate, 5α-cholest-2-ene (**1**), and benzeneselenenyl chloride as the electrophilic selenium source were unsuccessful, and the formation of only β-hydroxy and β-chloro selenides was observed. Running the reaction in the presence of silica gel was also unpromising.[9] An increase in electrophilic nature of the selenium reagent has been reported when benzeneselenenyl halides are combined with different silver salts.[10] Increase in the *N*-selectivity of several ambident nucleophiles has also been observed in the presence of mercury salts.[5,6] We therefore decided to try the system PhSeCl–$AgBF_4$ in order to achieve the carbamatoselenenylation of alkenes.†

In a typical experiment (Scheme 2), a solution of benzeneselenenyl chloride (1.1 mmol) in dichloromethane was added



Scheme 2. *Reagents:* i, PhSeCl, $AgBF_4$, H_2NCO_2Et.

dropwise, at 25 °C, under argon, and in the dark, to a well stirred suspension of 5α-cholest-2-ene (**1**) (1 mmol), ethyl carbamate (40 mmol),‡ and silver tetrafluoroborate (1.2 mmol) in dichloromethane. After 1 h at 25 °C 3α-ethoxycarbonylamino-2β-phenylseleno-5α-cholestane (**2**) was obtained in 83% yield. Results are summarized in Table 1 (Method A).§

The axial disposition of the substituents at C-2 and C-3 in the seleno compound (**2**) was clearly established from its ^1H NMR spectrum where two narrow multiplets ($w_{\frac{1}{2}}$ 9 and 14 Hz) at δ 3.60 and 4.05, corresponding to the C-2 and C-3 methine protons respectively, were observed. The phenylseleno group in compound (**2**) was oxidatively removed [H_2O_2, tetrahydrofuran (THF) 25 °C] to give the carbamate (**3**) which in turn was synthesized from 5α-cholest-1-en-3-one following a known procedure.[12]

Clean reactions with high yields were observed with monosubstituted and 1,2-disubstituted alkenes, with the exception of cyclododecene (**16**) (entry 9) that will be discussed below. The regioisomers (**6**), (**7**) and (**11**), (**12**) could be distinguished easily by ^1H NMR and ^{13}C NMR spectroscopy because chemical shifts (δ_H and δ_C) are shifted upfield when the nitrogen is replaced by selenium. Attempts to extend this reaction to 1,1-

† The choice of $AgBF_4$ was based on the one hand on the low nucleophilicity of BF_4^- and on the other that HBF_4 behaved as the best acid catalyst in the carbamatoselenenylation reaction when NPSP was used as the source of electrophilic selenium.

‡ When the reactions were performed with lesser amounts of carbamate (*e.g.*, 10 mmol) smaller yields were observed, even with longer reaction times.

§ For an intramolecular version of this reaction see refs. 9 and 11.

Table 1. Carbamatoselenenylation of alkenes.

Entry	Alkene	Group R in carbamate (H_2NCO_2R)	Method[a]	Temp. (°C); time (h)	Product(s), Yield (%)
1	(**1**)	Et	A	25; 1	(**2**), 83
2	(**1**)	Et	A	25; 24	*b*
3	(**1**)	Et	B	40–45; 7	(**2**), 80
4	(**5**)	Et	A	25; 6	(**6**), 24; (**7**), 56
5	(**5**)	Et	B	40–45; 10	(**6**), 23; (**7**), 55
6	(**10**)	Et	A	25; 7	(**11**), 58; (**12**), 25
7	(**10**)	Et	B	40–45; 10	(**11**), 61; (**12**), 25
8	(**10**)	Et	B	25; 7	(**13**), 65[c]
9	(**16**)	Et	A	25; 20	(**17**), 27; (**20**), 11 (**18**), 40[d]
10	(**16**)	Et	B	40–45; 11	(**17**), 21; (**20**), 10 (**18**), 54[e]
11	(**22**)	Et	A	40–45; 16	(**23**), 12; (**24**), 5; (**25**), 3[f] (**27**), 20; (**28**), 6
12	(**29**)	Et	A	25; 5	*erythro*-(**30**), 95
13	(**29**)	Et	B	40–45; 8	*erythro*-(**30**), 93
14	(**29**)	Cyclohexyl	A	25; 6	(**31**), 74
15	(**29**)	Cyclohexyl	B	40–45; 8	(**31**), 83
16	(**29**)	CH_2Ph	A	25; 6	(**32**), 76
17	(**29**)	CH_2Ph	B	40–45; 8	(**32**), 73
18	(**29**)	Bu^t	A	25; 19	(**33**), 20; (**34**), 17
19	(**36**)	Et	A	25; 7	*threo*-(**30**), 87
20	Cholesteryl ac.	Et	A	25; 20	

[a] Method A: Alkene (1 mmol), PhSeCl (1.2 mmol), $AgBF_4$ (1.3 mmol), H_2NCO_2R (40 mmol). Method B: Alkene (1 mmol), NPSP (1.5 mmol), HBF_4 (0.5–1 mmol), H_2NCO_2R (40 mmol). [b] $AgBF_4$ was omitted. [c] Traces of (**11**) and (**12**) were also detected. [d] Two stereoisomers in a 3:1 ratio. [e] Two stereoisomers in a 2:1 ratio. [f] The reaction products were separated into two unresolved mixtures comprised of (**23**) + (**24**) + (**25**) and (**27**) + (**28**).

disubstituted and trisubstituted alkenes are indicated in entries 11 and 20. Methylenecyclohexane (**22**) partially isomerizes under the reaction conditions used (40–45 °C, 16 h) to 1-methylcyclohexene (**42**), affording the seleno carbamates (**23**), (**24**), and (**25**) and the allylic carbamates (**27**) and (**28**). It is remarkable to note that the acid-catalysed elimination of the phenylseleno group, without the usual oxidation, observed in this case and also in the cyclododecene (**16**) reaction (entry 9) is almost unprecedented.[13] Cholesteryl acetate failed to react under different conditions and the only product detected was the 5α,6β-dihydroxy derivative in 29% yield.

The stereoespecificity of the carbamatoselenenylation reaction was evidenced when (*E*)- and (*Z*)-dec-5-ene were used as olefinic substrates (Scheme 3) to give the *erythro*-(**30**) and *threo*-(**30**) β-phenylseleno carbamates, respectively, in 95 and 87% yield (entries 12 and 19); these stereoisomers show different ^1H and ^{13}C NMR spectral patterns.*

With regard to the regiochemistry of this reaction, we observed that monosubstituted alkenes gave a mixture of regioisomers. Although dodec-1-ene (**10**) yielded predominantly the Markovnikov adduct, the most sterically hindered vinylcyclohexane (**5**) gave mainly the *anti*-Markovnikov product (compare entries 4 and 6). This behaviour indicates that the reaction is highly dependent on steric factors. Thus, the reaction with 5α-cholest-2-ene (**1**) afforded only the regioisomer (**2**) as the carbamate approaches exclusively by the less hindered face of the molecule (α face). Furthermore, in the reaction with 1,1-disubstituted and trisubstituted alkenes, where electronic factors are very important, the *anti*-Markovnikov adducts predominate over the Markovnikov ones (*ca.* 2:1) (entry 11).

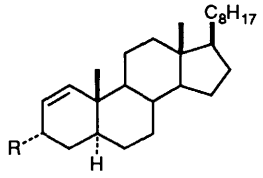
With the aim of facilitating a subsequent deprotection of the amino group, we used cyclohexyl, benzyl, and t-butyl carbamates in the reaction. As shown in Table 1 for (*E*)-dec-5-ene (**29**) (entries 14 and 16), cyclohexyl and benzyl β-phenylseleno carbamates (**31**) and (**32**) were produced in good yield. However, the t-butyl β-phenylseleno carbamate (**33**) (entry 18) was obtained in low yield (20%), in addition to the β-hydroxy selenide (**34**) (17%); the results were not improved when the temperature was increased.

N-(Phenylseleno)phthalimide (NPSP) was also used as the source of electrophilic selenium. The catalytic action of several acids was tested [CF_3SO_3H, HBF_4, camphor-10-sulphonic acid, toluene-*p*-sulphonic acid (PTSA)], tetrafluoroboric acid being the most effective. The system NPSP–HBF_4 overcomes the difficulty of working with the very hygroscopic and expensive silver tetrafluoroborate, and provides an easier work-up procedure. Results are displayed in Table 1 (Method B).

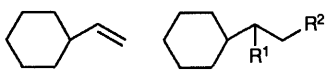
The reaction proceeds stereoselectively and works well with monosubstituted and 1,2-disubstituted alkenes. Although the required reaction temperature is higher than in the preceding reaction (40–45 °C), we found that this carbamatoselenenylation reaction afforded the adducts in similar yields to those obtained with the system PhSeCl–$AgBF_4$, as well as similar regioisomer ratios to those found for the reaction of PhSeCl–$AgBF_4$ with monosubstituted alkenes.

The yields of β-phenylseleno carbamates decreased when the reaction temperature or the reaction time was diminished, and a concomitant increase in the yield of β-hydroxy selenides was observed (compare entries 7 and 8). Owing to the ambident nature of carbamates, compounds (**38**) and (**39**) can be formed by *O*- or *N*-attack, respectively (Scheme 4). The kinetically favoured intermediates (**38**) underwent hydrolysis during the work-up to give β-hydroxy selenides. Nucleophilic *N*-attack on the episelenonium ion (**37**) to produce β-phenylseleno carbamates (**39**) seemed to be an irreversible process under the reaction conditions. Only in the case of cyclododecene (**16**) (entries 9 and 10) did the isomerization (**38**) ⟶ (**39**) turn out

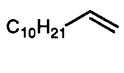
* The *erythro* and *threo* stereochemistries were assigned on the basis of mechanistic considerations: antiperiplanar opening by the carbamate of the episelenonium ion.



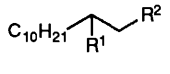
(3) R = $NHCO_2Et$
(4) R = NHCN



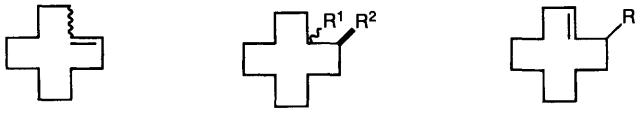
(5) (6) $R^1 = NHCO_2Et$, R^2 = SePh
(7) R^1 = SePh, $R^2 = NHCO_2Et$
(8) R^1 = NHCN, R^2 = SePh
(9) R^1 = SePh, R^2 = NHCN



(10)



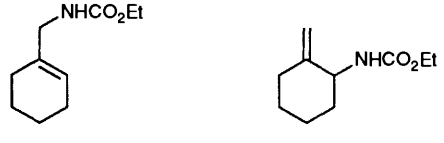
(11) $R^1 = NHCO_2Et$, R^2 = SePh
(12) R^1 = SePh, $R^2 = NHCO_2Et$
(13) R^1 = OH, R^2 = SePh
(14) R^1 = NHCN, R^2 = SePh
(15) R^1 = SePh, R^2 = NHCN



(16) *erythro* – (17) R^1 = SePh, $R^2 = NHCO_2Et$ (20) $R = NHCO_2Et$
(18) R^1 = OH, R^2 = SePh (21) R = NHCN
(19) R^1 = NHCN, R^2 = SePh

(22)

(23) R^1 = SePh, $R^2 = NHCO_2Et$, R^3 = H
(24) R^1 = H, R^2 = SePh, $R^3 = NHCO_2Et$
(25) R^1 = H, $R^2 = NHCO_2Et$, R^3 = SePh
(26) R^1 = SePh, R^2 = NHCN, R^3 = H

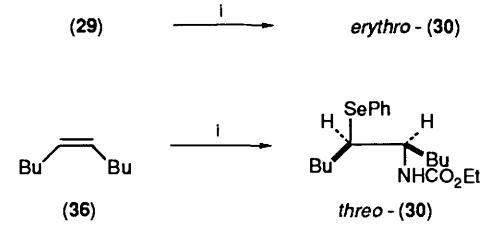


(27) (28)

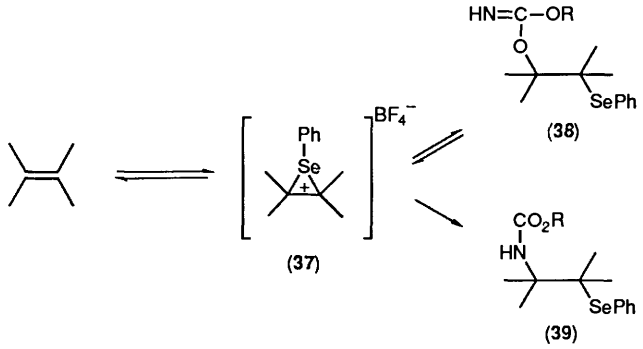
(29)

(30) R = $NHCO_2Et$
(31) R = $NHCO_2C_6H_{11}$
(32) R = $NHCO_2CH_2Ph$
(33) R = $NHCO_2Bu^t$
(34) R = OH
(35) R = NHCN

* Although the reaction was performed with the alkene stereoisomeric mixture (*E*:*Z* 7:3) the β-phenylseleno carbamate (**17**) is a single stereoisomer, for which we tentatively propose the *erythro* stereochemistry.



Scheme 3. *Reagents:* i, PhSeCl, $AgBF_4$, H_2NCO_2Et.



Scheme 4.

to be extremely slow regardless of the system used (Methods A and B), and the reaction product was mostly the β-hydroxy selenide (**18**) (mixture of stereoisomers) with lesser amounts of the carbamate (**17**)* and the allylic carbamate (**20**). This particular situation is presumably associated with conformational factors that hinder the antiperiplanar disposition of the substituents in intermediate (**38**)[14] and therefore the equilibrium (**38**) $\rightleftharpoons$ (**37**).

Cyanamidoselenenylation of Alkenes.—Cyanamide (H_2NCN) can also be used efficiently as a nucleophile in selenium-promoted additions to non-activated alkenes. Thus, in a typical reaction, NPSP (1.3 mmol) was added to a mixture of 5α-cholest-2-ene (**1**) (1 mmol), cyanamide (20 mmol), and PTSA (1 mmol) in dry dichloromethane, in the dark and under argon, and the resulting solution was stirred at 25 °C for 18 h to afford, after column chromatography, the β-phenylseleno cyanamide regioisomers (**40**) and (**41**) in 92% yield [ratio (**40**):(**41**) 3:2].† The results obtained with different alkenes are shown in Table 2.

This reaction was efficiently applied to mono-, di-, and trisubstituted alkenes. Nevertheless, the tetrasubstituted alkene tetrahydroindan (**50**) did not undergo the cyanamidoselenenylation reaction under different reaction conditions (entry 15). The stereochemistry of the products (**47**)–(**49**) (entries 9–11) was confirmed to be *trans* by the wide signal observed in the ^1H NMR spectra (multiplets with $w_{\frac{1}{2}}$ 30–50 Hz) for the protons attached to carbons bearing the phenylseleno and cyanamido groups.

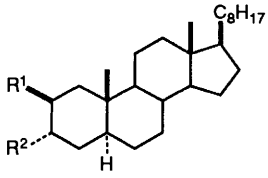
The cyclic diene cyclo-octa-1,5-diene (**51**) gave, after reaction with NPSP–H_2NCN (Scheme 5) the regioisomeric 9-azabicyclo[3.3.1]- and 9-azabicyclo[4.2.1]-nonane (**52**) and (**53**) in 83% yield (ratio 3:2) as the result of a combined process of inter- and intra-molecular nucleophilic addition of cyanamide. The

† The proposed structures for both regioisomers were confirmed by the synthesis of the allylic cyanamide (**4**) [through oxidation to the selenoxide and pyrolysis of the regioisomer (**40**)], also obtained from 3α-amino-5α-cholest-1-ene[12] (i, NaOCN, AcOH, EtOH; ii, $MeSO_2Cl$, pyridine).[15]

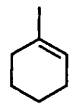
Table 2. Cyanamidoselenenylation of alkenes.[a]

Entry	Alkene	Temp. (°C); time (h)	Product(s), Yield (%)
1	(**1**)	25; 18	(**40**), 55; (**41**), 37
2	(**1**)	25; 3	(**40**), 25; (**41**), 16[b]
3	(**5**)	25; 22	(**8**), 25; (**9**), 25
4	(**5**)	25; 24	(**8**), 41; (**9**), 40[c]
5	(**10**)	25; 24	(**14**), 71; (**15**), 17[c]
6	(**29**)	25; 22	*erythro*-(**35**), 78
7	(**29**)	25; 5	*erythro*-(**35**), 62[b]
8	(**36**)	25; 22	*threo*-(**35**), 81
9	(**44**)	25; 18	(**47**), 74[c]
10	(**45**)	25; 18	(**48**), 65[c]
11	(**46**)	25; 18	(**49**), 44[c]
12	(**16**)	25; 24	(**19**), 76[d]
13	(**22**)	25; 24	(**26**), 71
14	(**42**)	25; 24	(**43**), 78
15	(**50**)	80; 16	*e*
16	(**51**)	25; 18	(**52**), 50; (**53**), 33

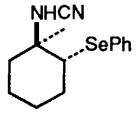
[a] Alkene (1 mmol), H_2NCN (20 mmol), PTSA (1 mmol), NPSP (1.3 mmol), CH_2Cl_2 (30 ml). [b] PhSeCl (1.2 mmol) and $AgBF_4$ (1.3 mmol) were used instead of NPSP–PTSA. [c] Only 0.5 mmol of PTSA per mmol of alkene was employed. [d] Unresolved mixture of diastereoisomers; ratio *erythro*:*threo* 7:3. [e] 1,2-Dichloroethane was used as solvent.



(**40**) R^1 = SePh, R^2 = NHCN
(**41**) R^1 = NHCN, R^2 = SePh

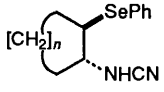


(**42**)

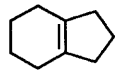


(**43**)

(**44**) *n* = 2
(**45**) *n* = 3
(**46**) *n* = 4



(**47**) *n* = 2
(**48**) *n* = 3
(**49**) *n* = 4



(**50**)

Table 3. Oxidative fragmentation of β-phenylseleno carbamates.[a]

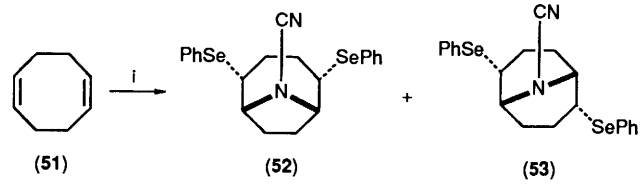
Entry	Carbamate	Temp. (°C); time (h)	Allylic carbamate, Yield (%)
1	(**2**)	25; 25	(**3**), 71
2	(**30**)	25; 19	(**56**), 79
3	(**31**)	25; 18	(**57**), 84
4	(**32**)	25; 14	(**58**), 81

[a] Reactions were carried out in THF with 30% aq. H_2O_2 (2 mmol) as oxidant.

isomer ratio was deduced from the ^1H NMR spectrum of the reaction mixture.[16]

The system PhSeCl–$AgBF_4$ can also be used instead of NPSP–PTSA to promote the cyanamidoselenenylation of alkenes; however, although the reaction times were shorter (3–5 h) lower yields were observed (entries 2 and 7).

The stereospecifity of the reaction is shown in entries 6–8 for (*E*)- and (*Z*)-dec-5-ene. In the case of cyclododecene (**16**) a mixture of isomers (*E*:*Z* 7:3) was used as the starting substrate, and a mixture of isomers (**19**) in the same ratio was formed (entry 12). However, steric hindrance is not so important in this reaction as in the carbamatoselenenylation reaction. Thus, the monosubstituted alkene (**10**) gave mainly the Markovnikov



(**51**) (**52**) (**53**)

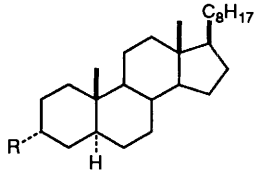
Scheme 5. *Reagents:* i, NPSP, PTSA, H_2NCN.

adduct (entry 5), vinylcyclohexane (**5**) a 1:1 mixture of regioisomers (entries 3 and 4), and the 1,2-disubstituted alkene (**1**) two regioisomers (**40**) and (**41**) in a 3:2 ratio (entries 1 and 2). In addition, the 1,1-disubstituted and trisubstituted alkenes (**22**) and (**42**) (entries 13 and 14) gave exclusively the Markovnikov adducts.

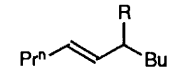
All attempts to use other *N*-nucleophiles such as $MeCONH_2$ and H_2NCONH_2 in the aminoselenenylation reaction were unsuccessful.

Reductive and Oxidative Removal of the Phenylseleno Group.—Treatment of β-phenylseleno carbamate (**2**) and β-phenylseleno cyanamide (**40**) with triphenyltin hydride[17] in toluene at 120 °C for 2–3 h gave the selenium-free compounds (**54**) and (**55**) in 88 and 94% yield, respectively, the carbamate and cyanamide functions remaining unaffected.[18]

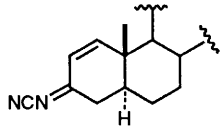
It is well established that the regiochemistry in the selenoxide fragmentation of β-hetero-substituted alkyl phenyl selenides is highly dependent on the nature of the heteroatom.[19] In the particular case of the nitrogen atom it has been reported that β-phenylseleno amides[20] and nitro selenides[5] afford exclusively allyl and vinyl compounds, respectively, while β-phenylseleno dimethylamines,[21] azides,[4] and isothiocyanates[6] lead to mixtures of regioisomers. The two types of adducts described in this paper exhibited different behaviour upon oxidative deselenation. As shown in Table 3, β-phenylseleno carbamates afforded exclusively allylic carbamates after oxidation with H_2O_2 and subsequent pyrolysis at 25 °C. No regioisomers were detected.*



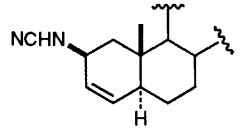
(**54**) R = $NHCO_2Et$
(**55**) R = NHCN



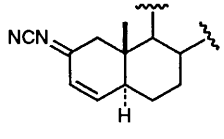
(**56**) R = $NHCO_2Et$
(**57**) R = $NHCO_2C_6H_{11}$
(**58**) R = $NHCO_2CH_2Ph$
(**59**) R = NH_2



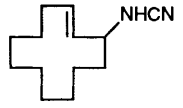
(**60**)



(**61**)



(**62**)



(**21**)

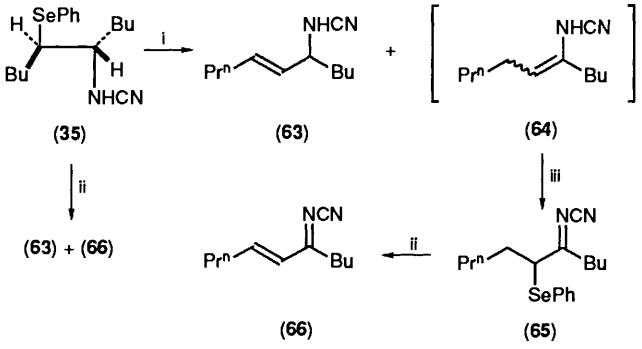
* Deprotection of the benzyl allylic carbamate (**58**) by treatment with Me_3SiCl–NaI in acetonitrile[22] at 30 °C afforded the primary allylic amine (**59**) in 70% yield.

Table 4. Oxidative fragmentation of β-phenylseleno cyanamides.

Entry	Cyanamide	Oxidant[a]	Solvent	Temp. (°C); time (h)	Yield (%) Allylic cyanamide	Yield (%) Cyanimide
1	(**35**)	O_3	CH_2Cl_2	40; 2	(**63**), 30	(**65**), 50
2	(**35**)	H_2O_2[b]	Et_2O	25; 4	(**63**), 30	(**66**), 58
3	(**35**)	H_2O_2[b]	THF	0; 48	(**63**), 59	
4	(**35**)	H_2O_2[b]	MeOH	0; 72	(**63**), 71	(**66**), 5
5	(**35**)	H_2O_2[b]	Et_2O	0; 48	(**63**), 77	
6	(**40**)	H_2O_2[b]	Et_2O	25; 2	(**4**), 22	(**60**), 31
7	(**40**)	H_2O_2[b]	Et_2O	0; 62	(**4**), 40	(**60**), 16
8	(**41**)	H_2O_2[b]	Et_2O	25; 1	(**61**), 40	(**62**), 43
9	(**41**)	O_3	Et_2O	−78; 7/0; 15	(**61**), 73	(**62**), 19
10	(**19**)	O_3	Et_2O	0; 20	(**21**), 61	
11	(**19**)	H_2O_2[b]	Et_2O	0; 24	(**21**), 86	

[a] Ozonizations were carried out at −78 °C. [b] 2–4 mmol of 15–30% aq. H_2O_2 per mmol of cyanamide.

On the other hand, ozonization of β-phenylseleno cyanamide *erythro*-(**35**) (Table 4, entry 1) followed by selenoxide fragmentation at 40 °C led to a mixture of allylic cyanamide (**63**) (30% yield) and β-phenylseleno cyanimide (**65**) (50% yield), the latter produced by addition of PhSeOH to the initially formed vinylic cyanamide (**64**) (Scheme 6).* Further oxidation of



Scheme 6. *Reagents:* i, O_3 (1 mol equiv.); ii, H_2O_2 (4 mol equiv.); iii, PhSeOH.

selenide (**65**) (4 mol equiv. of H_2O_2) gave rise to the unsaturated cyanimide (**66**) in 94% yield. The regioselectivity of the reaction could be improved by an appropriate choice of the reaction conditions as shown in Table 4 for *erythro*-(**35**) (entries 1–5). When the pyrolysis was performed at low temperature the yields of allylic cyanamides were increased and under suitable reaction conditions they were the only observed products. Likewise, Et_2O–H_2O_2 appeared to be the best solvent–oxidant combination for improvement of the yield of allylic cyanamides.

In summary, we describe in this paper two efficient syntheses of β-phenylseleno carbamates and cyanamides from non-activated alkenes. Reductive or oxidative removal of the phenylseleno group in the adducts formed in the carbamatoselenenylation reaction lead, after deprotection, to synthetically useful amines and β-functionalized amines. On the other hand, the cyanamidoselenenylation reaction, together with the thermal allylic transposition of allylic cyanamides that we reported recently,[25] provides a route to a variety of allylic cyanamides as well as cyanamides and cyanimides which can be easily synthesized; this complements the already known halogenocyanamination of alkenes.[26]

* Cyanimides are relatively unknown compounds. To our knowledge they have been prepared by addition of cyanogen azide to olefins[23] and by treatment of cyanamides with lead tetra-acetate.[24]

† Ethyl (2β-phenylseleno-5α-cholestan-3α-yl)carbamate.

Experimental

M.p.s were determined with a Mettler FP82 hot-stage apparatus and are uncorrected. Optical rotations were measured at room temperature for solutions in chloroform on a Perkin-Elmer 241 polarimeter. IR spectra were taken on a Perkin-Elmer 681 instrument for $CHCl_3$ solutions. ^1H and ^{13}C NMR spectra were recorded with a Bruker AC80 or a WP200SY instrument for solutions in $CDCl_3$ (unless otherwise stated) with Me_4Si as internal reference. Low- and high-resolution mass spectra were determined with a VG Micromass ZAB-2F spectrometer at 70 eV. UV spectra were taken on a Perkin-Elmer 550SE instrument for solutions in EtOH. TLC was performed on Merck silica gel 60, and column chromatography on Merck silica gel (0.063–0.2 mm). Circular layers of Merck silica gel 60 PF254 (1 mm) were used on a Harrison chromatotron for centrifugally assisted chromatography. The spray reagent for TLC was vanillin (1 g) in H_2SO_4–EtOH (4:1; 200 ml).

Carbamatoselenenylation of Alkenes. General Procedure.—Method A. To a solution of 5α-cholest-2-ene (**1**) (500 mg, 1.35 mmol), ethyl carbamate (4.75 g, 53.3 mmol), and silver tetrafluoroborate (312 mg, 1.6 mmol) in dry dichloromethane (50 ml) at 25 °C, in the dark, was added dropwise a solution of benzeneselenenyl chloride (285 mg, 1.5 mmol) in dry dichloromethane (8 ml) under argon during 20 min. The mixture was then stirred at 25 °C for 40 min, poured into aq. potassium hydroxide, and extracted with diethyl ether. The extract was filtered through Celite 545, washed with water, dried over Na_2SO_4, and the solvent was then evaporated off. Column chromatography of the residue (hexane–ethyl acetate; 9:1) gave 3α-ethoxycarbonylamino-2β-phenylseleno-5α-cholestane (**2**)† (690 mg, 83%), m.p. 168–172 °C (from MeOH); $[\alpha]_D$ +38° (*c* 0.19); ν_{max} 3 400, 1 705, 1 575, 1 500, and 690 cm^{-1}; δ_H(200 MHz; 50 °C) 7.61 and 7.24 (5 H, 2 m, each $w_{\frac{1}{2}}$ 10 Hz), 4.96 (1 H, br d, *J* 7.4 Hz, NH), 4.05 (1 H, m, $w_{\frac{1}{2}}$ 14 Hz), 4.01 (2 H, q, *J* 7 Hz), 3.60 (1 H, m, $w_{\frac{1}{2}}$ 9 Hz), 1.14 (3 H, t, *J* 7 Hz), 1.00 (3 H, s), 0.91 (3 H, d, *J* 7 Hz), 0.87 (6 H, d, *J* 7 Hz), and 0.66 (3 H, s); δ_C(50.3 MHz; 50 °C) 155.6, 132.0, 42.8, and 36.5 (C), 133.3 (× 2), 129.0 (× 2), 127.2, 56.6, 56.5, 55.5, 52.0, 41.0, 35.8, 35.3, and 28.0 (CH), 60.7, 40.2, 39.6 (× 2), 36.3, 31.9 (× 2), 29.6, 28.2, 24.2, 24.0, and 21.0 (CH_2), 22.7, 22.5, 18.8, 14.6, 14.3, and 12.2 (Me); *m/z* 615 and 613 (10, 5%, M^+), 569.3175 and 567.3304 (59, 34, M^+ − EtOH. $C_{34}H_{51}NOSe$ requires *m/z*, 569.3132 and 567.3139), 526.3115 and 524.2953 (13, 8, $C_{33}H_{50}Se$ requires *m/z*, 526.3076 and

524.3084), and 370.3610 (100, $C_{27}H_{46}$ requires *m/z*, 370.3597).

Method B. A solution of NPSP (51 mg, 0.17 mmol) in dry dichloromethane (1 ml) was added during 30 min, under argon, to a stirred solution of 5α-cholest-2-ene (**1**) (50 mg. 0.14 mmol), ethyl carbamate (506 mg, 5.6 mmol), and tetrafluoroboric acid (12 mg, 0.14 mmol) in dry dichloromethane (10 ml) at 40–45 °C. The mixture was stirred at the same temperature for 5.5 h, and then an additional solution of NPSP (13 mg, 0.04 mmol) in dry dichloromethane (0.3 ml) was added. After being further stirred for 2 h the mixture was poured into aqueous $NaHCO_3$ and extracted with diethyl ether. The extract was washed with water, dried over Na_2SO_4, and the solvent was then evaporated off. Column chromatography of the residue (hexane–ethyl acetate; 9:1) gave 3α-ethoxycarbonylamino-2β-phenylseleno-5α-cholestane (**2**) (66 mg, 80%).

The following β-phenylseleno carbamates were prepared in analogous fashion.

Ethyl [1-*cyclohexyl*-2-(*phenylseleno*)*ethyl*]*carbamate* (**6**). Prepared from vinylcyclohexane (**5**) and ethyl carbamate in 23–24% yield and separated from regioisomer (**7**) by column chromatography (hexane–ethyl acetate; 90:10), *oil*; ν_{max} 3 420, 1 700, 1 570, 1 500, and 690 cm^{-1}; δ_H(200 MHz) 7.53 and 7.24 (5 H, 2 × m, $w_{\frac{1}{2}}$ 12.5 and 10 Hz), 4.71 (1 H, br d, *J* 8 Hz, NH), 4.07 (2 H, q, *J* 7 Hz), 3.70 (1 H, m, $w_{\frac{1}{2}}$ 25 Hz), 3.10 (2 H, br d, *J* 5 Hz), and 1.21 (3 H, t, *J* 7 Hz); δ_C(20.1 MHz) 156.3 and 130.4 (C), 133.0 (× 2), 129.1 (× 2), 127.0, 55.6, and 41.4 (CH), 60.7, 32.2, 30.0, 28.5, 26.3, and 26.0 (× 2) (CH_2), and 14.6 (Me); *m/z* 355.1019 (6%, M^+. $C_{17}H_{25}NO_2Se$ requires *M*, 355.1048), 353 (7, M^+), 266.0547 (3, $C_{14}H_{18}Se$ requires *m/z*, 266.0572), 264 (2), 198.1476 (13, $C_{11}H_{20}NO_2$ requires *m/z*, 198.1493), 156.9538 (81, C_6H_5Se requires *m/z*, 156.9556), 155 (50), and 109 (100).

Ethyl [2-*cyclohexyl*-2-(*phenylseleno*)*ethyl*]*carbamate* (**7**). Prepared from vinylcyclohexane (**5**) and ethyl carbamate in 55–56% yield, *oil*; ν_{max} 3 400, 1 700, 1 570, 1 500, and 690 cm^{-1}; δ_H(200 MHz) 7.54 and 7.26 (5 H, 2 × m, $w_{\frac{1}{2}}$ 12.5 and 10 Hz), 5.08 (1 H, m, $w_{\frac{1}{2}}$ 20 Hz, NH), 4.06 (2 H, q, *J* 7 Hz), 3.54 (1 H, m, $w_{\frac{1}{2}}$ 30 Hz), 3.31 (1 H, ddd, *J* 13.4, 8.0, and 5.4 Hz), 3.17 (1 H, m, $w_{\frac{1}{2}}$ 19 Hz), and 1.20 (3 H, t, *J* Hz); δ_C(20.1 MHz) 156.4 and 129.7 (C), 134.3 (× 2), 129.0 (× 2), 127.3, 54.9, and 40.6 (CH), 60.7, 43.5, 31.3, 30.7, and 26.3 (× 3) (CH_2), and 14.5 (Me); *m/z* 355 (4%, M^+), 353.0972 (2, M^+. $C_{17}H_{25}NO_2Se$ requires *M*, 353.1057), 266.0522 (3, $C_{14}H_{18}Se$ requires *m/z*, 266.0572), 264 (2), 198.1461 (26, $C_{11}H_{20}NO_2$ requires *m/z*, 198.1493), 156.9528 (51, C_6H_5Se requires *m/z*, 156.9556), 155 (40), and 109 (100).

Ethyl [(1-*phenylselenomethyl*)*undecyl*]*carbamate* (**11**). Prepared from dodec-1-ene (**10**) and ethyl carbamate in 58–61% yield and separated from regioisomer (**12**) by chromatography on a chromatotron (hexane–ethyl acetate; 97:3), *oil*; ν_{max} 3 420, 1 700, 1 570, 1 500, and 690 cm^{-1}; δ_H(200 MHz) 7.52 and 7.24 (5 H, 2 × m, $w_{\frac{1}{2}}$ 12.5 and 10 Hz), 4.71 (1 H, br d, *J* 7.6 Hz, NH), 4.06 (2 H, q, *J* 7 Hz), 3.85 (1 H, m, $w_{\frac{1}{2}}$ 24 Hz), 3.10 (2 H, br d, *J* 5 Hz), 1.21 (3 H, t, *J* 7 Hz), and 0.88 (3 H, t, *J* 6.5 Hz); δ_C(20.1 MHz) 156.0 and 130.3 (C), 132.8 (× 2), 130.1 (× 2), 127.0 and 51.1 (CH), 60.7, 34.6, 34.2, 31.9, 29.5 (× 2), 29.4, 29.30, 29.32, 29.27, 25.9, and 22.4 (CH_2), 14.6 and 14.0 (Me); *m/z* 413.1836 and 411.1891 (1 and 1%, M^+. $C_{21}H_{35}NO_2Se$ requires *M*, 413.1831 and 411.1838), 367.1360 (66, $C_{19}H_{29}NOSe$ requires *m/z*, 367.1412), 365 (33), 256.2217 (4, $C_{15}H_{30}NO_2$ requires *m/z*, 256.2275), and 158 (100).

Ethyl [2-(*phenylseleno*)*dodecyl*]*carbamate* (**12**). Prepared from dodec-1-ene (**10**) and ethyl carbamate in 25% yield, *oil*; ν_{max} 3 430, 1 710, 1 570, 1 500, and 690 cm^{-1}; δ_H(200 MHz) 7.53 and 7.26 (5 H, 2 × m, each $w_{\frac{1}{2}}$ 12.5 Hz), 5.10 (1 H, m, $w_{\frac{1}{2}}$ 18 Hz, NH), 4.09 (2 H, q, *J* 7 Hz), 3.40 (1 H, m, $w_{\frac{1}{2}}$ *ca.* 30 Hz), 3.26 (1 H, q, *J* 7 Hz), 3.25 (1 H, m, $w_{\frac{1}{2}}$ *ca.* 8 Hz), 1.22 (3 H, t, *J* 7 Hz), and 0.88 (3 H, t, *J* 6.5 Hz); δ_C(50.3 MHz) 156.5 and 132.8 (C), 135.2 (× 2), 129.1 (× 2), 127.6, and 46.7 (CH), 60.8, 45.0, 32.8, 31.9, 29.6 (× 2), 29.4, 29.3, 27.7, and 22.7 (CH_2), 14.6 and 14.1 (Me); *m/z* 413.1811 and 411.1825 (4 and 2%, M^+), 367.1323 (35, $C_{19}H_{29}NOSe$ requires *m/z*, 367.1412), 365 (19), 324.1335 (2, $C_{18}H_{28}Se$ requires *m/z*, 324.1354), 256.2232 (37, $C_{15}H_{30}NO_2$ requires *m/z*, 256.2275), and 158 (100).

erythro-*Ethyl* [1-*butyl*-2-(*phenylseleno*)*hexyl*]*carbamate* (**30**). Prepared from (*E*)-dec-5-ene (**29**) and ethyl carbamate in 93–95% yield, *oil*; ν_{max} 3 420, 1 700, 1 570, 1 500, and 690 cm^{-1}; δ_H(200 MHz) 7.53 and 7.23 (5 H, 2 × m, $w_{\frac{1}{2}}$ 12.5 and 10 Hz), 4.90 (1 H, br d, *J* 9 Hz, NH), 4.02 (2 H, q, *J* 7 Hz), 3.81 (1 H, m, $w_{\frac{1}{2}}$ 26 Hz), 3.32 (1 H, m, $w_{\frac{1}{2}}$ 20 Hz), 1.18 (3 H, t, *J* 7 Hz), 0.88 (3 H, t, *J* 6 Hz), and 0.87 (3 H, t, *J* 7 Hz); δ_C(20.1 MHz) 156.2 and 130.6 (C), 134.1 (× 2), 129.0 (× 2), 127.2, 55.2, and 54.6 (CH), 60.6, 54.6, 33.8, 31.0, 30.4, 28.3, 22.4, and 22.3 (CH_2), 14.5, 13.9, and 13.8 (Me); *m/z* 385.1525 and 383.1572 (4 and 2%, M^+. $C_{19}H_{31}NO_2Se$ requires *M*, 385.1517 and 383.1526), 228.1951 (19, $C_{13}H_{26}NO_2$ requires *m/z*, 228.1962), and 158 (100).

erythro-*Cyclohexyl* [1-*butyl*-2-(*phenylseleno*)*hexyl*]*carbamate* (**31**). Prepared from (*E*)-dec-5-ene (**29**) and cyclohexyl carbamate in 74–83% yield, oil; ν_{max} 3 420, 1 700, 1 570, 1 500, and 690 cm^{-1}; δ_H(200 MHz) 7.54 and 7.24 (5 H, 2 × m, $w_{\frac{1}{2}}$ 12.5 and 10 Hz), 4.91 (1 H, d, *J* 9 Hz, NH), 4.58 (1 H, m, $w_{\frac{1}{2}}$ 30 Hz), 3.82 (1 H, m, $w_{\frac{1}{2}}$ 26 Hz), 3.30 (1 H, m, $w_{\frac{1}{2}}$ 20 Hz), 0.89 (3 H, t, *J* 6 Hz), and 0.87 (3 H, t, *J* 7 Hz); δ_C(20.1 MHz) 155.7 and 130.6 (C), 134.0 (× 2), 128.9 (× 2), 127.1, 72.7, 55.4, and 54.4 (CH), 33.9, 31.9 (× 2), 30.9, 30.3, 28.2, 25.4, 23.6 (× 2), 22.4, and 22.2 (CH_2), 13.8 and 13.7 (Me); *m/z* 439, 437 (9 and 4%, M^+), 339 (48), 337 (24), 296 (8), 294 (4), 282 (5), 182 (76), 157 (100), and 155 (65).

erythro-*Benzyl* [1-*butyl*-2-(*phenylseleno*)*hexyl*]*carbamate* (**32**). Prepared from (*E*)-dec-5-ene (**29**) and benzyl carbamate in 73–76% yield, *oil*; ν_{max} 3 420, 1 705, 1 575, 1 500, and 690 cm^{-1}; δ_H(200 MHz) 7.51, 7.32, and 7.20 (total 10 H, 3 × m, $w_{\frac{1}{2}}$ 12.5, 25, and 17.5 Hz), 5.05 (1 H, br d, overlapped with AB system, NH), 5.03 and 4.99 (2 H, AB. *J* 12 Hz), 3.84 (1 H, m, $w_{\frac{1}{2}}$ 25 Hz), 3.32 (1 H, m, $w_{\frac{1}{2}}$ 19 Hz), 0.88 (3 H, t, *J* 6 Hz), and 0.86 (3 H, t, *J* 7 Hz); δ_C(50.3 MHz) 155.9, 136.7, and 130.4 (C), 134.0, 129.0, 128.4, 127.9, 127.2, 55.2, and 54.7 (CH), 66.5, 33.8, 30.8, 30.3, 28.2, 22.4, and 22.3 (CH_2), 13.9 and 13.8 (Me); *m/z* 447.1657 and 445.1686 (5 and 3%, M^+. $C_{24}H_{33}NO_2Se$ requires *M*, 447.1673 and 445.1681), 339.1155 and 337.1081 (37 and 20, $C_{17}H_{25}NOSe$ requires *m/z*, 339.1099 and 337.1108), 296 (4), 294.1088 (2, $C_{16}H_{24}Se$ requires *m/z*, 294.1050), 290.2085 (12, $C_{18}H_{28}NO_2$ requires *m/z*, 290.2119), 157 (100), and 155 (60).

erythro-*t-Butyl* [1-*butyl*-2-(*phenylseleno*)*hexyl*]*carbamate* (**33**). Prepared from (*E*)-dec-5-ene (**29**) and t-butyl carbamate (Method A) in 20% yield as *crystals*, m.p. 46–47 °C (neat); ν_{max} 3 420, 1 700, 1 575, 1 495, and 690 cm^{-1}; δ_H(200 MHz) 7.55 and 7.24 (5 H, 2 × m, $w_{\frac{1}{2}}$ 12.5 and 10 Hz), 4.80 (1 H, br d, *J* 9 Hz, NH), 3.75 (1 H, m, $w_{\frac{1}{2}}$ 26 Hz), 3.30 (1 H, m, $w_{\frac{1}{2}}$ 19 Hz), 1.39 (9 H, s), 0.90 (3 H, t, *J* 6.5 Hz), and 0.86 (3 H, t, *J* 7 Hz); δ_C(50.3 MHz) 155.5, 130.9, and 79.1 (C), 134.1 (× 2), 129.0 (× 2), 127.2, 55.9, and 54.3 (CH), 34.2, 31.0, 30.4 (× 2), 22.5, and 22.4 (CH_2), 28.4 (× 3), 13.9, and 13.8 (Me); *m/z* 413.1784 and 411.1723 (22 and 11%, M^+. $C_{21}H_{35}NO_2Se$ requires *M*, 413.1830 and 411.1838), 339.1114 (74, $C_{17}H_{25}NOSe$ requires *m/z*, 339.1099), 337 (38), 296.1008 (10, $C_{16}H_{24}Se$ requires *m/z*, 296.1041), 294 (5), and 200 (100).

threo-*Ethyl* [1-*butyl*-2-(*phenylseleno*)*hexyl*]*carbamate* threo-(**30**). Prepared from (*Z*)-dec-5-ene (**36**) and ethyl carbamate in 87% yield, *oil*; ν_{max} 3 420, 1 705, 1 580, 1 500, and 690 cm^{-1}; δ_H(200 MHz) 7.58 and 7.25 (5 H, 2 × m, $w_{\frac{1}{2}}$ 12.5 and 15 Hz), 4.82 (1 H, br d, *J* 9.4 Hz, NH), 4.10 (2 H, q, *J* 7.1 Hz), 3.84 (1 H, m, $w_{\frac{1}{2}}$ 30 Hz), 3.25 (1 H, m, $w_{\frac{1}{2}}$ 20 Hz), 1.24 (3 H, t, *J* 7.2 Hz), 0.88 (3 H, t, *J* 7 Hz), and 0.79 (3 H, t, *J* 6.5 Hz); δ_C(50.3 MHz) 156.6 and 130.5 (C), 134.5 (× 2), 129.2 (× 2), 127.5, 55.1, and 53.4 (CH), 60.9, 34.3, 33.3, 30.6, 28.6, and 22.6 (× 2) (CH_2), 14.8, 14.13, and 14.06 (Me); *m/z* 385.1542 and 383.1548 (3 and 2%, M^+. $C_{19}H_{31}NO_2Se$ requires *M*, 385.1520 and 383.1528),

297.1191 and 295.1149 (3 and 2, $C_{16}H_{25}Se$ requires *m/z*, 297.1121 and 295.1130), 228.1943 (28, $C_{13}H_{26}NO_2$ requires *m/z*, 228.1963), and 158.1197 (100, $C_8H_{16}NO_2$ requires *m/z*, 158.1180).

Carbamatoselenenylation of Cyclododecene (**16**).—Cyclododecene (**16**) is a 7:3 mixture of *E*- and *Z*-stereoisomer (gas chromatography, 30% carbowax 1500 on chromosorb W; 130 °C). The procedure described for compound (**1**) (Method A) was followed using cyclododecene (**16**) (197 mg, 1.18 mmol), ethyl carbamate (4.2 g, 47.5 mmol), and silver tetrafluoroborate (300 mg, 1.54 mmol) in dry dichloromethane (30 ml), and benzeneselenenyl chloride (272 mg, 1.42 mmol) in dry dichloromethane (5 ml) (reaction time 20 h). Column chromatography of the residue (hexane–ethyl acetate; 97:3) gave erythro-*ethyl* [2-(*phenylseleno*)*cyclododecyl*]*carbamate* (**17**) (133 mg, 27%), the stereoisomers of 2-(*phenylseleno*)*cyclododecan*-**1**-*ol* (**18**) (41 mg, 10%; and 122 mg, 30%), and ethyl [(*E*)-cyclododec-2-enyl]carbamate (**20**) (33 mg, 11%).

Compound (**17**) is a single stereoisomer and the *erythro* stereochemistry was tentatively assigned, m.p. 80–81 °C (from pentane); ν_{max} 3 420, 1 710, 1 570, 1 500, and 690 cm^{-1}; δ_H(200 MHz) 7.57 and 7.27 (5 H, 2 × m, $w_{\frac{1}{2}}$ 12.5 and 10 Hz), 4.95 (1 H, br d, *J* 9 Hz, NH), 4.11 (2 H, q, *J* 7 Hz), *ca.* 4.1 (1 H, m, partially overlapped with signal at δ 4.11), 3.50 (1 H, m, $w_{\frac{1}{2}}$ 20 Hz), and 1.25 (3 H, t, *J* 7 Hz); δ_C(20.1 MHz) 156.4 and 129.7 (C), 134.8 (× 2), 129.1 (× 2), 127.6, 49.8, and 48.4 (CH), 60.8, 32.7, 32.5, 25.4, 25.3, 23.3, 23.0, 22.9, 21.8, and 14.6 (CH_2), and 14.4 (Me); *m/z* 411.1637 and 409.1639 (89 and 49%, M^+. $C_{21}H_{33}NO_2Se$ requires *M*, 411.1637 and 409.1681), 365.1221 (8, $C_{19}H_{27}NOSe$ requires *m/z*, 365.1255), 363 (4), 322.1187 (19, $C_{18}H_{26}Se$ requires *m/z*, 322.1199), 320 (11), 254.2084 (100, $C_{15}H_{28}NO$ requires *m/z*, 254.2119).

Compound (**18**) (minor), amorphous; ν_{max} 3 460, 1 570, and 690 cm^{-1}; δ_H(200 MHz) 7.58 and 7.27 (5 H, 2 × m, $w_{\frac{1}{2}}$ 12.5 and 10 Hz), 3.69 (1 H, m, $w_{\frac{1}{2}}$ 20 Hz), 3.35 (1 H, m, $w_{\frac{1}{2}}$ 25 Hz), and 2.27 (1 H, m, $w_{\frac{1}{2}}$ 7.5 Hz, OH); δ_C(50.3 MHz) 135.1 (× 2), 129.0 (× 2), 127.7, 70.1, and 53.2 (CH), 30.4, 29.3, 24.6, 24.2, 23.7, 23.4, 23.34, 23.30, 23.2, and 20.0 (CH_2); *m/z* 340.1328 and 338.1335 (53 and 26%, M^+. $C_{18}H_{28}OSe$ requires *M*, 340.1304 and 338.1311), 183.1742 (63, $C_{12}H_{23}O$ requires *m/z*, 183.1747), and 158 (100).

Compound (**18**) (major), m.p. 75–76 °C (from pentane); ν_{max} 3 500, 1 575, and 690 cm^{-1}; δ_H(200 MHz) 7.54 and 7.28 (5 H, 2 × m, $w_{\frac{1}{2}}$ 12.5 and 10 Hz), 3.74 (1 H, m, $w_{\frac{1}{2}}$ 21 Hz), 3.44 (1 H, ddd, *J* 1.9, 7.8, and 4.5 Hz), and 2.37 (1 H, d, *J* 4.7 Hz, OH); δ_C(20.1 MHz) 129.6 (C), 134.3 (× 2), 129.1 (× 2), 127.5, 71.7, and 51.7 (CH), 29.8, 26.0, 25.2, 25.0, 24.5, 24.1, 23.7, 22.4, 22.0, and 21.6 (CH_2); *m/z* 340.1303 and 338.1291 (37 and 19%, M^+), 183.1747 (61, $C_{12}H_{23}O$ requires *m/z*, 183.1747), and 158 (100).

Compound (**20**), m.p. 77–78 °C (from pentane); ν_{max} 3 425, 1 705, and 1 500 cm^{-1}; δ_H(200 MHz) 5.61 (1 H, ddd, *J* 16.0, 9.4, and 5.6 Hz), 5.24 (1 H, dd, *J* 16.0 and 8.4 Hz), 4.65 (1 H, m, $w_{\frac{1}{2}}$ 20 Hz, NH), 4.10 (2 H, q, *J* 7 Hz), *ca.* 4.0 (1 H, m, $w_{\frac{1}{2}}$ *ca.* 25 Hz, partially overlapped with a signal at δ 4.10), and 1.23 (3 H, t, *J* 7 Hz); δ_C(20.1 MHz) 154.6 (C), 133.0, 131.0, and 54.0 (CH), 60.6, 33.5, 31.7, 26.0, 25.7, 25.0, 24.5, and 22.8 (CH_2), and 14.6 (Me); *m/z* 253 (47%, M^+), 224 (32), 180 (50), and 164 (100).

Carbamatoselenenylation of Methylenecyclohexane (**22**).—The procedure employed for compound (**1**) (Method A) was followed using methylenecyclohexane (**22**) (66 mg, 0.69 mmol), ethyl carbamate (2.4 g, 27 mmol), and silver tetrafluoroborate (175 mg, 0.9 mmol) in dry dichloromethane (15 ml), and benzeneselenenyl chloride (159 mg, 0.83 mmol) in dry dichloromethane (4 ml) (reaction temperature 40–45 °C; reaction time 16 h). Column chromatography of the crude mixture (hexane; then hexane–ethyl acetate; 95:5) gave a mixture of ethyl [1-(phenylselenomethyl)cyclohexyl]carbamate (**23**), *trans*-ethyl [2-methyl-2-(phenylseleno)cyclohexyl]carbamate (**24**), and *trans*-ethyl [1-methyl-2-(phenylseleno)cyclohexyl]carbamate (**25**) in 12, 5, and 3% yield, respectively (determined by ^1H NMR spectroscopy), and a mixture of ethyl [(cyclohex-1-enyl)methyl]carbamate (**27**) and ethyl (2-methylenecyclohexyl)-carbamate (**28**) in 20 and 6% yield, respectively (^1H NMR spectroscopy). Compounds (**23**), (**24**), and (**25**) each showed ν_{max} 3 430, 1 710, 1 565, 1 500, and 690 cm^{-1}; *m/z* 341, 339 (8 and 4%, M^+), 295 and 293 (19 and 25), 252 and 250 (14 and 7), 184 (21), and 170 (100); δ_H(200 MHz) 7.53 and 7.23 (15 H, 2 × m, $w_{\frac{1}{2}}$ 25 and 20 Hz). Compound (**23**); δ_H(200 MHz) 4.55 (1 H, m, $w_{\frac{1}{2}}$ 7.5 Hz, NH), 3.90 (2 H, q, *J* 7 Hz), 3.41 (2 H, s), and 1.16 (3 H, t, *J* 7 Hz). Compound (**24**); δ_H(200 MHz) 4.5 (1 H, m, $w_{\frac{1}{2}}$ 18 Hz, NH), 4.06 (2 H, q, *J* 7 Hz), 3.98 (1 H, m, $w_{\frac{1}{2}}$ 8 Hz), 1.32 (3 H, s), and 1.19 (3 H, t, *J* 7 Hz). Compound (**25**); δ_H(200 MHz) 5.00 (1 H, m, $w_{\frac{1}{2}}$ 6 Hz, NH), 3.96 (2 H, q, *J* 7.2 Hz), 3.41 (1 H, m, $w_{\frac{1}{2}}$ 11.3 Hz), 1.36 (3 H, s), and 1.23 (3 H, t, *J* 7.2 Hz).

Compounds (**27**) and (**28**) each showed ν_{max} 3 440, 1 700, and 1 505 cm^{-1}; *m/z* 183 (42%, M^+), 154 (100), and 94 (52). Compound (**27**); δ_H(200 MHz) 5.57 (1 H, m, $w_{\frac{1}{2}}$ 10.4 Hz), 4.66 (1 H, m, $w_{\frac{1}{2}}$ 22 Hz, NH), 4.12 (2 H, q, *J* 7 Hz), 3.66 (2 H, d, *J* 6 Hz), and 1.24 (3 H, t, *J* 7 Hz). Compound (**28**): δ_H(200 MHz) 4.73 (2 H, m, $w_{\frac{1}{2}}$ 5 Hz), 4.14–4.07 (2 H, signals overlapped with q at δ 4.12), 4.12 (2 H, q, *J* 7 Hz), and 1.25 (3 H, t, *J* 7 Hz).

1-(*Phenylseleno*)*dodecan*-2-*ol* (**13**).—The procedure used for compound (**1**) (Method B) was followed using dodec-1-ene (**10**) (53 mg, 0.31 mmol), ethyl carbamate (1.12 g, 12.6 mmol), and tetrafluoroboric acid (27 mg, 0.31 mmol) in dry dichloromethane (10 ml), and NPSP (114 mg, 0.38 mmol) in dry dichloromethane (3 ml) (reaction temperature 25 °C; reaction time 7 h). No additional ammount of NPSP was added. Chromatography of the crude extract (hexane) on a chromatotron gave *compound* (**13**) (70 mg, 65%), oil; ν_{max} 3 500, 1 570, and 690 cm^{-1}; δ_H(200 MHz) 7.54 and 7.29 (5 H, 2 × m, $w_{\frac{1}{2}}$ 12.5 and 20 Hz), 3.67 (1 H, m, $w_{\frac{1}{2}}$ 29 Hz), 3.14 (1 H, dd, *J* 12.7 and 3.3 Hz), 2.87 (1 H, dd, *J* 12.7 and 8.7 Hz), 2.37 (1 H, br d, *J* 3.7 Hz, OH), and 1.86 (3 H, t, *J* 7 Hz); *m/z* 342.1453 and 340.1441 (27 and 14%, M^+. $C_{18}H_{30}OSe$ requires *M*, 342.1460 and 340.1467), 185.1807 (4, $C_{12}H_{25}O$ requires *m/z*, 185.1804), 183 (11), 181 (6), 172 (100), and 170 (50).

Cyanamidoselenenylation of Alkenes. Method A. General Procedure.—To a solution of 5α-cholest-2-ene (**1**) (52 mg, 0.14 mmol), cyanamide (118 mg, 2.8 mmol), and PTSA (27 mg, 0.14 mmol) in dry dichloromethane (5 ml) at 25 °C, in the dark, and under argon, was added a solution of NPSP (55 mg, 0.18 mmol) in dry dichloromethane (1.5 ml) during 1 h. The mixture was stirred at 25 °C for 17 h and then was poured into water and extracted with ethyl acetate; the extract was washed with water, and concentrated under reduced pressure. Chromatography of the extract on a chromatotron (benzene–ethyl acetate; 99:1) gave 3α-*cyanoamino*-2β-*phenylseleno*-5α-*cholestane* (**40**) (44 mg, 55%) and 2β-*cyanoamino*-3α-*phenylseleno*-5α-*cholestane* (**41**) (29 mg, 37%). *Compound* (**40**), m.p. 170–173 °C (from acetone–pentane); $[\alpha]_D$ +31° (*c* 0.20); ν_{max} 3 380, 2 210, 1 570, and 690 cm^{-1}; δ_H(C_6D_6; 200 MHz) 7.51 and 7.06 (5 H, 2 × m, $w_{\frac{1}{2}}$ 10 and 30 Hz), 3.52 (1 H, m, $w_{\frac{1}{2}}$ 11.6 Hz), 3.35 (1 H, m, $w_{\frac{1}{2}}$ 9.5 Hz), 2.46 (1 H, br d, *J* 3.5 Hz, NH), 1.04 (3 H, d, *J* 6.4 Hz), 0.94 (6 H, d, *J* 6.5 Hz), 0.91 (3 H, s), and 0.64 (3 H, s); δ_C(20.1 MHz) 131.0, 114.9, 42.6, and 36.5 (C), 133.9 (× 2), 129.3 (× 2), 127.6, 56.3 (× 3), 54.9, 42.6, 39.5, 35.7, 35.1, and 27.9 (CH), 39.9, 39.5, 39.4, 36.2, 31.7 (× 2), 28.8, 28.1, 24.1, 23.8, and 20.8 (CH_2), 22.7, 22.5, 18.6, 14.1, and 12.1 (Me); *m/z* 568.3264 and 566.3394 (41 and 30%, M^+. $C_{34}H_{52}N_2Se$ requires *M*, 568.3292 and 566.3301), 411.3695, (100, $C_{28}H_{47}N_2$ requires *m/z*, 411.3738), and 369.3511 (47, $C_{27}H_{45}$ requires *m/z*, 369.3520).

Compound (**41**), amorphous; $[\alpha]_D$ +15° (*c* 0.24); ν_{max} 3 390,

2 210, 1 570, and 690 cm^{-1}; δ_H(C_6D_6; 200 MHz) 7.52 and 7.06 (5 H, 2 × m, $w_{\frac{1}{2}}$ 12.5 and 25 Hz), 3.55 (1 H, m, $w_{\frac{1}{2}}$ 12 Hz), 3.50 (1 H, m, $w_{\frac{1}{2}}$ 9 Hz), 2.88 (1 H, br d, *J* 2.5 Hz, NH), 1.04 (3 H, d, *J* 6.4 Hz), 0.94 (6 H, d, *J* 6.5 Hz), 0.79 (3 H, s), and 0.65 (3 H, s); δ_C(20.1 MHz) 128.5, 114.9, 42.6, and 37.8 (C), 133.6 (× 2), 129.3 (× 2), 127.7, 56.3, 56.2 (× 2), 55.0, 44.5, 42.2, 35.7, 34.8, and 27.9 (CH), 39.9, 39.5, 37.7, 36.1, 31.5, 29.5, 28.1, 27.9, 24.0, 23.8, and 20.9 (CH_2), 22.7, 22.5, 18.6, 14.7, and 12.1 (Me); *m/z* 568.3267 and 566.3314 (36 and 19%, M^+), 411.3716 (100, $C_{28}H_{47}N_2$ requires *m/z*, 411.3739), and 369.3517 (55, $C_{27}H_{45}$ requires *m/z*, 369.3521).

The following β-phenylseleno cyanamides were prepared in an analogous manner.

[1-Cyclohexyl-2-(*phenylseleno*)*ethyl*]*cyanamide* (**8**). Prepared from vinylcyclohexane (**5**) in 41% yield [PTSA (0.5 mol equiv.); reaction time 24 h] and separated from regioisomer (**9**) by column chromatography (hexane; then hexane–ethyl acetate; 90:10), *oil*; ν_{max} 3 380, 2 210, 1 570, and 690 cm^{-1}; δ_H(200 MHz) 7.53 and 7.29 (5 H, 2 × m, $w_{\frac{1}{2}}$ 12.5 and 10 Hz), 4.02 (1 H, br d, *J* 3.7 Hz, NH), and 3.19–2.92 (3 H); δ_C(20.1 MHz) 128.9 and 115.2 (C), 133.3 (× 2), 129.3 (× 2), 127.6, 61.2, and 41.5 (CH), 30.9, 29.2, 28.5, 26.0, and 25.8 (× 2), (CH_2); *m/z* 308.0779 and 306.0802 (42 and 21%, M^+. $C_{15}H_{20}N_2Se$ requires *M*, 308.0792 and 306.0799), 171.9821 and 169.9851 (100 and 49, C_7H_8Se requires *m/z*, 171.9791 and 169.9799), 156.9558 and 154.9573 (45 and 27, C_6H_5Se requires *m/z*, 156.9556 and 154.9564), and 151.1228 (20, $C_9H_{15}N_2$ requires *m/z*, 151.1235).

[2-Cyclohexyl-2-(*phenylseleno*)*ethyl*]*cyanamide* (**9**) Prepared from vinylcyclohexane (**5**) in 40% yield, oil; ν_{max} 3 380, 2 220, 1 570, and 690 cm^{-1}; δ_H(200 MHz) 7.55 and 7.30 (5 H, 2 × m, $w_{\frac{1}{2}}$ 12.5 and 15 Hz), 4.15 (1 H, br t, $w_{\frac{1}{2}}$ 17 Hz, NH), 3.27 (2 H, m, $w_{\frac{1}{2}}$ 48 Hz), and 3.16 (1 H, m, $w_{\frac{1}{2}}$ 23 Hz); δ_C(20.1 MHz) 133.3 and 115.9 (C), 134.5 (× 2), 129.3 (× 2), 127.5, 54.2, and 39.8 (CH), 48.3, 31.3, 30.6, and 26.1 (× 3) (CH_2); *m/z* 308.0775 and 306.0819 (58 and 29%, M^+), 253.0455 (9, $C_{13}H_{17}Se$ requires *m/z*, 253.0459), 251 (5), 151.1283 (100, $C_9H_{15}N_2$ requires *m/z*, 151.1235), and 109 (94).

[1-(*Phenylselenomethyl*)*undecyl*]*cyanamide* (**14**). Prepared from dodec-1-ene (**10**) in 71% yield [PTSA (0.5 mol equiv.); reaction time 24 h] and separated from regioisomer (**15**) by column chromatography (hexane–ethyl acetate; 85:15), *oil*; ν_{max} 3 360, 2 220, 1 575, and 690 cm^{-1}; δ_H(200 MHz) 7.35 and 7.28 (5 H, 2 × m, $w_{\frac{1}{2}}$ 15 and 20 Hz), 4.09 (1 H, br d, *J* 4.5 Hz, NH), 3.2 (1 H, m, $w_{\frac{1}{2}}$ 25 Hz), 3.10–2.04 (2 H), and 0.88 (3 H, t, *J* 6.4 Hz); δ_C(20.1 MHz) 114.6 (C), 133.2 (× 2), 129.2 (× 2), 127.5, and 56.0 (CH), 33.8, 33.3, 31.7, 30.0, 29.4, 29.2, 29.14, 29.10, 25.6, and 22.5 (CH_2), and 13.9 (Me); *m/z* 366.1534 and 364.1542 (58 and 29%, M^+. $C_{19}H_{30}N_2Se$ requires *M*, 366.1573 and 364.1582), 325.1379 (1, $C_{18}H_{29}Se$ requires *m/z*, 325.1434), 209.2012 (13, $C_{13}H_{25}N_2$ requires *m/z*, 209.2018), 195.1896 (9, $C_{12}H_{23}N_2$ requires *m/z*, 195.1861), and 171.9832 and 169.9829 (100 and 48, C_7H_8Se requires *m/z*, 171.9791 and 169.9799).

[2-(*Phenylseleno*)*dodecyl*]*cyanamide* (**15**). Prepared from dodec-1-ene (**10**) in 17% yield, *oil*; ν_{max} 3 380, 2 220, 1 575, and 690 cm^{-1}; δ_H(200 MHz) 7.54 and 7.31 (5 H, 2 × m, $w_{\frac{1}{2}}$ 10.2 and 20.5 Hz), 4.02 (1 H, br t, $w_{\frac{1}{2}}$ 15.5 Hz, NH), 3.18 (3 H, m, $w_{\frac{1}{2}}$ 37 Hz), and 0.88 (3 H, t, *J* 6.5 Hz); δ_C(50.3 MHz) 133.3 and 115.8 (C), 135.5 (× 2), 129.3 (× 2), 128.4, and 46.2 (CH), 50.2, 46.2, 32.4, 31.9, 29.5 (× 2), 29.4, 29.2, 27.6, and 22.6 (CH_2), and 14.0 (Me); *m/z* 366.1556 and 364.1548 (78 and 41%, M^+), 325.1437 (8, $C_{18}H_{29}Se$ requires *m/z*, 325.1434), 323 (5), 311.1239 (30), $C_{17}H_{27}Se$ requires *m/z*, 311.1278), 309 (15), and 209.2012 (100, $C_{13}H_{25}N_2$ requires *m/z*, 209.2018).

erythro-[1-*Butyl*-2-(*phenylseleno*)*hexyl*]*cyanamide* (**35**). Prepared from (*E*)-dec-5-ene (**29**) in 78% yield (reaction time 22 h), oil; ν_{max} 3 340, 2 210, 1 570, and 690 cm^{-1}; δ_H(200 MHz) 7.55 and 7.30 (5 H, 2 × m, $w_{\frac{1}{2}}$ 12 and 17 Hz), 4.06 (1 H, br d, *J* 6 Hz, NH), 3.31 (1 H, ddd, *J* 8.9, 4.9, and 3.5 Hz), 3.19 (1 H, dddd, *J* 8.9, 4.9, 3.5, and 6.0 Hz), 0.90 (3 H, t, *J* 6.5 Hz), and 0.89 (3 H, t, *J* 6.5 Hz); δ_C(50.3 MHz) 128.9 and 115.4 (C), 134.5 (× 2), 129.2 (× 2), 127.8, 59.8, and 53.2 (CH), 31.0, 30.2, 28.2 (× 2), 22.2, and 22.1 (CH_2), and 13.7 (× 2) (Me); *m/z* 338 and 336 (62 and 31%, M^+), 227 and 225 (100 and 54), 181 (98), and 157 and 155 (87 and 55).

threo-[1-*Butyl*-2-(*phenylseleno*)*hexyl*]*cyanamide*, threo-(**35**). Prepared from (*Z*)-dec-5-ene (**36**) in 81% yield (reaction time 22 h), *oil*; ν_{max} 3 380, 2 225, 1 580, and 700 cm^{-1}; δ_H(200 MHz) 7.50 and 7.28 (5 H, 2 × m, $w_{\frac{1}{2}}$ 10 and 15 Hz), 4.02 (1 H, br d, *J* 6.5 Hz, NH), 3.22 (2 H, m, $w_{\frac{1}{2}}$ 27 Hz), 0.92 (3 H, t, *J* 7 Hz), and 0.83 (3 H, t, *J* 7 Hz); δ_C(20.1 MHz) 128.9 and 115.5 (C), 134.5 (× 2), 129.0 (× 2), 127.7, 60.7, and 52.2 (CH), 32.1, 31.8, 30.1, 28.0, 22.14, and 22.07 (CH_2), 13.7 and 13.6 (Me); *m/z* 338.1281 and 336.1294 (52 and 26%, M^+. $C_{17}H_{26}N_2Se$ requires *M*, 338.1261 and 336.1269), 297.1064 (7, $C_{16}H_{25}Se$ requires *m/z*, 297.1121), 227.0358 and 225.0355 (92 and 48, $C_{11}H_{15}Se$ requires *m/z*, 227.0339 and 255.0347), 181.1721 (78, $C_{11}H_{21}N_2$ requires *m/z*, 181.1785), and 156.9573 and 154.9529 (100 and 56, C_6H_5Se requires *m/z*, 156.9557 and 154.9556).

trans-[2-(*Phenylseleno*)*cyclohexyl*]*cyanamide* (**47**).[27] Prepared from cyclohexene (**44**) in 74% yield [PTSA (0.5 mol equiv.); reaction time 18 h], oil; ν_{max} 3 300, 2 220, 1 560, and 690 cm^{-1}; δ_H(200 MHz) 7.58 and 7.33 (5 H, 2 × m, $w_{\frac{1}{2}}$ 15 and 25 Hz), 4.68 (1 H, m, $w_{\frac{1}{2}}$ 25 Hz, NH), and 2.88 (2 H, m, $w_{\frac{1}{2}}$ 30 Hz); δ_C(50.3 MHz) 125.9 and 114.5 (C), 135.9 (× 2), 129.0 (× 2), 128.3, 57.0, and 48.4 (CH), 33.3, 31.6, 26.2, and 23.9 (CH_2); *m/z* 280.0489 and 278.0508 (29 and 14%, M^+. Calc, for $C_{13}H_{16}N_2Se$: *M*, 280.0478 and 278.0487), 158 (29), 157 (24), 156 (16), 155 (16), 123 (53), and 81 (100).

trans-[2-(*Phenylseleno*)*cycloheptyl*]*cyanamide* (**48**). Prepared from cycloheptene (**45**) in 65% yield [PTSA (0.5 mol equiv.); reaction time 18 h], *oil*; ν_{max} 3 290, 2 220, 1 575, and 690 cm^{-1}; δ_H(200 MHz) 7.57 and 7.32 (5 H, 2 × m, $w_{\frac{1}{2}}$ 15 and 25 Hz), 4.50 (1 H, m, $w_{\frac{1}{2}}$ 20 Hz, NH), and 3.08 (2 H, m, $w_{\frac{1}{2}}$ 50 Hz); δ_C(50.3 MHz) 127.3 and 115.0 (C), 135.3 (× 2), 129.2 (× 2), 128.2, 60.5, and 51.2 (CH), 32.7, 31.2, 27.4, 26.3, and 22.4 (CH_2); *m/z* 294.0674 and 292.0684 (20 and 10%, M^+. $C_{14}H_{18}N_2Se$ requires *M*, 294.0635 and 292.0643), 158 (22), 157 (17), 156 (11), 155 (11), 137 (37), and 95 (100).

trans-[2-(*Phenylseleno*)*cyclo-octyl*]*cyanamide* (**49**). Prepared from (*Z*)-cyclo-octene (**46**) in 44% yield [PTSA (0.5 mol equiv.); reaction time 18 h], *oil*; ν_{max} 3 300, 2 220, 1 580, and 690 cm^{-1}; δ_H(200 MHz) 7.57 and 7.31 (5 H, 2 × m, $w_{\frac{1}{2}}$ 15 and 25 Hz), 4.69 (1 H, m, $w_{\frac{1}{2}}$ 17 Hz, NH), and 3.24 (2 H, m, $w_{\frac{1}{2}}$ 40 Hz); δ_C(50.3 MHz) 127.2 and 115.0 (C), 135.3 (× 2), 129.2 (× 2), 128.3, 59.3, and 50.2 (CH), 31.7, 29.0, 26.8, 26.2, 25.1, and 23.8 (CH_2); *m/z* 308.0837 and 306.0828 (29 and 14%, M^+. $C_{15}H_{20}N_2Se$ requires *M*, 308.0791 and 306.0800), 158 (48), 157 (44), 156 (24), 155 (29), 151 (72), and 109 (100).

[2-(*Phenylseleno*)*cyclododecyl*]*cyanamide* (**19**). Prepared from cyclododecene (**16**) (7:3 mixture of *E*- and *Z*-stereoisomer) in 76% yield (reaction time 24 h). *Compound* (**19**) was a 7:3 mixture of stereoisomers as determined by ^1H NMR spectroscopy; ν_{max} 3 340, 2 220, 1 575, and 690 cm^{-1}; δ_H(200 MHz) 7.55 and 7.30 (10 H, 2 × m, $w_{\frac{1}{2}}$ 15 and 12.5 Hz), 4.47 (1 H, minor, m, $w_{\frac{1}{2}}$ 13 Hz, NH), 4.11 (1 H, major, m, $w_{\frac{1}{2}}$ 16 Hz, NH), 3.45 (1 H, major, m, $w_{\frac{1}{2}}$ 17 Hz), and 3.31 (3 H, m, $w_{\frac{1}{2}}$ 13 Hz); δ_C(20.1 MHz) 115.4 (C), 135.3, 134.5, 129.4, 129.3, 128.5, 128.2, 128.0, 57.0, 56.5, 49.0, and 48.3 (CH), 30.2, 29.4, 27.2, 26.6, 24.5, 24.1, 24.0, 23.8, 23.2, 22.1, 21.9, 21.8, and 20.1 (CH_2); *m/z* 364.1398 and 362.1512 (32 and 12%, M^+. $C_{19}H_{28}N_2Se$ requires *M*, 364.1418 and 362.1425), 207.1866 (31, $C_{13}H_{23}N_2$ requires *m/z*, 207.1861), 180.1805 (8, $C_{12}H_{22}N$ requires *m/z*, 180.1752), and 156.9564 and 154.9578 (100 and 51, C_6H_5Se requires *m/z*, 156.9556 and 154.9565).

[1-(*Phenylselenomethyl*)*cyclohexyl*]*cyanamide* (**26**).[27] Prepared from methylenecyclohexane (**22**) in 71% yield (reaction

time 24 h), oil; ν_{max} 3 360, 2 210, 1 570, and 690 cm^{-1}; δ_H(200 MHz) 7.57 and 7.28 (5 H, 2 × m, $w_{\frac{1}{2}}$ 12.5 and 10 Hz), 3.96 (1 H, m, $w_{\frac{1}{2}}$ 20 Hz, NH), and 3.15 (2 H, s); δ_C(20.1 MHz) 130.0, 113.7, and 57.7 (C), 133.1 (× 2), 129.2 (× 2), and 127.3 (CH), 40.9, 34.7 (× 2), 24.9, and 21.6 (× 2) (CH_2); *m/z* 294.0702 and 292.0642 (12 and 6%, M^+. Calc. for $C_{14}H_{18}N_2Se$: *M*, 294.0635 and 292.0643), 252.0448 and 250.0421 (3 and 2. Calc. for $C_{13}H_{16}Se$: *m/z*, 252.0417 and 250.0425), 171.9812 and 169.9838 (100 and 50. Calc. for C_7H_8Se: *m/z*, 171.9791 and 169.9799), 157.9622 and 155.9625 (78 and 41. Calc. for C_6H_6Se: *m/z*, 157.9635 and 155.9597), 156.9552 and 154.9631 (41 and 31. Calc. for C_6H_5Se: *m/z*, 156.9556 and 154.9564), 137.1088 (8. Calc. for $C_8H_{13}N_2$: *m/z*, 137.1079), and 123.0956 (80. Calc. for $C_7H_{11}N_2$: *m/z*, 123.0922).

trans-[1-*Methyl*-2-(*phenylseleno*)*cyclohexyl*]*cyanamide* (**43**).[27] Prepared from 1-methylcyclohexene (**42**) in 78% yield (reaction time 24 h), oil; ν_{max} 3 330, 2 210, 1 570, and 690 cm^{-1}; δ_H(80 MHz) 7.59 and 7.30 (5 H, 2 × m, $w_{\frac{1}{2}}$ 13 and 9 Hz), 4.38 (1 H, m, $w_{\frac{1}{2}}$ 12 Hz, NH), 3.19 (1 H, dd, *J* 12 and 5 Hz), and 1.32 (3 H, s); δ_C(20.1 MHz) 113.7 and 58.6 (C), 134.6 (× 2), 129.2 (× 2), 127.8, and 55.6 (CH), 37.3, 32.2, 26.3, and 22.2 (CH_2), and 21.5 (Me); *m/z* 294 and 292 (28 and 14%, M^+), 253 (1), 251 (1), 157 (22), 155 (15), and 137 (100).

endo,endo-N-*Cyano*-2,5-*bis*(*phenylseleno*)-9-*azabicyclo*-[4.2.1]*nonane* (**52**) *and* endo,endo-N-*cyano*-2,6-*bis*(*phenylseleno*)-9-*azabicyclo*[3.3.1]*nonane* (**53**). Obtained from cycloocta-1,5-diene (**51**) in 83% yield (reaction time 18 h) as an unresolved mixture [ratio (**52**):(**53**) 3:2]; ν_{max} 2 200, 1 570, and 690 cm^{-1}; *m/z* 462, 460, and 458 (3, 3, and 1%, M^+), 305 (53), 303 (26), 263 (4), 261 (2), 157 (100), 155 (51), 147 (79), and 105 (45); δ_H(200 MHz) 7.54 and 7.28 (20 H, 2 × m, $w_{\frac{1}{2}}$ 12.5 and 15 Hz). Compound (**52**); δ_H(200 MHz) 4.16 (2 H, m, $w_{\frac{1}{2}}$ 17 Hz) and 3.75 [2 H, m, $w_{\frac{1}{2}}$ 11 Hz, overlapped with m at δ 3.78 of (**53**)]. Compound (**53**); δ_H(200 MHz) 3.78 [2 H, m, $w_{\frac{1}{2}}$ 11 Hz, overlapped with m at δ 3.75 of (**52**)] and 3.43 (2 H, m, $w_{\frac{1}{2}}$ 12 Hz).

Cyanamidoselenenylation of Alkenes. Method B. General Procedure.—A solution of benzeneselenenyl chloride (76 mg, 0.4 mmol) in dry dichloromethane (2 ml) was added during 1 h, in the dark and under argon, to a stirred solution of 5α-cholest-2-ene (**1**) (121 mg, 0.33 mmol), cyanamide (275 mg, 6.5 mmol), and silver tetrafluoroborate (83 mg, 0.43 mmol) in dry dichloromethane (5 ml) at 0 °C. The mixture was then stirred at 25 °C for 2 h, poured into water, and extracted with ethyl acetate. The extract was filtered through Celite 545, washed with water, and dried over Na_2SO_4. Column chromatography of the residue (hexane; then benzene–ethyl acetate; 98:2) gave 3α-cyanoamino-2β-phenylseleno-5α-cholestane (**40**) (46 mg, 25%) and 2β-cyanoamino-3α-phenylseleno-5α-cholestane (**41**) (31 mg, 16%).

erythro[1-Butyl-2-(phenylseleno)hexyl]cyanamide (**35**) was also prepared by this method from (*E*)-dec-5-ene (**29**) in 62% yield (reaction time 1 h at 0 °C; 4 h at 25 °C).

Reductive Removal of the Phenylseleno Group.—To a solution of ethyl (2β-phenylseleno-5α-cholestan-3α-yl)carbamate (**2**) (51 mg, 0.08 mmol) in dry toluene (1 ml) at 120 °C was added, under argon and during 1 h, a solution of triphenyltin hydride (84 mg, 0.25 mmol) in dry toluene (1 ml). The reaction mixture was refluxed for an additional 2 h and then cooled, poured into water, and extracted with ethyl acetate; the extract was washed with water. Column chromatography (benzene) gave ethyl (5α-cholestan-3α-yl)carbamate (**54**) (32 mg, 88%), m.p. 119–121 °C (from MeOH); $[\alpha]_D$ +31° (*c* 0.08); ν_{max} 3 400, 1 700, and 1 500 cm^{-1}; δ_H(200 MHz) 4.93 (1 H, m, $w_{\frac{1}{2}}$ 22 Hz, NH), 4.10 (2 H, q, *J* 7 Hz), 3.88 (1 H, m, $w_{\frac{1}{2}}$ 17.5 Hz), 1.24 (3 H, t, *J* 7 Hz), 0.90 (3 H, d, *J* 7 Hz), 0.86 (6 H, d, *J* 6.5 Hz), 0.79 (3 H, s), and 0.65 (3 H, s); δ_C(50.3 MHz) 155.8, 42.6, and 36.0 (C), 56.6, 56.3, 54.6, 46.3, 42.3, 40.7, 35.8, 35.5, and 28.0 (CH), 60.5, 40.0, 39.5, 36.2, 33.3, 33.0, 32.0, 28.5, 28.2, 26.4, 24.1, 23.8, and 20.8 (CH_2), 22.8, 22.5, 18.7, 14.6, 12.1, and 11.4 (Me); *m/z* 459 (5, M^+), 413.3634 (82, M^+ − EtOH. $C_{28}H_{47}NO$ requires *m/z*, 413.3656), 398.3395 (93, $C_{27}H_{44}NO$ requires *m/z*, 398.3369), 370.3539 (100, $C_{27}H_{46}$ requires *m/z*, 370.3598), and 355.3342 (64, $C_{26}H_{43}$ requires *m/z*, 355.3363).

3α-*Cyanoamino*-5α-*cholestane* [(5α-*cholestan*-3α-*yl*)*cyanamide*] (**55**). To a solution of 3α-cyanoamino 1-2β-phenylseleno-5α-cholestane (**40**) (60 mg, 0.1 mmol) in dry toluene (1 ml) at 120 °C was added, under argon and during 1 h, a solution of triphenyltin hydride (111 mg, 0.32 mmol) in dry toluene (1 ml). The reaction mixture was refluxed for 1 h, and after usual work-up and column chromatography (hexane–ethyl acetate; 95:5 and 85:15), gave *compound* (**55**) (41 mg, 94%), m.p. 179–180 °C (from hexane); $[\alpha]_D$ +24° (*c* 0.2); ν_{max} 3 380 and 2 210 cm^{-1}; δ_H(200 MHz) 3.60 (1 H, m, $w_{\frac{1}{2}}$ 13.5 Hz), 3.44 (1 H, br d, *J* 3.5 Hz, NH), 0.90 (3 H, d, *J* 6.5 Hz), 0.86 (6 H, d, *J* 6.5 Hz), 0.79 (3 H, s), and 0.65 (3 H, s); δ_C(20.1 MHz) 115.5, 42.6, and 36.1 (C), 56.6, 56.4, 54.4, 51.6, 39.5, 35.8, 35.5, and 28.0 (CH), 40.0, 39.6, 36.2, 32.6, 32.2, 31.9, 28.3, 28.2, 25.7, 24.2, 23.9, and 20.8 (CH_2), 22.8, 22.5, 18.7, 12.1, and 11.4 (Me); *m/z* 412.3816 (25%, M^+. $C_{28}H_{48}N_2$ requires *M*, 412.3816), 397.3593 (27, $C_{27}H_{45}N_2$ requires *m/z*, 397.3580), 370.3622 (20, $C_{27}H_{46}$ requires *m/z*, 370.3597), and 257.2025 (100, $C_{17}H_{25}N_2$ requires *m/z*, 257.2016).

Oxidative Fragmentation of β-*Phenylseleno Carbamates. General Procedure.*—To a solution of ethyl (2β-phenylseleno-5α-cholestan-3α-yl)carbamate (**2**) (250 mg, 0.4 mmol) in THF (50 ml) at 0 °C was added 30% aq. H_2O_2 (0.09 ml, 0.8 mmol). After 25 h at 25 °C the reaction mixture was poured into water, extracted with ethyl acetate, and the extract was washed with water. Column chromatography of the residue (hexane–ethyl acetate; 95:5) gave *ethyl* (5α-*cholest*-1-*en*-3α-*yl*)*carbamate* (**3**) (132 mg, 71%), m.p. 93–94 °C (from MeOH); $[\alpha]_D$ −13° (*c* 0.28); ν_{max} 3 400, 1 705, and 1 500 cm^{-1}; δ_H(200 MHz) 6.05 (1 H, dd, *J* 10 and 1 Hz), 5.48 (1 H, dd, *J* 10 and 3.8 Hz), 4.83 (1 H, br d, *J* 8 Hz, NH), 4.11 (2 H, q, *J* 7 Hz), *ca.* 4.1 (1 H, m, $w_{\frac{1}{2}}$ *ca.* 15 Hz), 1.24 (3 H, t, *J* 7 Hz), 0.91 (3 H, d, *J* 7 Hz), 0.86 (6 H, d, *J* 6.5 Hz), 0.81 (3 H, s), and 0.67 (3 H, s); δ_C(50.3 MHz) 155.6, 42.6, and 37.7 (C), 140.3, 124.0, 56.5, 56.2, 51.2, 42.6, 39.9, 35.7, 35.6, and 27.9 (CH), 60.6, 39.9, 39.5, 36.1, 32.7, 31.9, 28.2, 27.9, 24.1, 23.8, and 21.1 (CH_2), 22.7, 22.5, 18.6, 14.6, 14.2, and 12.1 (Me); *m/z* 457.3907 (5%, M^+. $C_{30}H_{51}NO_2$ requires *M*, 457.3919), 442.3712 (2, $C_{29}H_{48}NO_2$ requires *m/z*, 442.3685), 428.3553 (16, $C_{28}H_{46}NO_2$ requires *m/z*, 428.3528), 411.3522 (20, $C_{28}H_{45}NO$ requires *m/z*, 411.3501), 368.3452 (100, $C_{27}H_{44}$ requires *m/z*, 368.3443), and 353.3184 (22, $C_{26}H_{41}$ requires *m/z*, 353.3209).

The following allylic carbamates were prepared by an analogous procedure.

Ethyl [(E)-1-*Butylhex*-2-*enyl*]*carbamate* (**56**). Prepared from *erythro*-ethyl [1-butyl-2-(phenylseleno)hexyl]carbamate (**30**) in 79% yield, *oil*; ν_{max} 3 430, 1 700, and 1 500 cm^{-1}; δ_H(200 MHz) 5.57 (1 H, dt, *J* 15.3 and 6.6 Hz), 5.31 (1 H, dd, *J* 15.3 and 6.3 Hz), 4.63 (1 H, m, $w_{\frac{1}{2}}$ 25 Hz, NH), 4.11 (2 H, q, *J* 7 Hz), *ca.* 4.1 (1 H, m, $w_{\frac{1}{2}}$ *ca.* 30 Hz), 1.23 (3 H, t, *J* 7 Hz), 0.89 (3 H, t, *J* 6.5 Hz), and 0.88 (3 H, t, *J* 7 Hz); δ_C(50.3 MHz) 156.0 (C), 131.1, 130.7, and 52.8 (CH), 60.5, 35.3, 34.2, 27.8, 22.4, and 22.3 (CH_2), 14.5, 13.9, and 13.5 (Me); *m/z* 227.1871 (3%, M^+. $C_{13}H_{25}NO_2$ requires *M*, 227.1884), 198 (6), 184 (21), 170.1177 (100, $C_9H_{16}NO_2$ requires *m/z*, 170.1180), 154 (6), and 139 (10).

Cyclohexyl [(E)-1-*Butylhex*-2-*enyl*]*carbamate* (**57**). Prepared from *erythro*-cyclohexyl[1-butyl-2-(phenylseleno)hexyl]carbamate (**31**) in 84% yield, oil; ν_{max} 3 430, 1 695, and 1 500 cm^{-1}; δ_H(200 MHz) 5.57 (1 H, dt, *J* 15.3 and 6.5 Hz), 5.31 (1 H, dd, *J* 15.3 and 6.3 Hz), 4.63 (1 H, m, $w_{\frac{1}{2}}$ 27 Hz), 4.48 (1 H, m, $w_{\frac{1}{2}}$ 27 Hz, NH), 4.05 (1 H, m, $w_{\frac{1}{2}}$ 30 Hz), and 0.88 (6 H, t, *J* 7.3 Hz); δ_C(50.3 MHz) 155.4 (C), 130.8, 130.6, 72.5, and 52.6 (CH), 35.1, 34.0,

31.8, 27.6, 25.2, 23.5, 22.2, and 22.1 (CH_2), 13.7 and 13.3 (Me); *m/z* 281.2372 (1%, M^+. $C_{17}H_{31}NO_2$ requires *M*, 281.2353), 224.1652 (32, $C_{13}H_{22}NO_2$ requires *m/z*, 224.1649), 142.0814 (100, $C_7H_{12}NO_2$ requires *m/z*, 142.0866), and 138 (6).

Benzyl [(E)-1-*Butylhex*-2-*enyl*]*carbamate* (**58**). Prepared from *erythro*-benzyl [1-butyl-2-(phenylseleno)hexyl]carbamate (**32**) in 81% yield, *oil*; ν_{max} 3 420, 1 700, 1 500, and 690 cm^{-1}; δ_H(200 MHz) 7.33 (5 H, m, $w_{\frac{1}{2}}$ 12.5 Hz), 5.57 (1 H, dt, *J* 15.3 and 6.6 Hz), 5.31 (1 H, dd, *J* 15.3 and 6.3 Hz), 5.10 (2 H, s), 4.64 (1 H, m, $w_{\frac{1}{2}}$ 20 Hz, NH), 4.09 (1 H, m, $w_{\frac{1}{2}}$ 30 Hz), and 0.88 (6 H, t, *J* 7 Hz); δ_C(20.1 MHz) 155.8 (C), 131.3, 130.7, 128.4, 128.0, and 53.0 (CH), 66.5, 35.3, 34.2, 27.8, 22.4, and 22.3 (CH_2), 13.9 and 13.5 (Me); *m/z* 289.2006 (1%, M^+. $C_{18}H_{27}NO_2$ requires *M*, 289.2042), 232.1355 (78, $C_{14}H_{18}NO_2$ requires *m/z*, 232.1337), 198.1494 (23, $C_{11}H_{20}NO_2$ requires *m/z*, 198.1494), 188 (100), and 154.1602 (11, $C_{10}H_{20}N$ requires *m/z*, 154.1596).

(E)-*Dec*-6-*en*-5-*amine* (**59**).—To a mixture of benzyl [(*E*)-1-butylhex-2-enyl]carbamate (**58**) (45 mg, 0.16 mmol) and dry NaI (94 mg, 0.62 mmol) in dry acetonitrile (0.4 ml) was added trimethylsilyl chloride (67 mg, 0.63 mmol) and the reaction mixture was stirred at 30 °C for 6.5 h. After the mixture had cooled to 25 °C, a saturated solution of hydrogen chloride (0.47 mmol) in methanol was added and the mixture was stirred for 30 min. The reaction mixture was then poured into ethyl acetate and extracted with 0.1% aq. HCl. The aqueous layer was saturated with NaCl, basified with aq. KOH, and extracted with ethyl acetate. The extract was dried over Na_2SO_4 and the solvent was evaporated off to give amine (**59**) (17 mg, 70%), oil; ν_{max} 3 300 and 1 590 cm^{-1}; δ_H(200 MHz) 5.70 (1 H, m, $w_{\frac{1}{2}}$ 32 Hz), 5.39 (1 H, m, $w_{\frac{1}{2}}$ 32 Hz), 3.60 (3 H, m, $w_{\frac{1}{2}}$ 80 Hz), and 0.89 (6 H, t, *J* 7 Hz). *Acetamide derivative* of (**59**), *oil*; ν_{max} 3 430, 1 720, 1 650, and 1 505 cm^{-1}; δ_H(200 MHz) 5.58 (1 H, dt, *J* 15.5 and 6.6 Hz), 5.32 (1 H, dd, *J* 15.5 and 6.3 Hz), 4.38 (1 H, m, $w_{\frac{1}{2}}$ 32 Hz), 1.98 (3 H, s), 0.91 (3 H, t, *J* 7 Hz), and 0.88 (3 H, t, *J* 7 Hz); *m/z* 197.1844 (8%, M^+. $C_{12}H_{23}NO$ requires *M*, 197.1779), 140.1090 (100, $C_8H_{14}NO$ requires *m/z*, 140.1069), and 128.1084 (6, $C_7H_{14}NO$ requires *m/z*, 128.1075).

Oxidative Fragmentation of β-*Phenylseleno Cyanamides. General Procedure.*—(a) *With* O_3. A solution of *erythro*-[1-butyl-2-(phenylseleno)hexyl]cyanamide (**35**) (110 mg, 0.32 mmol) in dichloromethane (60 ml) was cooled to −78 °C under argon, and ozone was introduced into the solution until the colour of the solution became blue. Then argon was bubbled through the solution to expel excess of ozone and the mixture was heated under reflux for 2 h, then poured into water, and extracted with dichloromethane; the extract was washed with water, and column chromatography of the residue (hexane–ethyl acetate; 9:1) gave (*E*)-1-butylhex-2-enylcyanamide (**63**) (18 mg, 30%) and [1-*butyl*-2-(*phenylseleno*)*hexylidene*]*cyanamide* (**65**) (55 mg, 50%. Compound (**63**), oil; ν_{max} 3 380, 3 330, and 2 210 cm^{-1}; δ_H(200 MHz) 5.69 (1 H, dt, *J* 15.3 and 6.7 Hz), 5.32 (1 H, dd, *J* 15.3 and 7.7 Hz), 3.57 (2 H, m, $w_{\frac{1}{2}}$ 24 Hz), and 0.91 (6 H, t, *J* 7 Hz); δ_C(20.1 MHz) 134.5, 129.0, and 58.4 (CH), 34.3, 34.1, 27.7, 22.2, and 22.0 (CH_2), 13.7 and 13.4 (Me); *m/z* 180 (1%, M^+), 151 (7), 139 (15), 137 (12), and 123 (100).

Compound (**65**), oil; ν_{max} 2 180, 1 590, and 690 cm^{-1}; λ_{max} 225 (9 360) and 240 (10 110) nm; δ_H(200 MHz) 7.38 (5 H, m, $w_{\frac{1}{2}}$ 50 Hz), 3.73 (1 H, t, *J* 7.4 Hz), 2.78 (2 H, m, $w_{\frac{1}{2}}$ 24 Hz), and 0.92 (6 H, t, *J* 7.2 Hz); δ_C(50.3 MHz) 136.6, 129.5, 129.4, and 50.5 (CH), 39.0, 31.0, 30.3, 29.3, and 22.4 (× 2) (CH_2), 13.9 and 13.6 (Me); *m/z* 336.1096 and 334.1083 (33 and 16%, M^+. $C_{17}H_{24}N_2Se$ requires *M*, 336.1104 and 334.1113), 225 (20), and 230 (100).

(b) *With* H_2O_2. To a solution of *erythro*-[1-butyl-2-(phenylseleno)hexyl]cyanamide (**35**) (100 mg, 0.29 mmol) in diethyl ether (50 ml) at 0 °C was added 30% aq. H_2O_2 (0.06 ml. 1.16 mmol). After 4 h at 25 °C the reaction mixture was poured into water, extracted with diethyl ether, and the extract was washed with water. Chromatography of the extract on a chromatotron (hexane–ethyl acetate; 95:5) gave [(*E*)-1-butylhex-2-enyl]cyanamide (**63**) (16 mg, 30%) and [(E)-1-*butyl*-2-*hex*-2-*enylidene*]*cyanamide* (**66**) (31 mg, 58%). Compound (**66**), from NMR data, was shown to be a *ca.* 1:1 mixture of the stereoisomers in the cyanimide group; oil; ν_{max} 2 180, 1 630, and 1 555 cm^{-1}; λ_{max} 260 nm (18 540); δ_H(200 MHz) 7.02–6.17 (2 H), 2.85–2.61 (2 H), 2.30 (2 H, m, $w_{\frac{1}{2}}$ 24 Hz), and 0.96 (6 H, t, *J* 7 Hz); δ_C(50.3 MHz) 151.5, 150.7, 130.0, and 127.3 (CH), 36.3, 35.4, 35.3, 35.1, 30.3, 29.2, 22.8, 22.5, and 21.5 (CH_2), and 13.8 (Me); *m/z* 179.1532 (2%, $M^+ + 1$. $C_{11}H_{19}N_2$ requires $M^+ + 1$, 179.1548), 135.0892 (100, $C_8H_{11}N_2$ requires *m/z*, 135.0922), and 121.0776 (45, $C_7H_9N_2$ requires *m/z*, 121.0765).

As shown in Table 4, the following cyanamides and cyanimides were prepared in an analogous way.

3α-*Cyanoamino*-5α-*cholest*-1-*ene* (**4**). M.p. 125 °C (from hexane); $[\alpha]_D$ −14° (*c* 0.25); ν_{max} 3 390 and 2 200 cm^{-1}; δ_H(200 MHz) 6.19 (1 H, d, *J* 10 Hz), 5.22 (1 H, ddd, *J* 10, 4.4, and 1.5 Hz), 3.73 (1 H, m, $w_{\frac{1}{2}}$ 10 Hz), 3.42 (1 H, br d, *J* 6 Hz, NH), 0.90 (3 H, d, *J* 7 Hz), 0.86 (6 H, d, *J* 6.8 Hz), 0.81 (3 H, s), and 0.66 (3 H, s); *m/z* 410.3635 (100%, M^+. $C_{28}H_{46}N_2$ requires *M*, 410.3659), 395.3440 (35, $C_{27}H_{43}N_2$ requires *m/z*, 395.3425), 368.3472 (67, $C_{27}H_{44}$ requires *m/z*, 368.3440), and 255 (93).

3-*Cyanoimino*-5α-*cholest*-1-*ene* (**60**). From ^1H NMR data it was shown that, in solution, this *compound* was a *ca.* 7:3 mixture of the stereoisomers in the cyanimide group; m.p. 111–112 °C (from MeOH); $[\alpha]_D$ +108° (*c* 0.1); ν_{max} 2 180, 1 700, and 1 565 cm^{-1}; λ_{max} 267 nm (20 810); δ_H(200 MHz) 7.20 and 7.14 (1 H, 2 × d, each *J* 10.1 Hz), 6.60 and 6.16 (1 H, 2 × d, each *J* 10.1 Hz), 0.98 and 0.97 (3 H, 2 × s), 0.91 (3 H, d, *J* 7 Hz), 0.86 (6 H, d, *J* 6.6 Hz), and 0.69 (3 H, s); *m/z* 408.3514 (60%, M^+. $C_{28}H_{44}N_2$ requires *M*, 408.3504), 393.3262 (25, $C_{27}H_{41}N_2$ requires *m/z*, 393.3270), 365.2943 (9, $C_{25}H_{37}N_2$ requires *m/z*, 365.2957), 323.2488 (14, $C_{22}H_{31}N_2$ requires *m/z*, 323.2478), 300.2832 (26, $C_{22}H_{36}$ requires *m/z*, 300.2817), 295.2189 (38, $C_{20}H_{27}N_2$ requires *m/z*, 295.2174), and 146.0841 (100, $C_9H_{10}N_2$ requires *m/z*, 146.0844).

2β-*Cyanoamino*-5α-*cholest*-3-*ene* (**61**). Amorphous; $[\alpha]_D$ +25° (*c* 0.13); ν_{max} 3 390 and 2 210 cm^{-1}; δ_H(200 MHz) 5.62 (2 H, m, $w_{\frac{1}{2}}$ 7.5 Hz), 3.88 (1 H, m, $w_{\frac{1}{2}}$ 20 Hz), 3.42 (1 H, br d, *J* 7 Hz, NH), 0.90 (3 H, d, *J* 7 Hz), 0.86 (6 H, d, *J* 6.6 Hz), 0.85 (3 H, s), and 0.66 (3 H, s); δ_C(50.3 MHz) 115.5, 42.7, and 33.7 (C), 136.7, 123.0, 56.2 (× 2), 53.5, 51.1, 45.5, 35.7, 35.0, and 28.0 (CH), 41.3, 39.8, 39.5, 36.1, 31.8, 28.2, 27.1, 24.1, 23.8, and 21.1 (CH_2), 22.8, 22.5, 18.6, 13.8, and 12.1 (Me); *m/z* 410.3655 (100%, M^+. $C_{28}H_{46}N_2$ requires *M*, 410.3658), 395.3437 (41, $C_{27}H_{43}N_2$ requires *m/z*, 395.3424), 368.3421 (36, $C_{27}H_{44}$ requires *m/z*, 368.3441), and 255 (64).

2-*Cyamoimino*-5α-*cholest*-3-*ene* (**62**). From NMR data it was shown that this compound in solution was a *ca.* 7:3 mixture of stereoisomers in the cyanimide group; m.p. 115–115.5 °C (from MeOH); $[\alpha]_D$ +89° (*c* 0.21); ν_{max} 2 180, 1 610, and 1 560 cm^{-1}; λ_{max} 267 nm (15 830); δ_H(200 MHz) 6.75–6.24 (2 H), 0.90 (3 H, d, *J* 6.5 Hz), 0.86 (6 H, d, *J* 6.8 Hz), 0.84 and 0.82 (3 H, 2 × s), and 0.66 (3 H, s); δ_C(50.3 MHz) 190.8, 188.8, 114.5, 42.8, and 40.5 (C), 156.2, 155.8, 128.0, 123.8, 56.4, 56.3, 53.5, 47.4, 35.9, 35.1, and 28.1 (CH), 48.3, 47.8, 39.7, 36.3, 31.9, 28.2, 26.5, 26.4, 24.2, 24.0, and 21.2 (CH_2), 22.9, 22.7, 18.8, 12.8, 12.6, and 12.2 (Me); *m/z* 408.3486 (10%, M^+. $C_{28}H_{44}N_2$ requires *M*, 408.3504), 393.3281 (4, $C_{27}H_{41}N_2$ requires *m/z*, 393.3269), 253.1658 (26, $C_{17}H_{21}N_2$ requires *m/z*, 253.1705), 231 (37), 145.0798 (20, $C_9H_9N_2$ requires *m/z*, 145.0765), and 123.1160 (100, C_9H_{15} requires *m/z*, 123.1174).

[(E)-*Cyclododec*-2-*enyl*]*cyanamide* (**21**). M.p. 51–52 °C (from pentane); ν_{max} 3 380, 3 220, and 2 220 cm^{-1}; δ_H(200 MHz) 5.70 (1 H, ddd, *J* 15.2, 9.9, and 4.8 Hz), 5.32 (1 H, ddd, *J* 15.2, 8.8, and 1.2 Hz), and 3.65 (2 H, m, $w_{\frac{1}{2}}$ 34 Hz); δ_C(20.1 MHz) 115.5 (C), 135.8, 129.1, and 59.1 (CH), 32.6, 31.5, 25.7 (× 2), 24.9, 24.6, 24.3 (× 2),

and 22.7 (CH_2); *m/z* 206.1781 (40%, M^+. $C_{13}H_{22}N_2$ requires *M*, 206.1783), 205.1704 (40, $C_{13}H_{21}N_2$ requires *m/z*, 205.1704), 165 (100), and 163 (73).

[(E)-1-*Butylhex*-2-*enylidene*]*cyanamide* (**66**) *from Selenide* (**65**).—To a solution of [1-butyl-2-(phenylseleno)hexylidene]-cyanamide (**65**) (60 mg, 0.17 mmol) at 0 °C was added 30% aq. H_2O_2 (0.072 ml, 0.71 mmol) and the reaction mixture was stirred at 25 °C for 3 h. The usual work-up and chromatography on a chromatotron (hexane–ethyl acetate; 95:5) gave compound (**66**) (25 mg, 78%).

3α-*Cyanoamino*-5α-*cholest*-1-*ene* (**4**).—A mixture of 3α-amino-5α-cholest-1-ene (162 mg, 0.42 mmol),[12] acetic acid (0.03 ml, 0.56 mmol), and sodium cyanate (43 mg, 0.66 mmol) was refluxed for 1 h. After usual work-up, the crude urea (180 mg) was dissolved in dry pyridine (2.5 ml) and methanesulphonyl chloride (0.06 ml, 0.82 mmol) was added to the mixture at 0 °C. After 1 h at 0 °C, followed by the usual work-up and column chromatography (hexane–ethyl acetate; 9:1), the allylic cyanamide (**4**) (155 mg, 90%) was obtained.

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