the oily residue was chromatographed (CH_2Cl_2/acetone, 25:1) to afford **29** as a colorless oil (0.16 g, 51%) as a mixture of two stereoisomers (~1:1). ^1H NMR: δ (isomer I) 4.19 (H-7a, dd, J = 12, 5.5 Hz, 1 H), 4.25, 3.97 ($CO_2CH_2CH_3$, AB q split into q, J = 10.5, 7 Hz, 2 H), 2.89 (H-4 eq, dm, J = 13.5 Hz, 1 H), 2.4–1.4 (H-4–H-7a, m, 7 H), 1.81 (Me s, 3 H), 1.27 ($CO_2CH_2CH_3$, t, J = 7 Hz, 3 H); (isomer II) 4.16 (H-7a, dd, J = 12, 5.5 Hz, 1 H), 4.21, 3.95 ($CO_2CH_2CH_3$, AB q split into q, J = 10.5 7 Hz, 2 H), 2.89, (H-4 eq, dm, J = 13.5 Hz, 1 H), 2.4-1.4 (H-4–H-7a, m, 7 H), 1.87 (Me, s, 3 H), 1.25 ($CO_2CH_2CH_3$, t, J = 7 Hz, 3 H). ^{13}C NMR (isomer I): δ 176.32 (C=N), 171.66 (CO_2Et), 86.61 (C-2), 61.60 ($CO_2CH_2CH_3$), 60.25 (C-7a), 37.61 (C-7), 32.64 (C-4), 27.76[a] (C-5), 26.76[a] (C-6), 25.14 (CH_3), 13.88 ($CO_2CH_2CH_3$); (isomer II) 176.43 (C=N), 172.03 (CO_2Et), 87.68 (C-2), 61.60 ($CO_2CH_2CH_3$), 59.78 (C-7a), 37.96 (C-7), 32.25 (C-4), 29.90[b] (C-5), 27.19[b] (C-6), 25.46 (CH_3), 13.88 ($CO_2CH_2CH_3$). IR (neat): ν max 1725 (C=O), 1665 (C=N) cm^{-1}. MS (m/e): 228 (MH^+), 154 (MH^+-HCO_2Et). HRMS: calcd for $C_9H_{12}NS$ (M – CO_2Et) 154.0690, found 154.0661. Anal. (mixture of isomers) Calcd for $C_{11}H_{17}NO_2S$: C, 58.13; H, 7.54. Found: C, 58.23; H, 7.48.

2-Methyl-2-carbethoxycyclopenta[*d*]-2,6a-dihydrothiazole (28). Prepared from **16a**, n = 3, as described above. The two isomers were obtained as a colorless oil (42% yield, ratio ~1:1); after chromatography (ether/hexane, 6:1) each stereoisomer was isolated. ^1H NMR: δ (isomer I) 4.49 (H-6, dd, J = 11.5, 7 Hz, 1 H), 4.25 ($CO_2CH_2CH_3$, q, J = 7 Hz, 2 H), 2.5–2.0, 1.65–1.55 (H-4–H-6, m, 6 H), 1.83 (Me, s, 3 H) 1.30 ($CO_2CH_2CH_3$, t, 3 H). ^{13}C NMR: δ 185.68 (C=N), 172.04 (CO_2Et), 98.30 (C-2), 61.77 ($CO_2CH_2CH_3$), 60.41 (C-6a), 32.12 (C-6), 27.91 (C-4), 25.06 (C-5), 24.91 (CH_3), 14.06 ($CO_2CH_2CH_3$). ^1H NMR: δ (isomer II) 4.55 (H-6a, dd, J = 12, 7 Hz, 1 H), 4.20 ($CO_2CH_2CH_3$, AB q split into q, J = 11, 7 Hz, 2 H), 2.61 (H-4, eq, ddm, J = 17.5, 10 Hz, 1 H), 2.5–1.6 (H-4–H-6, m, 5 H), 1.92 (CH_3, s, 3 H), 1.28 ($CO_2CH_2CH_3$, t, J = 7 Hz, 3 H). ^{13}C NMR: δ 188.77 (C=N), 171.38 (CO_2Et), 95.71 (C-2), 62.42 (CO_2CHCH_3), 61.73 (C-6a), 32.10 (C-6), 27.25 (C-4), 25.60 (C-5), 25.12 (CH_3), 14.00 ($CO_2CH_2CH_3$). IR (neat): ν max 1725 br (C=O), 1655 br (C=N) cm^{-1}. MS (m/e): 214 (MH^+), 140 (MH^+ – HCO_2Et). HRMS: calcd for $C_7H_{10}NS$ (M – CO_2Et) 140.0534, found 140.0555.

2-Methyl-1,2-dicarbethoxycyclopenta[*d*]-2,6a-dihydroimidazole (30). A solution of aldehyde **16a** (0.14 g, 0.71 mmol), ethyl carbamate (0.15 g, 2.4 equiv), and a catalytic amount of p-toluenesulfonic acid (0.01 g) in benzene (6 mL) was heated under reflux in a Dean–Stark system for 2.5 h. The colorless solution turned black. The reaction mixture was filtered through basic alumina. The solvent was removed and the dark oil residue was sublimed to yield **30** as a thick yellow oil at 160 °C (2 mmHg) (0.082 g, 43%). The product was obtained as a mixture of four isomers. ^1H NMR: δ 4.86, 4.79, 4.70, 4.62 (H-6, four dd, J = 11, 7.5 Hz, 1 H), 4.15 ($CO_2CH_2CH_3$, m, 4 H), 2.50–2.10 ($CH_2CH_2CH_2$, m, 6 H), 1.91, 1.83, 1.77, 1.73 (Me, s, 3 H), 1.30 ($CO_2CH_2CH_3$, m, 6 H). ^{13}C NMR: δ 186.34, 184.74, 184.61 (C=N), 169.47, 169.20 (CO_2Et), 154.52, 152.76 (NCO_2Et), 126.32, 124.72 (C-2), 99.81, 99.14 (C-6a), 72.08, 70.97, 69.17, 68.44 ($NCO_2CH_2CH_3$), 61.76, 61.56, 61.33, 61.17 ($CO_2CH_2CH_3$), 30.80–21.11 ($CH_2CH_2CH_2$), 14.55–14.00 ($NCO_2CH_2CH_3$, $CO_2CH_2CH_3$). IR (neat): ν max 1747 (CO_2Et), 1709 (NCO_2Et), 1674 (C=N) cm^{-1}. MS: 269 (MH^+), 195 (MH^+ – CO_2Et). HRMS: calcd for $C_{10}H_{15}N_2O_2$ (M – CO_2Et) 195.1129, found 195.1196.

2-Methyl-1,2-dicarbethoxycyclohexano[*d*]-2,7a-dihydroimidazole (31). The product obtained, following the above procedure, was a mixture of **31** and **27** in a ratio of 18:82 according to GC/MS. Complete separation of **31** by flash chromatography was not successful. The data given below are for a mixture enriched in **31**. Total yield 41%. ^1H NMR: δ 4.48, 4.40, 4.33, 4.25 (H-7a, 4 dd, J = 1.1, 6 Hz, 1 H), 2.4–1.4 (H-4–H-7, m, 7 H), 1.82, 1.77, 1.71, 1.66 (Me, 4 s, 3 H), 1.25 ($CO_2CH_2CH_3$, $NCO_2CH_2CH_3$, m, 6 H). ^{13}C NMR: δ 176.89, 176.74 (C=N), 170.39 (CO_2Et), 108.45 (C-2), 67.51, 66.44, 66.42, 65.82 (C-7a), 61.72, 61.70, 61.27, 61.12 (CO_2Et, NCO_2Et), 35.42, 33.70, 32.71, 31.34, 26.61, 26.26, 24.67, 23.11, 22.53, 21.88 (C-7–C-4), 14.54, 14.37 (CO_2Et, NCO_2Et). MS (m/e): 283 (MH^+), 209 (MH^+ – HCO_2Et). IR (neat): ν max 1735 (CO_2Et), 1700 (NCO_2Et), 1655 (C=N) cm^{-1}.

Acknowledgment. Support of this work by a grant from the US–Israel Binational Science Foundation is gratefully acknowledged. We thank Dr. H. E. Gottlieb for his help with NMR spectra.

Supplementary Material Available: ^1H and ^{13}C NMR spectra for compounds **21a**, **21b**, **28a**, **28b**, and **30** (10 pages). Ordering information is given on any current masthead page.

Organoselenium- and Proton-Mediated Cyclization Reactions of Allylic Amides and Thioamides. Syntheses of 2-Oxazolines and 2-Thiazolines

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A variety of allylic amides and thioamides were treated with phenylselenenyl bromide in chloroform to give, via 5-exo cyclization, 2-oxazolines and 2-thiazolines, respectively, carrying a (phenylselenenyl)methyl substituent in the 5-position. In some cases (*N*-crotyl- and *N*-cinnamylamides/thioamides), dihydro-1,3-oxazines/-thiazines were formed via 6-endo cyclization. The phenylselenenyl group of the cyclofunctionalization products was slowly eliminated by treatment with *m*-chloroperbenzoic acid to introduce unsaturation in the resulting oxazoline/thiazoline. Reductive removal of the phenylselenenyl group was effected by treatment with triphenyltin hydride. This reaction was sometimes accompanied by a rearrangement of the heterocyclic ring. Proton-induced cyclizations of allylic thioamides to give 2-thiazolines was slowly but efficiently effected in boiling toluene containing a catalytic amount of *p*-toluenesulfonic acid.

Introduction

Organoselenium-mediated cyclization reactions have been very useful in organic syntheses over the last decade. Conceptually, the reactions involve addition of electrophilic selenium to an unsaturated site in the molecule, followed by intramolecular attack by a suitably positioned nucleophile. Cyclization of unsaturated alcohols, thiols, carboxylic acids, and amine derivatives are all well-represented in the literature. In addition, it is possible, with certain substrates, to form new carbon–carbon bonds in the reaction.[1]

Ethylurethanes of 4-pentenamines and 5-hexenamines, when treated with phenylselenenyl chloride, gave pyrrol-

(1) Nicolaou, K. C.; Petasis, N. A.; Claremon, D. A. In *Organoselenium Chemistry*; Liotta, D., Ed.; Wiley: New York, 1987; p 127.

0022-3263/91/1956-3425$02.50/0

Scheme I

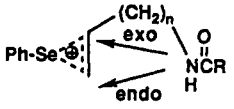


Table I. Phenylselenenyl Bromide Induced Cyclizations of Allylic Amides and Thioamides

entry	starting material	X	R	R_1	R_2	R_3	product	yield[a] (%)
1	1a	O	Ph	H	H	H	2a	97
2	1b	O	Ph	CH_3	H	H	2b	100
3	1c	O	Ph	H	H	CH_3	2c/3c = 1/2[b]	98
4	1d	O	Ph	H	H	Ph	c	
5	1e	O	Ph	H	CH_3	CH_3	c	
6	1f	O	CH_3	H	H	H	2f	70
7	1g	O	CH_3	CH_3	H	H	2g	94
8	1h	S	Ph	H	H	H	2h	85
9	1i	S	Ph	CH_3	H	H	2i	54
10	1j	S	Ph	H	H	CH_3	2j/3j = 87/13[b]	85
11	1k	S	Ph	H	H	Ph	3k	76
12	1l	S	Ph	H	CH_3	CH_3	2l	71
13	1m	S	CH_3	H	H	H	2m	87

[a] Isolated yield. [b] Isomeric composition of crude product as determined by ^1H NMR. [c] No product isolated.

idines and piperidines, respectively, via exo ring closures.[2] However, certain olefinic substituents can also direct the nucleophilic attack to occur in an endo fashion (Scheme I). Similar results were obtained with unsaturated amines protected as carboxamides.[3]

The situation is further complicated in cyclofunctionalization reactions of 4-pentenoic amides and related compounds. With these substrates, the cyclization can either occur from nitrogen, to give a lactam, or, from oxygen, to give an iminolactone (Scheme II).[4]

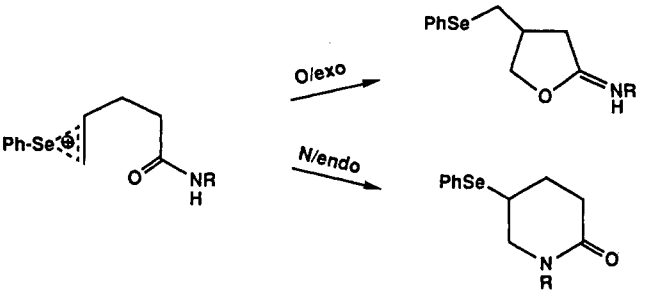
When the carbon chain connecting the nitrogen atom and the olefin was shortened in *N*-alkenylcarboxamides (Scheme I; R = CH_3, n = 2) the exo O-cyclization mode, leading to a dihydrooxazine, was the only one observed.[3] Allylic ureas, when treated with phenylselenenyl chloride, similarly afforded only products of O-cyclization (oxazolines).[5] The formation of oxazolines from *N*-allylbenzamides and *N*-(phenylseleno)phthalimide was recently observed during attempts to prepare tetrahydroisoquinoline-type ring systems.[6] A similar ring-closure reaction also occurred when *N*-allylbenzamide was treated with diphenyl diselenide/ammonium peroxydisulfate.[7]

In the following we report phenylselenenyl bromide and proton-induced cyclizations of allylic amides and thioamides for the preparation of 2-oxazolines and 2-thiazolines.

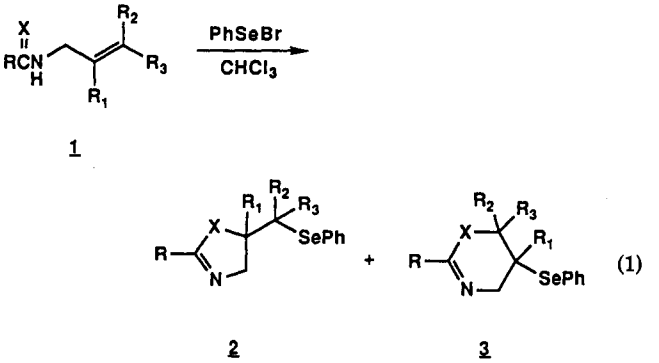
Results

Phenylselenenenyl Bromide Induced Cyclizations. When *N*-allylbenzamide (**1a**) was treated in chloroform at ambient temperature with a stoichiometric amount of

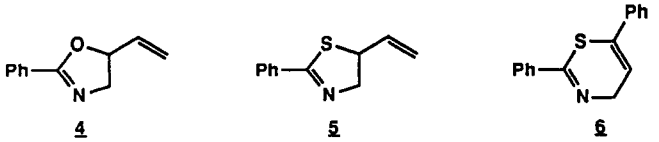
Scheme II



phenylselenenyl bromide, compound **2a** was isolated as the only product in 97% yield after aqueous workup (eq 1; Table I). The assignment of the compound as an exo



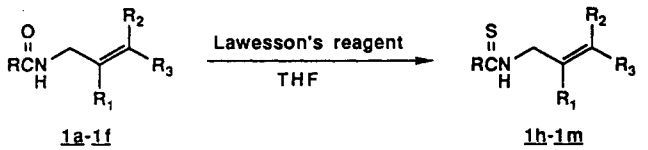
cyclization product rather than an endo one (**3a**) is based on ^1H NMR data (the methine proton R_1 of compound **2a** resonated at δ 4.89, which is in agreement with literature data[7] and ~1.5 ppm more downfield from TMS than proton R_1 of compound **3a**). Cyclofunctionalization of *N*-(2-methylallyl)benzamide (**1b**) similarly afforded 2-oxazoline **2b** in excellent yield. When *N*-crotylbenzamide (**1c**) was submitted to the usual reaction conditions, mixtures of compounds **2c** and **3c** were formed, the ratio varying from one experiment to another. However, by using a basic workup procedure (Na_2CO_3 (aq)) and a short reaction time, a 1:2 mixture of compounds **2c** and **3c** was always obtained. The assignment of compounds **2c** and **3c** was not obvious from inspection of the spectroscopic data. This was instead based on chemical evidence: when compound **2c** was treated with *m*-chloroperbenzoic acid in chloroform, 2-phenyl-5-vinyl-2-oxazoline (**4**) was formed via a regiospecific elimination of the corresponding selenoxide (66% yield). The large vicinal coupling constant $^3J_{R_1-R_2}$ (eq 1) of compound **3c** (9.8 Hz) indicates that the methyl and phenylselenenyl groups are oriented trans to each other.



Cinnamylamine derivative **1d** failed to give any cyclized products under the usual reaction conditions. Attempts to run the reaction in the presence of pyridine or silica gel[5] also met with failure. Prenylamine derivative **1e** afforded an inseparable mixture of products when treated with PhSeBr. PhSeBr-induced cyclization of *N*-allylacetamide (**1f**) afforded oxazoline **2f** in poor yield. However, by using the basic workup procedure, the yield was significantly improved (70%). *N*-(2-Methylallyl)acetamide (**1g**) was treated with PhSeBr in the presence of 1 equiv of pyridine to give oxazoline **2g** in 94% yield.

(2) Clive, D. L. J.; Farina, V.; Singh, A.; Wong, C. K.; Kiel, W. A.; Menchen, S. M. *J. Org. Chem.* **1980**, *45*, 2120.
(3) Toshimitsu, A.; Terao, K.; Uemura, S. *J. Org. Chem.* **1986**, *51*, 1724.
(4) Toshimitsu, A.; Terao, K.; Uemura, S. *J. Org. Chem.* **1987**, *52*, 2018.
(5) Betancor, C.; Leŏn, E. I.; Prange, T.; Salazar, J. A.; Suárez, E. *J. Chem. Soc., Chem. Commun.* 1989, 450.
(6) Chrétien, F.; Chapleur, Y. *J. Org. Chem.* **1988**, *53*, 3615.
(7) Tiecco, M.; Testaferri, L.; Tingoli, M.; Bartoli, D.; Balducci, R. *J. Org. Chem.* **1990**, *55*, 429.

Encouraged by our results with allylic amides, we were curious to see if allylic thioamides would undergo similar cyclization reactions. The required starting materials **1h–1m** were obtained from the allylic amides **1a–1f** by treatment with an excess of Lawesson's reagent[8] in refluxing tetrahydrofuran (eq 2).



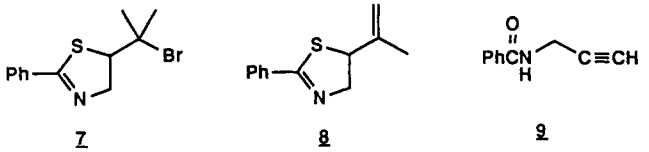
1a-1f 1h-1m (2)

On treatment with PhSeBr in $CHCl_3$, the allylic thioamides **1h** and **1i** afforded 2-thiazolines **2h** and **2i**, respectively, in good yields (eq 1, Table I). The cyclofunctionalization product obtained from crotylamine derivative **1j** consisted of an 87:13 mixture of 2-thiazoline **2j** and dihydrothiazine **3j**. A facile selenoxide elimination reaction of compound **2j** to give 2-phenyl-5-vinyl-2-thiazoline (**5**) in 66% yield, provided further support for the structural assignment.

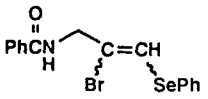
The coupling constant $^3J_{R_1-R_2}$ (eq 1) of compound **3j** (10.2 Hz) indicates a trans arrangement of the methyl and phenylselenenyl groups.

Acetonitrile was the solvent of choice for the cyclofunctionalization of compound **1k**. The assignment of the product as a dihydrothiazine **3k** ($^3J_{R_1-R_2}$ = 10.4 Hz) was based on a selenoxide elimination experiment: treatment of the compound with *m*-CPBA afforded 2,6-diphenyl-4*H*-1,3-thiazine (**6**) in 75% yield.

Prenylamine derivative **1l** was best cyclized in acetonitrile to give a 95:5 mixture of 2-thiazoline derivatives **2l** and **7**. As a proof of the structure, selenoxide elimination of compound **2l** afforded 2-thiazoline **8** in 81% of yield. *N*-Allylthioacetamide (**1m**) gave 2-thiazoline **2m** as the only cyclization product when treated with PhSeBr.



7 8 9



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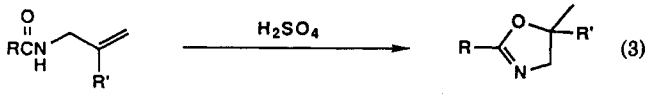
An attempt was also made to induce cyclization of propargylic amides with PhSeBr. However, when submitted to the usual cyclofunctionalization conditions, benzamide **9** afforded an addition compound **10** in 96% yield. The regio- and stereochemistry of addition was not determined (only one isomer is formed). Compound **9** did not give a thioamide when heated with Lawesson's reagent.

Proton-Induced Cyclizations of Allylic Thioamides. To study the role of the electrophile in the cyclofunctionalization reactions of allylic amides and thioamides, it would be interesting to determine the mode of cyclization for proton-induced reactions. Already 20 years ago, McManus and co-workers reported cyclizations of allylic amides to give oxazolines (eq 3).[9-11] Similar cyclizations



(3)

(8) Cava, M. P.; Levinson, M. I. *Tetrahedron* **1985**, *41*, 5061.

Table II. Proton-Induced Cyclizations of Allylic Thioamides 1h–1l

entry	starting material	R_1	R_2	R_3	product	yield[a] (%)
1	**1h**	H	H	H	**11h**	95
2	**1i**	CH_3	H	H	**11i**	79
3	**1j**	H	H	CH_3	**11j**	80
4	**1k**	H	H	Ph	**11k**	75
5	**1l**	H	CH_3	CH_3	**12l**[b]	83

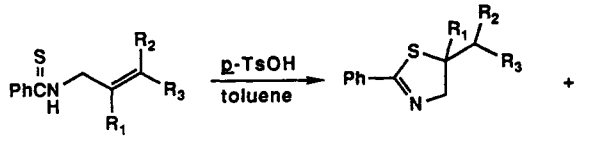
[a] Isolated yield. [b] A small amount of 5-isopropyl-2-phenyl-2-thiazoline (**11l**) was also formed in the reaction.

Table III. Hydrodeselenation Reactions of Compounds 2/3

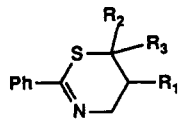
entry	starting material	product	yield[a] (%)
1	**2a**	**13**	80
2	**2b**	**14**	77
3	**2h**	**11h**	91
4	**2i**	**11i/15** = 14/9	61
5	**2j**	**11j**	83
6	**3k**	**11k**	93
7	**2l**	**11l**	60

[a] Isolated yield.

of allylic thioamides also occurred in the presence of Lewis acids.[12] However, the extreme reaction conditions and the low product yields of the previous methods made us look for alternative reaction conditions to bring about the desired transformations. We found that thioamides (but not amides[13]) were slowly but cleanly cyclized in refluxing toluene containing a catalytic (11–50%) amount of *p*-toluensulfonic acid (eq 4). As seen from Table II, all



1h-1l 11 +



(4)

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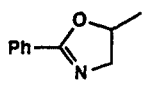
reactions resulted in the clean formation of thiazolines, except for compound **11**, which gave a dihydrothiazine derivative **12l** as the main product.

Hydrodeselenation Reactions. As demonstrated previously, the phenylselenenyl group is easily eliminated under oxidative conditions to introduce unsaturation in the product. Another useful reaction of the phenylselenenyl group is its reductive removal to introduce hydrogen. Hydrodeselenation of compound **2a** was best effected by treatment with excess triphenyltin hydride[14] in refluxing toluene to give oxazoline **13** in 80% isolated yield.

(9) McManus, S. P.; Carroll, J. T.; Grohse, P. M.; Pittman Jr., C.U. *Org. Prep. Proc.* **1969**, *1*, 183.
(10) McManus, S. P.; Carroll, J. T.; Grohse, P. M.; Pittman, C. U., Jr. *Org. Prep. Proc.* **1969**, *1*, 235.
(11) McManus, S. P.; Carroll, J. T. *J. Org. Chem.* **1970**, *35*, 3768.
(12) Smith, P. A. S.; Sullivan, J. M. *J. Org. Chem.* **1961**, *26*, 1132.
(13) The cyclization of allylic amides occurred considerably more slowly than the cyclization of the corresponding thioamides. Thus, *N*-allylbenzamide afforded a 38:62 mixture of 5-methyl-2-phenyl-2-oxazoline (**13**) and unreacted starting material after 24 h in refluxing toluene containing 50 mol % *p*-toluenesulfonic acid monohydrate. *N*-Cinnamylbenzamide was unchanged under the same conditions.
(14) 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.

Some other representative examples of reductive removal of the phenylselenenyl group are shown in Table III.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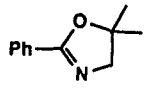
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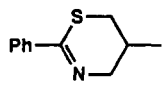
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As seen from entries 4 and 6 (Table III), the reaction sometimes yielded a rearranged product. Thus, thiazoline **2i** afforded a mixture of the expected compound **11i** and the ring-expanded compound **15**. Dihydrothiazine **3k** gave the ring-contracted thiazoline **11k** as the only product when subjected to hydrodeselenation.

Discussion

Cyclofunctionalization reactions of allylic amides and thioamides can, in principle, result in the formation of three-, four-, five-, or six-membered heterocycles. However, due to the unfavorable ring-size, N-cyclization to give three- and four-membered compounds does not occur. As for the remaining ring-closure problem, exo-O/S-cyclization to give an oxazoline/thiazoline seems to predominate, both in organoselenium- and proton-induced cyclizations. However, with some substrates (entries 3, 10, and 11, Table I; entry 5, Table II) fair amounts of endo-cyclization products were isolated.

The varying product ratios in the cyclofunctionalization of compound **1c** may indicate isomerization of a kinetic product to a thermodynamic one. Further support for this idea was obtained from the following result: treatment of compound **3c** with BF_3/etherate (0.87 equiv) in $CHCl_3$ afforded a 92:8 mixture of compounds **2c** and **3c**. All other cyclizations of allylic amides failed to give any isolable amounts of dihydrooxazines. It is believed that the five-membered heterocycle is formed as the primary product in these reactions (kinetic and thermodynamic product).

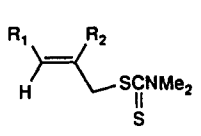
Attempts to isomerize the dihydrothiazines **3j** and **3k** to thiazolines by using BF_3 etherate were unsuccessful. Since the thiazoline **2j** was also inert toward BF_3 treatment, we conclude that the interconversion is not a reversible process.

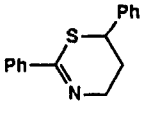
N-Allylbenzamide derivatives were previously cyclized by treatment with halogens.[15,16] In contrast to our selenium-mediated cyclizations, substantial amounts of addition to the double bond (without cyclization) was observed in these reactions. However, the isomeric composition of the halocyclization products was similar to that observed in our selenium-induced cyclizations of allylic amides and thioamides. Thus, derivatives of crotylamine gave mixtures of endo and exo products whereas the cinnamylamine derivatives afforded only endo products. Since a positive charge is probably developed in both kinds of cyclofunctionalization reactions (see Scheme I and ref 16), an olefinic substituent capable of stabilizing a carbocation γ to nitrogen would direct the nucleophilic attack to this position rather than the β-position. However, the formation of a thiazoline in the PhSeBr-induced cyclization of compound **11** shows that the substituent effect can sometimes be overruled by the preference for exo cyclization. Halocyclization of a compound similar to **11** has been reported to give only the product of endo-cyclization.[16]

Allylic thioamides have, to the best of our knowledge, not been previously submitted to selenium-induced cyclofunctionalization reactions. As judged from the examples shown in Table I, the reaction is more general with thioamides than with amides. This probably stems from the higher nucleophilicity of the sulfur atom.

With regard to the stereochemistry of addition in the cyclizations, all reactions leading to dihydrooxazines/dihydrothiazines occur by trans addition of the elements of oxygen/sulfur and selenium to the double bond. These results are consistent with a mechanism involving selenonium ion formation and attack by an O/S-nucleophile from the opposite side of the olefin.

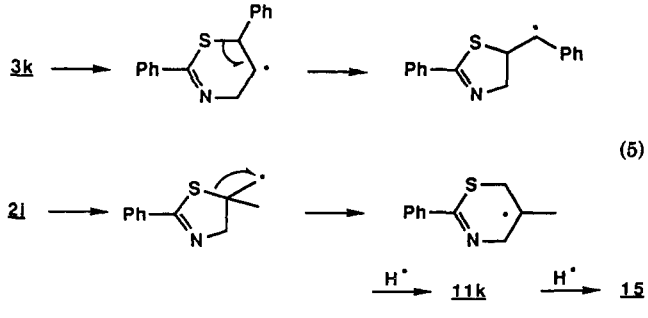
The replacement of the large selenium electrophile by a proton in the cyclofunctionalizations of allylic thioamides generally gives a higher preference for the exo cyclization mode. However, for some substrates carrying olefinic substituents (compounds **1k** and **1l**; Tables I and II), the mode of cyclization was dramatically dependent on the electrophile. Nakai and co-workers[17] reported that bromine-induced cyclofunctionalization reactions of *S*-allylic *N,N*-dimethyldithiocarbamates **16** occurred exo, irrespective of the substituents R_1 and R_2, whereas the mode of cyclization for the corresponding proton-induced reactions was highly substrate dependent.


16


17

The clean formation of a thiazoline **11k** in the proton-mediated cyclization of compound **1k** is especially noteworthy. Proton-[18] and selenium-induced[5] cyclizations of similar cinnamylamine derivatives were reported to give only products of endo cyclization. For reference purposes, the $AlCl_3$-induced cyclization of compound **1k** was repeated as described by Smith and Sullivan.[12] As reported, dihydrothiazine **17** is the principal cyclization product formed in the reaction. Interestingly, thiazoline **11k** did not isomerize to a dihydrothiazine when submitted to the reaction conditions for the formation of compound **17** ($AlCl_3$, nitrobenzene, 125 °C/2 h). Since the thiazoline and the dihydrothiazine do not interconvert, they must be formed as primary products during treatment of compound **1k** with protons and $AlCl_3$, respectively.

The triphenyltin hydride induced reductive removal of the phenylselenenyl group is probably a radical-chain process.[14] The formation of anomalous products **11k** and **15**, respectively, during hydrodeselenation of compounds **2i** and **3k** can occur via rearrangements of carbon-centered radicals as shown in eq 5. The driving force for the process is, in both cases, the formation of a more stable radical.


(5)

As shown in this paper, organoselenium- and proton-mediated cyclizations of allylic amides and thioamides can

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be performed under mild conditions in high yields to give, in most cases, derivatives of 2-oxazoline and 2-thiazoline. Due to the easily manipulated nature of the phenylselenenyl group (oxidative or reductive removal), the selenium-containing products can be further transformed into more or less elaborate structures. In spite of the many methods available for oxazoline[19] and thiazoline synthesis,[20] we feel that the present methods should be a useful addition to them.

Experimental Section

Melting points (uncorrected) were determined by using a Büchi 510 melting point apparatus. ^1H and ^{13}C NMR spectra were obtained with Bruker WP 200 and WP 400 instruments and recorded in $CDCl_3$ solutions containing tetramethylsilane as the internal standard. High-resolution mass spectra were obtained with a Kratos MS 25 RFA instrument (R = 5000; EI 70 eV). Elemental analyses were performed by Analytical Laboratories, Engelskirchen, Germany. Chloroform was washed several times with water to remove ethanol and was dried over $CaCl_2$. Pyridine was dried over KOH, distilled, and kept over molecular sieves (4 Å). Acetonitrile was dried over molecular sieves (4 Å). Crotylamine, cinnamylamine, and prenylamine were prepared by literature methods[16] and converted (together with the commercially available allylamine, (2-methylallyl)amine, and propargylamine) by analogy with a literature method[16] into *N*-crotylbenzamide, mp 46–7 °C (NMR δ 1.70 (dd, 3 H), 4.00 (m, 2 H), 5.51–5.77 (several peaks, 2 H), 6.25 (s, 1 H), 7.37–7.53 (several peaks, 3 H), 7.78 (m, 2 H). Anal. Calcd for $C_{11}H_{13}NO$: C, 75.40; H, 7.48. Found: C, 75.50; H, 7.45. *N*-cinnamylbenzamide, mp 91–2 °C (lit.[21] mp 93–4 °C); *N*-prenylbenzamide, bp 125–30 °C (0.01 mmHg (lit.[22] bp 120–6 °C (0.1 mmHg)) (^1H NMR δ 1.73 (s, 3 H), 1.76 (s, 3 H), 4.04 (m, 2 H), 5.30 (m, 1 H), 6.02 (s, 1 H), 7.38–7.49 (several peaks, 3 H), 7.76 (m, 2 H)); *N*-allylbenzamide, mp 23 °C (lit.[15] mp 22.5 °C); *N*-(2-methylallyl)benzamide, mp 70 °C (lit.[23] mp 68–9 °C); and *N*-propargylbenzamide, mp 110–11 °C (lit.[24] mp 111–12 °C). *N*-Allylacetamide, bp 106–9 °C (12 mmHg) (lit.[25] bp 109–12 °C (13 mmHg)), and *N*-(2-methylallyl)acetamide, bp 116–7 °C (13 mmHg) (lit.[26] bp 113 °C (9 mmHg)), were prepared by heating the amines in acetic anhydride at 100 °C for 1 h followed by distillation. 5,6-Dihydro-2,3-diphenyl-4*H*-1,3-thiazine was prepared according to a literature procedure.[12]

Phenylselenenyl Bromide Induced Cyclizations of Allylic Amides and Thioamides. Typical Procedure. 2-Phenyl-5-[(phenylselenenyl)methyl]-2-oxazoline (2a). To a stirred suspension of PhSeBr (2.0 g 8.5 mmol) in $CHCl_3$ (15 mL) was added dropwise *N*-allylbenzamide (1.40 g, 8.7 mmol) at ambient temperature. After 20 h, the reaction mixture was shaken with water (20 mL) in a separatory funnel and the organic phase separated, dried, and evaporated. Flash chromatography (SiO_2; CH_2Cl_2) afforded 2.61 g (97%) of compound **2a**, mp 47–9 °C. Anal. Calcd for $C_{16}H_{15}NOSe$: C, 60.76; H, 4.78. Found: C, 60.42; H, 4.84. The ^1H NMR spectrum of compound **2a** was in good agreement with literature data.[7]

N-Crotylbenzamide was stirred for 50 min with PhSeBr in $CHCl_3$ and the reaction mixture treated with Na_2CO_3 (5% aq). Isomers **2c** and **3c** were separated by flash chromatography (SiO_2; hexanes/EtOAc = 9/1).

The reaction product of *N*-allylacetamide and PhSeBr was shaken with Na_2CO_3 (5% aq) to obtain a good yield of compound **2f**.

The reaction of *N*-(2-methylallyl)acetamide with PhSeBr was performed in the presence of 1 equiv of pyridine.

All reactions of allylic thioamides with PhSeBr were run for 3 h before treatment with water.

Compounds **2j** and **3j** were separated by flash chromatography (SiO_2; hexanes/EtOAc = 9/1). Workup using Na_2CO_3 (aq) did not change the isomeric composition much (**2j**/**3j** = 82/18).

Allylic thioamides **1k** and **1l** were treated with PhSeBr with acetonitrile as solvent instead of chloroform.

Compound **2l** was separated from a small amount (5%) of compound **7** by using HPLC (Waters M-45 instrument; μ-Porasil column; hexanes/EtOAc = 95/5). **7**: ^1H NMR δ 1.68 (s, 3 H), 1.84 (s, 3 H), 4.41–4.50 (several peaks, 2 H), 4.80 (m, 1 H), 7.39–7.50 (several peaks, 3 H), 7.81 (m, 2 H). Exact mass calcd for $C_{12}H_{14}BrNS$ 283.0069, found 283.0050.

Compounds **3c**, **3j**, and **3k** were recrystallized from hexanes.

Physical, ^1H NMR, and analytical data for compounds **2** and **3** are reported as follows. For yields and isomer ratios, see Table I.

2b: oil; ^1H NMR δ 1.54 (s, 3 H), 3.24 (s, 2 H), 3.76 (d, 1 H, J = 14.9 Hz), 4.00 (d, 1 H J = 14.9 Hz), 7.16–7.54 (several peaks, 8 H), 7.82 (m, 2 H). Anal. Calcd for $C_{17}H_{17}NOSe$: C, 61.82; H, 5.19. Found: C, 61.89; H, 5.22.

2c: oil; ^1H NMR δ 1.53 (d, 3 H), 3.33 (m, 1 H), 3.90 (dd, 1 H, J = 7.4 Hz and 15.1 Hz), 4.15 (dd, 1 H, J = 9.5 and 15.1 Hz), 4.73 (m, 1 H), 7.21–7.50 (several peaks, 6 H), 7.60 (m, 2 H), 7.87 (m, 2 H). Anal. Calcd for $C_{17}H_{17}NOSe$: C, 61.82; H, 5.19. Found: C, 61.71; H, 5.23.

3c: mp 57 °C; ^1H NMR δ 1.59 (d, 3 H), 3.16 (ddd, 1 H, J = 5.2, 9.8, and 10.6 Hz), 3.53 (dd, 1 H, J = 10.6 and 16.9 Hz), 3.91 (dd, 1 H, J = 5.2 and 16.9 Hz), 4.28 (dq, 1 H, J = 6.3 and 9.8 Hz), 7.25–7.45 (several peaks, 6 H), 7.62 (m, 2 H), 7.86 (m, 2 H). Anal. Calcd for $C_{17}H_{17}NOSe$: C, 61.82; H, 5.19. Found: C, 61.83; H, 5.11.

2f: oil; ^1H NMR δ 1.92 (s, 3 H), 2.97 (dd, 1 H, J = 7.2 and 12.6 Hz), 3.16 (dd, 1 H J = 5.5 and 12.6 Hz), 3.56 (m, 1 H), 3.90 (m, 1 H), 4.67 (m, 1 H), 7.26–7.31 (several peaks, 3 H), 7.52–7.57 (m, 2 H). Anal. Calcd for $C_{11}H_{13}NOSe$: C, 51.98; H, 5.16. Found: C, 51.71; H, 5.25.

2g: oil; ^1H NMR δ 1.47 (s, 3 H), 1.86 (s, 3 H), 3.16 (s, 2 H), 3.54 (d, 1 H, J = 14.2 Hz), 3.76 (d, 1 H, J = 14.2 Hz), 7.24–7.30 (several peaks, 3 H), 7.55 (m, 2 H). Anal. Calcd for $C_{12}H_{15}NOSe$: C, 53.74; H, 5.64. Found: C, 53.56; H, 5.52.

2h: oil; ^1H NMR δ 3.04 (dd, 1 H, J = 9.2 and 12.6 Hz), 3.15 (dd, 1 H, J = 6.1 and 12.6 Hz), 4.04 (m, 1 H), 4.30 (dd, 1 H, J = 7.9 and 16.2 Hz), 4.60 (dd, 1 H, J = 3.1 and 16.2 Hz), 7.28–7.46 (several peaks, 6 H), 7.55 (m, 2 H), 7.81 (m, 2 H). Anal. Calcd for $C_{16}H_{15}NSSe$: C, 57.83; H, 4.55. Found: C, 57.75; H, 4.57.

2i: oil; ^1H NMR δ 1.66 (s, 3 H), 3.40 (s, 2 H), 4.09 (d, 1 H, J = 15.9 Hz), 4.42 (d, 1 H J = 15.9 Hz), 7.23–7.42 (several peaks, 6 H), 7.54 (m, 2 H), 7.76 (m, 2 H). Anal. Calcd for $C_{17}H_{17}NSSe$: C, 58.95; H, 4.95. Found: C, 58.77; H, 4.92.

2j: oil; ^1H NMR δ 1.45 (d, 3 H), 3.33 (m, 1 H), 4.12 (m, 1 H), 4.40 (dd, 1 H, J = 8.6 and 16.5 Hz), 4.56 (dd, 1 H, J = 4.3 and 16.5 Hz), 7.29–7.46 (several peaks, 6 H), 7.59 (m, 2 H), 7.82 (m, 2 H). Anal. Calcd for $C_{17}H_{17}NSSe$: C, 58.95; H, 4.95. Found: C, 58.79; H, 4.89.

3j: mp 50 °C; ^1H NMR δ 1.56 (d, 3 H), 3.10 (m, 1 H), 3.49 (m, 1 H), 3.76 (dd, 1 H, J = 10.4 and 16.9 Hz), 4.48 (dd, 1 H, J = 3.6 and 16.9 Hz), 7.28–7.42 (several peaks, 6 H), 7.63 (m, 2 H), 7.74 (m, 2 H). Anal. Calcd for $C_{17}H_{17}NSSe$: C, 58.95; H, 4.95. Found: C, 59.04; H, 4.92.

3k: mp 114–5 °C; ^1H NMR δ 3.60 (ddd, 1 H, J = 3.7, 10.2, and 10.4 Hz), 3.92 (dd, 1 H, J = 10.2 and 17.1 Hz), 4.51 (dd, 1 H, J = 3.7 and 17.1 Hz), 4.57 (d, 1 H, J = 10.4 Hz), 7.17–7.45 (several peaks, 13 H), 7.77 (m, 2 H). Anal. Calcd for $C_{22}H_{19}NSSe$: C, 64.70; H, 4.69. Found: C, 64.52; H, 4.72.

2l: oil; ^1H NMR δ 1.33 (s, 3 H), 1.44 (s, 3 H), 4.11 (dd, 1 H, J = 4.1 and 9.2 Hz), 4.36 (dd, 1 H, J = 9.2 and 16.8 Hz), 4.79 (dd, 1 H, J = 4.1 and 16.8 Hz), 7.32–7.45 (several peaks, 6 H), 7.65 (m, 2 H), 7.82 (m, 2 H). Anal. Calcd for $C_{18}H_{19}NSSe$: C, 59.99; H, 5.31. Found: C, 59.84; H, 5.31.

2m: oil; ^1H NMR δ 2.22 (s, 3 H), 2.97 (dd, 1 H, J = 9.0 and 12.5 Hz), 3.08 (dd, 1 H, J = 6.1 and 12.5 Hz), 3.95 (m, 1 H), 4.07 (m, 1 H), 4.29 (m, 1 H), 7.26–7.30 (several peaks, 3 H), 7.52 (m, 2 H). Anal. Calcd for $C_{11}H_{13}NSSe$; C, 48.89; H, 4.85. Found: C, 48.63; H, 4.78.

N-Propargylbenzamide (**9**) afforded the addition compound **10** when submitted to the usual reaction conditions for cyclo-

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functionalization: ^{1}H NMR δ 4.45 (dd, 2 H, J = 1.1 and 5.7 Hz), 6.32 (m, 1 H), 6.65 (t, 1 H, J = 1.1 Hz), 7.28–7.66 (several peaks, 10 H). Anal. Calcd for $C_{16}H_{14}BrNOSe$: C, 48.63; H, 3.57. Found: C, 48.50; H, 3.52.

Preparation of Allylic Thioamides. Typical Procedure. *N*-Cinnamylthiobenzamide (1k). *N*-Cinnamylbenzamide (0.50 g, 2.1 mmol) was heated at reflux with Lawesson's reagent (1.3 g, 3.2 mmol) in dry THF (15 mL) for 4 h. Evaporation of the solvent and flash chromatography (SiO_2; CH_2Cl_2/hexanes = 3/1) afforded 0.49 g (92%) of compound **1k**: mp 80 °C (lit.[12] mp 88–9 °C); ^{1}H NMR δ 4.62 (m, 2 H), 6.35 (dt, 1 H), 6.68 (d, 1 H), 7.25–7.48 (several peaks, 8 H), 7.63 (br s, 1 H), 7.76 (m, 2 H). Anal. Calcd for $C_{16}H_{15}NS$: C, 75.85; H, 5.97. Found: C, 75.99; H, 6.04.

The following compounds were similarly prepared (yields, physical, analytical, and ^{1}H NMR data are presented as follows).

1h: 85% yield; bp 125 °C (0.2 mmHg) (lit.[27] mp 214–5 °C (17 mmHg)); ^{1}H NMR δ 4.47 (m, 2 H), 5.27–5.41 (several peaks, 2 H), 6.02 (m, 1 H), 7.34–7.65 (several peaks, 4 H), 7.76 (m, 2 H).

1i: 33% yield; oil; ^{1}H NMR δ 1.86 (s, 3 H), 4.43 (d, 2 H), 4.97–4.99 (several peaks, 2 H), 7.38–7.70 (several peaks, 4 H), 7.76 (m, 2 H). Anal. Calcd for $C_{11}H_{13}NS$: C, 69.07; H, 6.85. Found: C, 68.87; H, 6.75.

1j: 82% yield; mp 33–5 °C; bp 105 °C (0.01 mmHg) (lit.[12] bp 156–7 °C (0.9 mmHg)); ^{1}H NMR δ 1.75 (d, 3 H), 4.37 (m, 2 H), 5.66 (m, 1 H), 5.84 (m, 1 H), 7.36–7.50 (several peaks, 4 H), 7.74 (m, 2 H).

1l: 92% yield; mp 43–5 °C; ^{1}H NMR δ 1.76 (s, 3 H), 1.80 (s, 3 H), 4.36 (m, 2 H), 5.41 (m, 1 H), 7.36–7.50 (several peaks, 4 H), 7.74 (m, 2 H). Anal. Calcd for $C_{12}H_{15}NS$: C, 70.20; H, 7.36. Found: C, 70.08; H, 7.33.

1m: 83% yield; oil. ^{1}H NMR data were in good agreement with literature data.[28]

Selenoxide Elimination Reactions. Typical Procedure. 2-Phenyl-5-vinyl-2-oxazoline (4). 2-Phenyl-5-[1-(phenylselenenyl)ethyl]-2-oxazoline (0.46 g, 1.39 mmol) and *m*-CPBA (0.30 g; 80–90%, 1.40 mmol) were dissolved in $CHCl_3$ (5 mL) and left for 5 days at ambient temperature. During this period, the solution gradually turned light yellow. After extraction with $NaHCO_3$ (5% aq), drying ($CaCl_2$), and evaporation, the residue was purified by flash chromatography (SiO_2; hexanes/EtOAc = 9/1) to give 0.16 g (66%) of compound **4**: ^{1}H NMR δ 3.78 (dd, 1 H, J = 7.9 and 14.7 Hz), 4.22 (dd, 1 H, J = 9.8 and 14.7 Hz), 5.13 (m, 1 H), 5.26 (d, 1 H, J = 10.3 Hz), 5.38 (d, 1 H, J = 17.1 Hz), 5.97 (m, 1 H), 7.37–7.49 (several peaks, 3 H), 7.97 (m, 2 H). Anal. Calcd for $C_{11}H_{11}NO$: C, 76.27; H, 6.40. Found: C, 76.05; H, 6.46.

Compounds **5**, **6**, and **8** were similarly prepared. The reaction times allowed for selenoxide elimination were 48, 3, and 48 h, respectively. Yields, physical, ^{1}H NMR and analytical/GC/MS data for the compounds are reported as follows.

5: 66% yield; oil; ^{1}H NMR δ 4.30 (m, 1 H), 4.46–4.55 (several peaks, 2 H), 5.08 (d, 1 H, J = 10.0 Hz), 5.23 (d, 1 H, J = 16.8 Hz), 5.92 (m, 1 H), 7.38–7.46 (several peaks, 3 H), 7.82 (m, 2 H). Anal. Calcd for $C_{11}H_{11}NS$: C, 69.80; H, 5.86. Found: C, 69.67; H, 5.79.

6: yield 75%; mp 57 °C; ^{1}H NMR δ 4.45 (d, 2 H, J = 4.9 Hz), 6.19 (t, 1 H, J = 4.9 Hz), 7.36–7.46 (several peaks, 6 H), 7.58 (m, 2 H), 8.01 (m, 2 H). Anal. Calcd for $C_{16}H_{13}NS$: C, 76.46; H, 5.21. Found: C, 76.53; H, 5.28.

8: yield 91%; oil; ^{1}H NMR 1.78 (s, 3 H), 4.40–4.48 (several peaks, 2 H), 4.62 (m, 1 H), 4.80 (s, 1 H), 4.98 (s, 1 H), 7.38–7.46 (several peaks, 3 H), 7.83 (m, 2 H). The material was contaminated by a small amount of compound **7** and a satisfactory elemental analysis was not obtained. Exact mass calcd for $C_{12}H_{13}NS$ 203.0758, found 203.0763.

Proton-Induced Cyclizations of Allylic Thioamides. Typical Procedure. 5-Methyl-2-phenyl-2-thiazoline (11h). *N*-Allylthiobenzamide (0.10 g, 0.56 mmol) and *p*-toluenesulfonic acid monohydrate (0.011 g, 0.058 mmol) were heated at reflux for 23 h in toluene (5 mL). After washing with $NaHCO_3$ (5% aq), drying of the organic phase ($CaCl_2$), and evaporation, the residue was purified by flash chromatography (SiO_2; hexanes/EtOAc = 9/1) to give 0.095 g (95%) of compound **11h**:[12] ^{1}H NMR δ 1.40 (d, 3 H), 4.03 (m, 1 H), 4.20 (dd, 1 H, J = 4.4 and 15.7 Hz), 4.41 (dd, 1 H, J = 7.9 and 15.7 Hz), 7.38–7.45 (several peaks, 3 H), 7.83 (m, 2 H); ^{13}C NMR δ 22.01, 45.77, 72.09, 128.14, 128.31, 130.90, 133.40, 167.52. Anal. Calcd for $C_{10}H_{11}NS$: C, 67.76; H, 6.26. Found: C, 67.69; H, 6.21.

The following compounds were similarly prepared (reaction time and amount of catalyst shown in parentheses): **11i** (4 h; 19%), **11j** (20 h; 50%), **11k** (48 h; 50%), and **11l** (29 h; 50%). ^{1}H and ^{13}C NMR and analytical data are shown as follows. For yields, see Table II.

11i: ^{1}H NMR data were in excellent agreement with literature data,[29] ^{13}C NMR δ 28.80, 58.71, 77.55, 127.94, 128.29, 130.87, 133.73, 168.36.

11j:[12] ^{1}H NMR δ 1.00 (t, 3 H), 1.68 (m, 2 H), 3.88 (m, 1 H), 4.25 (dd, 1 H, J = 4.7 and 15.9 Hz), 4.39 (dd, 1 H, J = 8.0 and 15.9 Hz), 7.36–7.46 (several peaks, 3 H), 7.83 (m, 2 H); ^{13}C NMR δ 12.14, 29.49, 53.39, 70.07, 128.20, 128.41, 130.99, 133.45, 167.72. Anal. Calcd for $C_{11}H_{13}NS$: C, 69.07; H, 6.85. Found: C, 68.93; H, 6.87.

11k: ^{1}H NMR δ 2.95 (d, 2 H), 4.17 (m, 1 H), 4.29 (dd, 1 H, J = 7.7 and 15.8 Hz), 4.39 (dd, 1 H, J = 4.3 and 15.8 Hz), 7.22–7.48 (several peaks, 8 H), 7.83 (m, 2 H); ^{13}C NMR δ 42.23, 52.69, 69.28, 126.65, 128.20, 128.38, 128.49, 128.96, 131.04, 133.36, 138.73, 167.63. Anal. Calcd for $C_{16}H_{15}NS$: C, 75.85; H, 5.97. Found: C, 75.67; H, 5.98.

11l: ^{1}H NMR δ 1.43 (s, 6 H), 1.70 (t, 2 H), 4.05 (t, 2 H), 7.36–7.43 (several peaks, 3 H), 7.77 (m, 2 H); ^{13}C NMR δ 31.11, 34.43, 42.07, 47.05, 126.39, 128.21, 130.15, 139.57, 158.79. Anal. Calcd for $C_{12}H_{15}NS$: C, 70.20; H, 7.36. Found: C, 70.00; H, 7.18.

In the preparation of compound **12l** a small amount (<5%) of compound **11l** was also formed. The compounds were easily separable by flash chromatography. ^{1}H NMR **11l**: ^{1}H NMR δ 0.97 (d, 6 H), 1.85 (m, 1 H), 3.88 (m, 1 H), 4.30 (dd, 1 H, J = 5.3 and 16.1 Hz), 4.40 (dd, 1 H, J = 8.7 and 16.1 Hz), 7.38–7.46 (several peaks, 3 H), 7.83 (m, 2 H). Exact mass calcd for $C_{12}H_{15}NS$ 205.0928, found 205.0927.

For reference purposes the ^{1}H NMR spectrum of 5,6-dihydro-2,6-diphenyl-4*H*-1,3-thiazine (**17**) is reported below: δ 1.98 (m, 1 H), 2.23 (m, 1 H), 3.86 (ddd, 1 H, J = 3.7, 10.6, and 17.1 Hz), 4.26 (ddd, 1 H, J = 4.0, 4.0, and 17.1 Hz), 4.54 (dd, 1 H, J = 3.7 and 10.6 Hz), 7.24–7.60 (several peaks, 8 H), 7.82 (m, 2 H).

Hydrodeselenation reactions were carried out essentially as described in the literature.[14] Listed below are the reaction times, mmol Ph_3SnH/mmol substrate, and presence/absence of AIBN for each substrate: Product yields are found in Table III:

2a (3 h, 3.2, AIBN), **2b** (4 h, 2.0, AIBN), **2h** (1 h, 3.6), **2i** (4 h, 2.0, AIBN), **2j** (2 h, 4.0, AIBN), **3k** (2 h, 2.0), **2l** (2 h, 4.0).

Compounds **11h**, **11i**, **11j**, **11k**, and **11l** were compared with authentic samples prepared as described previously.

The picrate of compound **13** melted at 170–2 °C (lit.[9] mp 168–9 °C). Compound **14** melted at 36 °C (lit.[30] mp 36–7 °C). **15**: ^{1}H NMR δ 1.11 (d, 3 H), 1.96 (m, 1 H), 2.87 (dd, 1 H, J = 10.0 and 11.9 Hz), 3.05 (ddd, 1 H, J = 2.4, 3.9, and 11.9 Hz), 3.41 (dd, 1 H, J = 9.5 and 16.6 Hz), 4.06 (ddd, 1 H, J = 2.5, 3.6, and 16,6 Hz), 7.34–7.42 (several peaks, 3 H), 7.76 (m, 2 H). Exact mass calcd for $C_{11}H_{13}NS$ 191.0781, found 191.0775.

BF_3-Promoted Isomerization of Compound 3c. Compound **3c** (0.050 g, 0.15 mmol) was treated with BF_3/etherate (0.018 g, 0.13 mmol) in $CHCl_3$ for 3 h. Extraction with water, drying and evaporation gave 0.046 g (92%) of a 92:8 mixture of compounds **2c** and **3c**.

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Supplementary Material Available: ^{1}H NMR spectra for compounds **7**, **8**, **11l**, and **15** (4 pages). Ordering information is given on any current masthead page.

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