Functional Group Manipulation via Organoselenium- and Halogen-Induced Cyclofunctionalization/Hydrolysis of Allylic Benzimidates, Tertiary Benzamides, and Benzamidines. Regioflexible Synthesis of Amino Alcohol Derivatives

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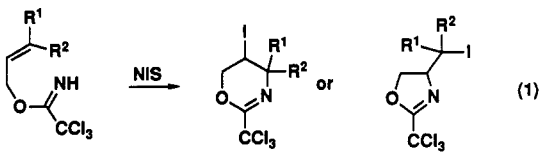
Allylic benzimidates were treated with benzeneselenenyl halides in chloroform or acetonitrile to give, via 5-exo cyclofunctionalization/hydrolysis, 3-(benzoyloxy)-2-(phenylamino)-1-(phenylselenenyl)-alkanes in fair yields. Allylic tertiary benzamides afforded 2-(benzoyloxy)-3-(phenylamino)-1-(phenylselenenyl)alkanes when submitted to similar reaction conditions. Bromoalkanes, functionalized in an analogous way, were obtained after hydrolytic workup when bromine was added to allylic benzimidates and tertiary benzamides. In some of these reactions, products of 6-endo cyclofunctionalization/hydrolysis (1-(benzoyloxy)-3-(phenylamino)-2-bromoalkanes) were also formed. The addition of benzeneselenenyl bromide to some α-substituted allylic benzimidates and tertiary benzamides was diastereoselective ($0 < de < 90\%$, depending on conditions) with a preference for threo isomer formation. Hydrodeselenation/hydrodebromination of the cyclofunctionalization/hydrolysis products was efficiently effected (88–100% yield) by treatment of the products with triphenyltin hydride in refluxing benzene containing a catalytic amount of azobis(isobutyronitrile). The proper choice of allylic benzimidate/tertiary benzamide allowed the preparation of amino alcohol derivatives in which the 1,2-orientation of the functional groups, relative to the carbon backbone, could be varied in a controlled and predictable manner. The regioflexibility of the process was demonstrated for primary, secondary, and tertiary positions. When allylic benzamidines were submitted to the cyclofunctionalization/hydrolysis reaction conditions using benzeneselenenyl bromide as the electrophilic reagent, 5-phenylselenenyl(methyl)-substituted dihydroimidazoles were obtained.

Introduction

The study and synthetic use of electrophilic addition of X-Y reagents (halogens; interhalogens; pseudohalogens; di- and tetravalent sulfur, selenium, and tellurium compounds; and mercury and thallium compounds) to alkenes has been the subject of a considerable number of recent publications.[1-3] With simple olefins, these reactions result in the 1,2-addition of the elements of X and Y to the double bond (Scheme I, part a). Depending on the nature of the alkene and the electrophile used, the process is more or less selective with respect to regiochemistry and stereochemistry of addition. If the olefinic substrate contains a nucleophilic group Z, treatment with an X-Y reagent usually results in a cyclofunctionalization reaction where the elements of Z and the more electropositive of X and Y (Y in the example) adds to the double bond, as shown in Scheme I part b. This process also occurs with varying degree of regio- and stereocontrol.

Imidates[4-14] and related compounds[15-19] have been used as nucleophiles in a variety of cyclofunctionalization reactions leading to nitrogen heterocycles. The treatment of allylic trichloroacetimidates with *N*-iodosuccinimide (NIS) to give dihydrooxazines or dihydrooxazoles illustrates this concept (eq 1).[20]



(1)

Amides are ambident nucleophiles in cyclofunctional-

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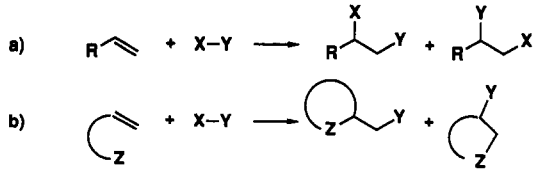
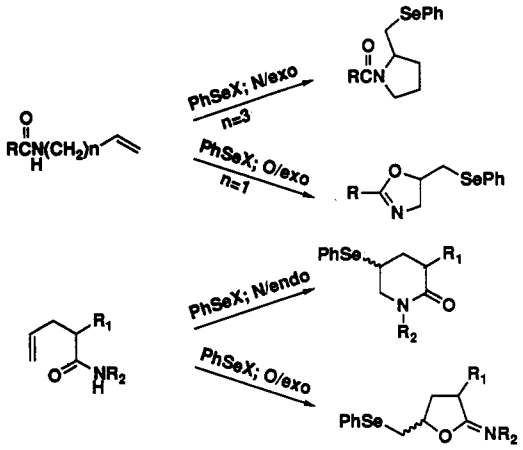
0022-3263/93/1958-2394$04.00/0

Scheme I



Scheme II



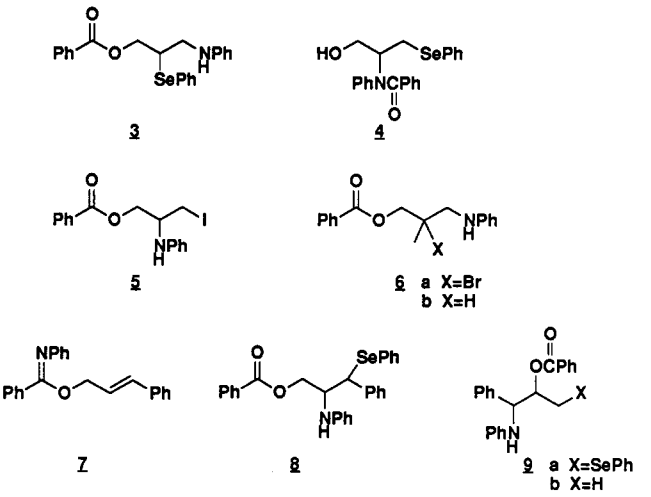
ization reactions giving *N*-heterocycles[21] and *N,O*-heterocycles,[5-7,22-24] via N- and O-cyclization of *N*-alkenyl carboxamides, respectively, and lactams [11,25] and iminolactones,[11,17,26] via N- and O-cyclization of unsaturated carboxylic acid amides, respectively (Scheme II). The situation is often further complicated by the formation of mixtures of endo and exo cyclization products.

In the following, we describe novel organoselenium- and halogen-induced cyclofunctionalization/hydrolysis reactions of readily available N-substituted allylic benzimidates and allylic tertiary benzamides. The two reactions are complementary in the sense that they provide access, in a regiocontrolled fashion, to a variety of N-substituted 1,2-amino alcohol derivatives.

Results

N-Substituted Allylic Benzimidates. When allyl (*N*-phenyl)benzimidate (**1a**) was treated in dry chloroform at ambient temperature with a stoichiometric amount of phenylselenenyl bromide and the reaction mixture hydrolyzed after 24 h with aqueous sodium hydrogen carbonate, 3-(benzoyloxy)-2-(phenylamino)-1-(phenylselenenyl)propane (**2a**) was isolated in 55% yield (eq 2, Table I). The assignment of the compound as an exo-cyclization/hydrolysis product rather than as endo product **3** was based on results from a hydrodeselenation experiment (vide infra). A carbonyl absorption at 1700 cm^{-1} in the infrared spectrum of the compound indicated the presence of benzoate ester/secondary amine rather than primary alcohol/tertiary amide functionalities (as in isomeric compound **4**).

As shown in Table I, the reactions of phenylselenenyl bromide with allylic benzimidates substituted in positions 1, 2, or 3 of the allyl group always resulted in the formation of exo-cyclization/hydrolysis products (Table I, entries 1, 3–5, 7) in fair yields. It was sometimes found to be beneficial to use acetonitrile as solvent and to hydrolyze the reaction mixture shortly (5 min) after completion of the addition of the electrophilic reagent. The diastereoselectivity for addition to 1-substituted allylic benzimidate **1c** was only moderate, with 76/24 and 66/34 preferences for formation of the threo product in $CHCl_3$ and CH_3CN, respectively. The diastereoselectivity was determined by hydrodeselenation (vide infra) of the purified diastereomer mixtures, hydrolysis of the benzoate esters, and comparison of the resulting amino alcohols with authentic samples.[27]



Cyclofunctionalization/hydrolysis according to eq 2 was also carried out using bromine and iodine in chloroform or acetonitrile as the electrophilic reagents. Although iodide **5** could be prepared in 60% yield from allyl *N*-phenylbenzimidate, other imidates afforded complex reaction mixtures when treated with I_2 under the standard reaction conditions. The reactions of Br_2 with benzimidates **1a** and **1c** proceeded in analogy with the corresponding PhSeBr reactions. Compound **1c** in CH_3CN afforded a 48/52 mixture of erythro and threo isomers of compound **2e**. The diastereoselectivity was determined by hydrodebromination (vide infra) of the crude isomer mixture and comparison with authentic samples. In contrast to the other benzimidates, benzimidate **1d** (Table I) afforded only 6-endo-cyclization/hydrolysis product **6a**, isolated in 48% yield, when treated with Br_2 under the standard reaction conditions. According to ^1H NMR analysis of an experiment carried out in deuterated chloroform, the material was *not* present in the organic phase immediately after hydrolysis but slowly formed on standing over the next 48 h.

When (*E*)-3-phenylallyl (*N*-phenyl)benzimidate (**7**) was subjected to the standard cyclofunctionalization/hydrol-

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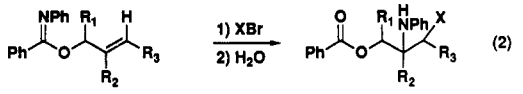
Table I. Phenylselenenyl Bromide- and Bromine-Induced Cyclofunctionalization/Hydrolysis of Allylic Benzimidates 1

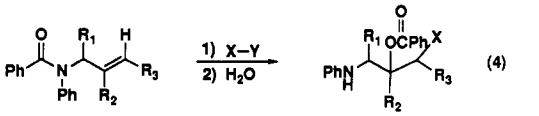


1 2 X=PhSe or Br

entry	starting material	solvent	X	R_1	R_2	R_3	product	yield (%)[a]
1	**1a**	$CHCl_3$	SePh	H	H	H	**2a**	55
2	**1a**	$CHCl_3$	Br	H	H	H	**2b**	44
3	**1b**[b]	CH_3CN	SePh	H	H	CH_3	**2c**	82[c]
4	**1c**	$CHCl_3$	SePh	CH_3	H	H	**2d**	64[d]
5	**1c**	CH_3CN	SePh	CH_3	H	H	**2d**	83[e]
6	**1c**	CH_3CN	Br	CH_3	H	H	**2e**	79[f]
7	**1d**	$CHCl_3$	SePh	H	CH_3	H	**2f**	62

[a] Isolated yield. [b] Isomeric mixture $E/Z \simeq 80/20$. [c] Diastereomeric mixture. [d] threo/erythro = 76/24. [e] threo/erythro = 66/34. [f] threo/erythro = 52/48.

Table II. Phenylselenenyl Halide- and Bromine-Induced Cyclofunctionalization/Hydrolysis of Allylic Tertiary Benzamides 11



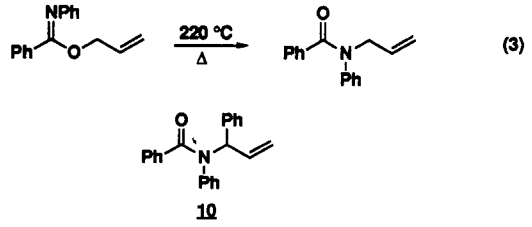
11 12 X=PhSe; Y=Br,Cl X=Br; Y=Br

entry	starting material	solvent	electrophilic reagent	X	R_1	R_2	R_3	product	yield (%)[a]
1	**11a**	$CHCl_3$	PhSeCl	PhSe	H	H	H	**12a**	51
2	**11a**	CH_3CN	Br_2	Br	H	H	H	**12b**	64
3	**11b**	CH_2Cl_2	PhSeCl	PhSe	H	H	CH_3	**12c**	45
4	**11b**	CH_3CN	Br_2	Br	H	H	CH_3	**12d+13a**	74[b]
5	**11c**	CH_3CN	PhSeBr	PhSe	CH_3	H	H	**12e**	68[c]
6	**11c**	CH_3CN	PhSeBr	PhSe	CH_3	H	H	**12e**	74[d]
7	**11c**	CH_3CN	Br_2	Br	CH_3	H	H	**12f**	76[e]
8	**11d**	CH_3CN	PhSeCl	PhSe	H	CH_3	H	**12g**	52
9	**11d**	CH_3CN	Br_2	Br	H	CH_3	H	**12h**	75

[a] Isolated yield. [b] Isomeric ratio **12d**/**13a** 62/38. [c] Reaction time = 24 h; threo/erythro > 95/5. [d] Reaction time = 5 min; threo/erythro = 50/50. [e] Reaction time = 20 h; threo/erythro = 40/60.

ysis reaction conditions using PhSeBr as the electrophilic reagent, the isolated selenide product (74% yield) did not show ^1H NMR characteristics in accord with the expected structure **8** (methylene protons resonated at 3.2–3.3 ppm rather than at 4.3–4.7 ppm). Instead, an isomer of the product (**9a**) was indicated and further corroborated from the results of a hydrodeselenation experiment (vide infra). Only one diastereomer of the compound was detected (configuration not determined).

Allylic Tertiary Benzamides. Allylic benzimidates are known to thermally rearrange at 220 °C to give tertiary allylic benzamides (eq 3).[28] In the presence of transition



10

metal catalysts, this rearrangement occurs at a considerably lower temperature.[29] It is conceivable that imidate **7** is rapidly rearranged in the presence of PhSeBr to give tertiary allylic benzamide **10**, which then undergoes 5-exo-O-cyclofunctionalization/hydrolysis to give observed selenide **9a**. In support of this idea, an authentic sample of benzamide **10**, prepared in situ by thermal rearrangement of benzimidate **7**, afforded selenide **9a** in 60% yield when treated with PhSeBr in $CHCl_3$ and submitted to a hydrolytic workup.

As shown in eq 4 and Table II, the 5-exo-O-cyclofunctionalization/hydrolysis reaction of tertiary allylic benzamides **11** is a quite general process that can be performed using phenylselenenyl halides or bromine as the electrophilic reagents. Acetonitrile was often the solvent of choice for the reactions with hydrolytic workup shortly (5 min) after completion of the addition of the electrophilic reagent.

The required allylic tertiary benzamides **11** were conveniently prepared from allylic benzimidates in analogy with eq 3.[28]

With PhSeBr and PhSeCl, allylic benzamides **11** afforded only products from 5-exo-O-cyclization/hydrolysis (Table II). However, when *N*-crotyl-*N*-phenylbenzamide (**11b**) was treated with bromine in CH_3CN, an inseparable 62/38 mixture of compounds **12d** and **13a** was obtained in 74% yield. The structural assignments were supported by the results of hydrodebromination experiments (vide infra).

The cyclofunctionalization/hydrolysis reaction of benzamide **11c** did not show any diastereoselectivity when PhSeBr was used under the standard reaction conditions (Table II). However, with a longer reaction time (24 h) the threo isomer was almost exclusively formed (threo/erythro >95/5). The use of Br_2 under the latter conditions resulted in the formation of a mixture (40/60) of threo/

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(29) Ikariya, T.; Ishikawa, Y.; Hirai, K.; Yoshikawa, S. *Chem. Lett.* **1982**, 1815.

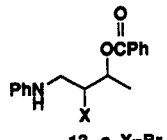
Table III. Hydrodehalogenation and Hydrodeselenation Reactions. Preparation of Amino Alcohol Derivatives

starting material	X	R_1	R_2	R_3	product	yield (%)[a]
2a	SePh	H	H	H	**14a**	97
12a	SePh	H	H	H	**15a**	96
2b	Br	H	H	H	**14a**	93
12b	Br	H	H	H	**15a**	90
2c	SePh	H	H	CH_3	**14b**	90
12c	SePh	H	H	CH_3	**15b**	97
12d+13a	Br	H	H	CH_3	**15b+13b**	98
threo-**2d**	SePh	CH_3	H	H	*threo*-**14c**[d]	88
erythro-**2d**	SePh	CH_3	H	H	*erythro*-**14c**[d]	91
threo-**12e**	SePh	CH_3	H	H	*threo*-**15c**[d]	95
2e[b]	Br	CH_3	H	H	**14c**[b,d]	100
12f[c]	Br	CH_3	H	H	**15c**[c,d]	90
2f	SePh	H	CH_3	H	**14d**	88
12g	SePh	H	CH_3	H	**15d**	97
12h	Br	H	CH_3	H	**15d**	90
5		H	H	H	**14a**	85
6a					**6b**	86
9a					**9b**	99

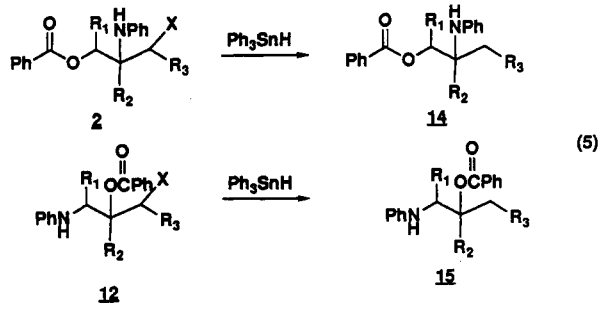
[a] Isolated yield. [b] threo/erythro mixture, see Table I. [c] threo/erythro mixture, see Table II. [d] Note that structures **14c** and **15c** are identical.

erythro isomers of compound **12f**. The diastereoselectivities were determined by hydrodeselenation/hydrodebromination (vide infra).

Hydrodeselenation/Hydrodebromination Reactions. The reductive removal of halogen[30] and phenylselenenyl[31] substituents to introduce hydrogen is conveniently performed by treatment of the cyclofunctionalization/hydrolysis products with organotin hydrides. Products **2** and **12** were efficiently (88–100% yield) hydrodeselenated/hydrodebrominated to give amino alcohol derivatives **14** and **15**, respectively, in refluxing benzene containing a 2-fold excess of triphenyltin hydride and a catalytic amount of azobis(isobutyronitrile) (AIBN) (eq 5; Table III). Also



13 a X=Br
b X=H

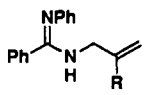


(5)

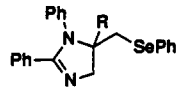
2 **14** **12** **15**

included in Table III are the hydrodeselenation/hydrodebromination reactions of compounds **5**, **6a**, **9**, and **13a**.

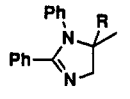
Allylic Benzamidines. We have recently shown that allylic amides, in the presence of phenylselenenyl bromide, are readily converted (5-exo-O-cyclization) to 2-oxazoline derivatives substituted in the 5-position with a phenylselenenyl(methyl) group.[24] Although protons,[32] halogens,[33,34] and NIS[34] have been used to similarly induce cyclization of allylic amidines to dihydroimidazoles, no such reactions seem to be known with electrophilic organoselenium reagents. We found that benzamidines **16a** and **16b** readily furnished dihydroimidazole derivatives **17a** (87% yield) and **17b** (94% yield), respectively, when treated in chloroform with phenylselenenyl bromide and submitted to an aqueous workup. Hydrodeselenation of compound **17a** afforded dihydroimidazole derivative **18a**, mp 68 °C, in 94% yield. The formation of **18a** confirms the 5-exo mode of cyclization for compound **16a**. However, when submitted to the ordinary hydrodeselenation conditions, compound **17b** yielded a high-melting material (mp 249 °C) that was clearly distinct from compound **18b**.[35]



16 a R=H
b R=CH_3



17 a R=H
b R=CH_3



18 a R=H
b R=CH_3

Discussion

The organoselenium- and halogen-induced cyclofunctionalization/hydrolysis reactions of N-substituted allylic benzimidates **2** and allylic tertiary benzamides **11** are complementary in the sense that they provide access, after hydrodeselenation/hydrodehalogenation, to amino alcohol derivatives **14** and **15** whereby the 1,2-orientation of the functional groups, relative to the carbon backbone, can be varied in a controlled manner. This regioflexibility has been demonstrated for primary, secondary, and tertiary positions (compounds **14a**/**15a**, **14b**/**15b**, **14c**/**15c**, **14d**/**15d**). In contrast to the 5-exo-specific organoselenium-induced reactions, the bromine-induced reactions sometimes afforded products resulting from 6-endo-cyclofunctionalization/hydrolysis (compounds **6a** and **13a**). These cyclizations could be useful for the preparation of N-substituted 1,3-amino alcohol derivatives.

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(31) 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.
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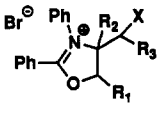
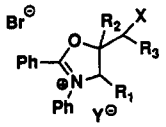
(35) At present we have no suggestion as to the structure of this material. Both ^1H NMR and MS data are consistent with structure **18b**, but the high melting point and the analytical data are indicative of another structure: ^1H NMR δ 1.50 (s, 6 H), 4.08 (s, 2 H), 7.05–7.58 (several peaks, 10 H); mass spectrum *m/e* (rel inten) 250(8), 236(4), 235(24), 132(11), 118(15), 117(100), 116(3), 105(3), 104(11). Anal. Calcd for $C_{17}H_{18}N_2$: C, 81.32; H, 6.82; N, 11.85. Found: C, 70.06; H, 6.54; N, 9.55.

N-substituted 1,2-amino alcohol derivatives related to compounds **14** and **15** have previously been prepared by phenylaminolysis of oxiranes[36] and hydroxyphenylamination of alkenes via organomercury intermediates.[37] Neither of these methods offers the kind of regiocontrol demonstrated in the present work. However, a similar regioflexible synthesis of N-unsubstituted 1,2-amino alcohol derivatives (dihydrooxazoles) was previously reported by Cardillo and co-workers in NIS-induced cyclofunctionalization reactions of allylic trichloroacetimidates/trichloroacetamides.[5-7,38]

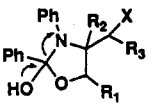
The mechanism of the organoselenium- and bromine-induced cyclofunctionalization/hydrolysis reactions of allylic benzimidates **1** and allylic tertiary benzamides **11** most probably involves dihydrooxazolium species **19** and **20**, respectively, formed via addition of N/X and O/X across the double bonds. The subsequent hydrolytic workup results in the selective rupture of the C–N bond as shown for proposed intermediate **21** in the hydrolytic transformation **19** → **2**. The formation of a secondary



19



20



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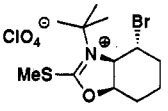

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amine/benzoate ester rather than a tertiary amide/alcohol is noteworthy in view of the results from mild hydrolysis of oxazoline derivatives.[8,9,13] The formation of the amine/ester may be attributed to a stabilizing effect of the *N*-phenyl group. A dihydrooxazolium species (**22**), related to compound **19**, was isolated in one case during bromine-induced cyclofunctionalization of an allylic thiocarbamidate[15] and has been suggested as an intermediate in other related processes.[10,16-18,22,39]

The regioselectivity of the cyclization step depends, to a large extent, on the olefinic substituents. Cardillo and co-workers found[20] (eq 1) that (*E*)-allylic imidates, for steric reasons, underwent 6-endo ring closure, whereas (*Z*)-allylic imidates preferentially gave products of 5-exo cyclization. Similar results were also reported for halonium-initiated cyclizations of allylic urethanes.[40] The few examples with (*E*)-allylic benzimidates (Table I, entry 3) and tertiary benzamides (Table II, entries 3 and 4) reported in this work indicate that 5-exo cyclization is often highly favored over 6-endo cyclization. However, bromine-induced cyclization of compound **11b** afforded a fair amount of endo-cyclization product **13a**. The exo mode of cyclization was also often observed for organoselenium-induced cyclization reactions of allylic amides and thioamides.[24] The ability of a substituent to stabilize an incipient carbocation intermediate could sometimes affect the regioselectivity of the cyclization step. This could be the reason why allylic benzimidate **1d** with Br_2 afforded only a 6-endo-cyclization/hydrolysis product. However, it is difficult to rationalize the dramatic influence of the electrophile on the exo/endo selectivity for the selenium- and halogen-induced reactions of compounds **1d** and **11b**.

The hydrolysis intermediate, observed by ^1H NMR spectroscopy in the preparation of compound **6a** may be of structure **23**.[41] A similar 5-membered compound (**21**)

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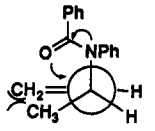
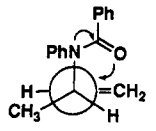


24



25

(X = SePh; $R_1 = R_3 = H$; $R_2 = CH_3$) could not be detected when imidate **1d** was treated with phenylselenenyl bromide in an NMR experiment under similar reaction conditions. Hydrolysis in this case resulted in the prompt formation of selenide **2f**. However, the similarities in the ^1H NMR spectra of the addition products prior to hydrolysis, relative to imidate **1d** (downfield shifts of protons α to oxygen and ortho to the amino group), seem to support the idea that compounds **2f** and **6a** are formed via dihydrooxazolium and dihydrooxazinium compounds, respectively.

The high threo selectivity in the formation of compound **12e** (Table II, entries 5 and 6) in a 24-h experiment as compared to a 5-min experiment performed under otherwise similar conditions, seems to indicate that the threo compound is the favored product in a thermodynamically controlled reaction. The selective formation of this material may reflect the increased steric strain in conformer **24** (leading to erythro product after cyclization) as compared to conformer **25** (leading to threo product).

As shown in this paper, the organoselenium- and halogen-induced cyclofunctionalization/hydrolysis of N-substituted allylic benzimidates and allylic tertiary benzamides can be used, after hydrodeselenation/hydrodehalogenation, for the preparation of N-substituted amino alcohol derivatives that are difficult to obtain by other methods. Because phenylselenenyl and halogen groups are easily manipulated, we feel that the cyclofunctionalization/hydrolysis products would find use as building blocks for the construction of more elaborated structures.

Experimental Section

Melting points are uncorrected. ^1H NMR spectra[24] were obtained at 250 MHz in $CDCl_3$ solutions containing Me_4Si as an internal standard. IR spectra were recorded in KBr. Elemental analyses were performed by Analytical Laboratories, Engelskirchen, Germany. Chloroform was washed several times with water to remove ethanol and dried over $CaCl_2$. Acetonitrile was dried over molecular sieves (4Å). Triphenyltin hydride was prepared according to a literature procedure.[42]

Allylic benzimidates **1a–c** were prepared according to a literature procedure.[28] New compounds **1d** and **7** were prepared using a slight modification of this preparation (the sodium salt of the allylic alcohol was prepared in benzene by the addition of a stoichiometric amount of sodium hydride). Reported below are ^1H NMR data for all compounds and physical and analytical data for new compounds:

(36) Iqbal, J.; Pandey, A. *Tetrahedron Lett.* **1990**, *31*, 575. Chini, M.; Crotti, P.; Macchia, F. *Tetrahedron Lett.* **1990**, *31*, 4661.
(37) Barluenga, J.; Fañanas, F. J.; Yus, M. *J. Org. Chem.* **1979**, *44*, 4798. Barluenga, J.; Alonso-Cires, L.; Asensio, G. *Synthesis* **1981**, 376.
(38) Cardillo, G.; Orena, M.; Sandri, S. *Pure Appl. Chem.* **1988**, *60*, 1679.
(39) Takano, S.; Iwabuchi, Y.; Ogasawara, K. *J. Chem. Soc. Chem. Commun.* **1988**, 1527.
(40) Parker, K. A.; O'Fee, R. *J. Am. Chem. Soc.* **1983**, *105*, 654.
(41) For an example of a related compound, see ref 12.
(42) Kuivila, H. G.; Beumel Jr., O. F. *J. Am. Chem. Soc.* **1961**, *83*, 1246.

1a: ^{1}H NMR δ 4.87 (d, 2 H, J = 4.3 Hz), 5.28 (d, 1 H, J = 10.4 Hz), 5.44 (d, 1 H, J = 17.2 Hz), 6.12 (m, 1 H), 6.71 (d, 2 H, J = 8.1 Hz), 6.95 (t, 1 H, J = 7.5 Hz), 7.13–7.34 (several peaks, 7 H). When commercial crotyl alcohol (E/Z mixture) was used for its preparation, compound **1b** was obtained as a 1/4 mixture of Z and E isomers. Doublets in the ^{1}H NMR spectrum at 4.79 and 4.93 ppm, respectively, were characteristic of the E and Z isomers.

1c: ^{1}H NMR δ 1.49 (d, 3 H, J = 6.5 Hz), 5.19 (d, 1 H, J = 10.6 Hz), 5.36 (d, 1 H, J = 17.3 Hz), 5.74 (m, 1 H), 6.05 (m, 1 H), 6.70 (d, 2 H, J = 7.8 Hz), 6.93 (t, 1 H, J = 7.4 Hz), 7.12–7.33 (several peaks, 7 H).

1d: yield 69%; oil, bp 134–6 °C/1 mmHg; ^{1}H NMR δ 1.89 (s, 3 H), 4.78 (s, 2 H), 4.99 (s, 1 H), 5.14 (s, 1 H), 6.72 (d, 2 H, J = 7.7 Hz), 6.95 (t, 1 H, J = 7.4 Hz), 7.14–7.35 (several peaks, 7 H). Anal. Calcd for $C_{17}H_{17}NO$: C, 81.24; H, 6.82. Found: C, 81.11; H, 6.89.

7: yield 34%, mp 68 °C; ^{1}H NMR δ 5.03 (dd, 2 H, J = 1.1, 6.1 Hz), 6.52 (dt, 1 H, J = 6.1, 15.9 Hz), 6.72–6.81 (several peaks, 3 H), 6.96 (t, 1 H, J = 6.7 Hz), 7.14–7.46 (several peaks, 12 H). Anal. Calcd for $C_{22}H_{19}NO$: C, 84.31; H, 6.11. Found: C, 84.20; H, 6.12.

Allylic tertiary benzamides **11a–c** were prepared according to a literature procedure.[28] New compounds **11d** and **10** were prepared in analogy with this preparation. Reported below are ^{1}H NMR data for all compounds and physical and analytical data for compound **11d**.

11a: ^{1}H NMR δ 4.53 (d, 2 H, J = 5.9 Hz), 5.15–5.24 (several peaks, 2 H), 6.00 (m, 1 H), 7.03 (d, 2 H, J = 6.9 Hz), 7.13–7.33 (several peaks, 8 H).

11b: ^{1}H NMR δ 1.67 (d, 3 H, J = 4.5 Hz), 4.44 (d, 2 H, J = 4.4 Hz), 5.59–5.65 (several peaks, 2 H), 7.01 (d, 2 H, J = 6.9 Hz), 7.12–7.32 (several peaks, 8 H).

11c: ^{1}H NMR δ 1.28 (d, 3 H, J = 6.9 Hz), 5.14–5.24 (several peaks, 2 H), 5.54 (m, 1 H), 6.00 (m, 1 H), 7.01 (m, 2 H, J = 6.9 Hz), 7.09–7.28 (several peaks, 8 H).

11d: yield 91%; oil, bp 125 °C/0.01 mmHg; ^{1}H NMR δ 1.83 (s, 3 H), 4.51 (s, 2 H), 4.91 (s, 2 H), 7.03 (d, 2 H J = 7.1 Hz), 7.11–7.34 (several peaks, 8 H). Anal. Calcd for $C_{17}H_{17}NO$: C, 81.24; H, 6.82. Found: C, 81.07; H, 6.97.

Compound **10** was obtained by heating compound **7** for 1 h at 210 °C. The crude product was used for cyclofunctionalization/hydrolysis reactions: ^{1}H NMR δ 5.36 (d, 1 H, J = 10.1 Hz), 5.47 (d, 1 H, J = 17.1 Hz), 6.14 (m, 1 H), 6.60 (d, 1 H, J = 8.1 Hz), 6.78 (m, 2 H), 7.05–7.36 (several peaks, 13 H).

***N*-Allyl-*N'*-phenylbenzamidine (16a).** To a stirred solution of *N*-phenylbenziminoyl chloride[43] (3.0 g, 13.9 mmol) in benzene (20 mL) was added dropwise allylamine (1.60 g, 29.1 mmol) in benzene (3 mL). The reaction mixture was then heated at reflux for 3 h, cooled, and extracted with water. After separation, drying, evaporation, and flash chromatography (SiO_2; CH_2Cl_2 with 0–5% MeOH) 2.63 g (80%) of compound **16a**, mp 69 °C (hexanes), was isolated: ^{1}H NMR δ 4.13 (br s, 2 H), 4.61 (br s, 1 H), 5.19 (d, 1 H, J = 10.1 Hz), 5.31 (d, 1 H, J = 17.1 Hz), 6.04 (m, 1 H), 6.63 (d, 2 H), 6.79 (t, 1 H), 7.01–7.07 (several peaks, 2 H), 7.15–7.30 (several peaks, 5 H). The broad peaks and the presence of small peaks other than those listed above seem to indicate the presence of syn/anti isomers of the amidine. Anal. Calcd for $C_{16}H_{16}N_2$: C, 81.32; H, 6.82. Found: C, 81.11; H, 6.63.

***N*-(2-Methylallyl)-*N'*-phenylbenzamidine (16b)** mp 85 °C, was prepared in 96% yield using the procedure for compound **16a**. Allylamine was replaced by 2-methylallylamine, prepared in situ by treatment of 2-methylallylamine hydrochloride (7.0 g, 65.1 mmol) with NaOH in water/benzene: ^{1}H NMR 1.87 (s, 3 H), 4.10 (br s, 2 H), 4.63 (br s, 1 H), 4.91 (s, 1 H), 4.99 (s, 1 H), 6.63 (d, 2 H), 6.79 (t, 1 H), 7.04 (t, 2 H), 7.24–7.35 (several peaks, 5 H). The broad peaks and the presence of small peaks other than those listed above seem to indicate the presence of syn/anti isomers of the amidine. Anal. Calcd for $C_{17}H_{18}N_2$: C, 81.56; H, 7.25. Found: C, 81.42; H, 7.11.

PhSeBr/Br_2-Induced Cyclofunctionalization/Hydrolysis of Allylic Benzimidates. Typical Procedure, 3-(Benzoyloxy)-2-(phenylamino)-1-(phenylselenenyl)propane (2a). To a stirred solution of PhSeBr (0.50 g, 2.1 mmol) in $CHCl_3$ (10 mL) at 0 °C was added dropwise a solution of allyl *N*-phenylbenzimidate (0.50 g, 2.1 mmol) in $CHCl_3$ (1 mL). After removal of the ice bath, the reaction mixture was stirred for 24 h and shaken in a separatory funnel with $NaHCO_3$ (5% aqueous). Separation of the organic phase, drying ($CaCl_2$), evaporation, and flash chromatography (SiO_2; CH_2Cl_2/hexanes = 3/1) afforded 0.48 g (55%) of compound **2a** as a white solid, mp 108–9 °C (CH_2Cl_2/hexanes): ^{1}H NMR δ 3.12–3.30 (several peaks, 2 H), 4.00 (br s, 2 H), 4.35 (dd, 1 H, J = 4.4 and 14.8 Hz), 4.64 (dd, 1 H, J = 3.6 and 14.8 Hz), 6.50 (d, 2 H, J = 8.2 Hz), 6.71 (t, 1 H), 7.10–7.27 (several peaks, 5 H), 7.44 (t, 2 H), 7.54–7.61 (several peaks, 3 H), 7.96 (m, 2 H); IR (cm^{-1}) 3356, 1700. Anal. Calcd for $C_{22}H_{21}NO_2Se$: C, 64.39; H, 5.16. Found: C, 64.27; H, 5.07.

In the bromination experiments, bromine, dissolved in $CHCl_3$ (1 mL), was added dropwise to a stirred solution of the allylic imidate in $CHCl_3$ (10 mL).

In the preparation of selenide **2c** and bromide **2e** the workup procedure (involving addition of 20 mL of H_2O, stirring for 30 min, and CH_2Cl_2 extraction) was carried out only 5 min after completion of the addition reaction.

The diastereomers of compounds **2c** and **2e** were not separated. Hydrodeselenation of the isomeric mixtures obtained after flash chromatography (vide infra) provided evidence for the assigned structures/isomeric composition of the cyclofunctionalization/hydrolysis products.

Physical, analytical, and ^{1}H NMR data for compounds **2**, **5**, **6a**, and **9a**, obtained from allylic benzimidates, are reported as follows. For solvents and electrophilic reagents used, yields, and isomeric ratios, see Table I.

3-(Benzoyloxy)-1-bromo-2-(phenylamino)propane (2b): oil; ^{1}H NMR δ 3.60–3.74 (several peaks, 2 H), 4.08 (br s, 2 H), 4.41 (dd, 1 H, J = 5.9 and 11.3 Hz), 4.69 (dd, 1 H J = 4.7 and 11.3 Hz), 6.70–6.81 (several peaks, 3 H), 7.21 (t, 2 H), 7.46 (t, 2 H), 7.60 (m, 1 H), 8.04 (m, 2 H). Anal. Calcd for $C_{16}H_{16}BrNO_2$: C, 57.50; H, 4.83. Found: C, 57.77; H, 4.76.

4-(Benzoyloxy)-3-(phenylamino)-2-(phenylselenenyl)butane (2c) was obtained as a mixture of diastereomers (80/20) because the allylic imidate **1b**, from which it was prepared, was a mixture of E and Z isomers ($E/Z \simeq$ 80/20). Doublets at 1.61 and 1.54 ppm in the ^{1}H NMR spectrum of the mixture were characteristic of the two diastereomers.

3-(Benzoyloxy)-2-(phenylamino)-1-(phenylselenenyl)butane (2d) was obtained as a mixture of erythro and threo isomers, which were separable by flash chromatography (SiO_2; CH_2Cl_2/hexanes = 3/1). ***threo*-2d**: mp 64–5 °C, ^{1}H NMR δ 1.40 (d, 3 H, J = 6.4 Hz), 3.02 (dd, 1 H, J = 5.3 and 12.8 Hz), 3.07 (dd, 1 H, J = 5.9 and 12.8 Hz), 3.70 (m, 1 H), 3.95 (d, 1 H, J = 9.3 Hz), 5.63 (m, 1 H), 6.50 (d, 2 H), 6.70 (t, 1 H), 7.09–7.27 (several peaks, 5 H), 7.43–7.62 (several peaks, 5 H), 8.00 (m, 2 H). Anal. Calcd for $C_{23}H_{23}NO_2Se$: C, 65.09; H, 5.46. Found: C, 64.82; H, 5.39. ***erythro*-2d**: mp 88–9 °C; ^{1}H NMR δ 1.41 (d, 3 H, J = 6.4 Hz), 3.25 (d, 2 H, J = 5.3 Hz), 3.86–3.93 (several peaks, 2 H), 5.30 (m, 1 H), 6.54 (d, 2 H), 6.71 (t, 1 H), 7.10–7.23 (several peaks, 5 H), 7.40–7.60 (several peaks, 5 H), 7.97 (m, 2 H). Anal. Calcd for $C_{23}H_{23}NO_2Se$: C, 65.09; H, 5.46. Found: C, 64.89; H, 5.37.

3-(Benzoyloxy)-1-bromo-2-(phenylamino)butane (2e) was obtained as a mixture of diastereomers after flash chromatography (doublets at 1.46 and 1.50 ppm in the ^{1}H NMR spectrum of the mixture were characteristic of the two isomers).

3-(Benzoyloxy)-2-methyl-2-(phenylamino)-1-(phenylselenenyl)propane (2f): mp 67–8 °C; ^{1}H NMR δ 1.51 (s, 3 H), 3.28 (d, 1 H, J = 12.5 Hz), 3.46 (d, 1 H, J = 12.5 Hz), 3.94 (br s, 1 H), 4.34 (d, 1 H, J = 11.2 Hz), 4.46 (d, 1 H, J = 11.2 Hz), 6.83–6.91 (several peaks, 3 H), 7.15–7.21 (several peaks, 5 H), 7.41–7.58 (several peaks, 5 H), 7.96 (m, 2 H). Anal. Calcd for $C_{23}H_{23}NO_2Se$: C, 65.09; H, 5.46. Found: C, 65.00; H, 5.38.

The addition of PhSeBr (0.050 g, 0.21 mmol) to compound **1d** (0.053 g, 0.21 mmol) was also studied in $CDCl_3$ (3 mL) by ^{1}H NMR. After 24 h, the spectrum indicated the formation of a cyclofunctionalization product: ^{1}H NMR δ 1.85 (s, 3 H), 3.29 (d, 1 H, J = 13.5 Hz), 3.65 (d, 1 H, J = 13.5 Hz), 5.18 (d, 1 H, J = 9.2 Hz), 5.68 (d, 1 H, J = 9.2 Hz), 7.29–7.74 (several peaks, 15 H). After hydrolysis and rapid drying of the organic phase, the ^{1}H NMR spectrum showed the presence of compound **2f** as the main product.

3-(Benzoyloxy)-1-iodo-2-(phenylamino)propane (5) was prepared according to the typical procedure described above

(43) von Braun, J.; Pinkernelle, W. *Ber. Dtsch. Chem. Ges.* **1934**, *67*, 1218.

(benzimidate in $CHCl_3$, 2 mL, was added to a suspension of I_2 in $CHCl_3$, 10 mL): yield 60%, oil; ^1H NMR δ 3.43 (dd, 1 H, J = 6.2 and 10.3 Hz), 3.50 (dd, 1 H, J = 4.0 and 10.3 Hz), 3.78 (m, 1 H), 4.03 (d, 1 H), 4.35 (dd, 1 H, J = 5.8 and 11.4 Hz), 4.67 (dd, 1 H, J = 5.1 and 11.4 Hz), 6.68–6.80 (several peaks, 3 H), 7.21 (m, 2 H), 7.46 (m, 2 H), 7.59 (m, 1 H), 8.04 (m, 2 H). Anal. Calcd for $C_{16}H_{16}INO_2$: C, 50.41; H, 4.23. Found: C, 50.55; H, 4.19.

1-(Benzoyloxy)-2-bromo-2-methyl-3-(phenylamino)propane (6a) was prepared according to the typical procedure given above. However, the $CHCl_3$ solution was left over $CaCl_2$ for 3 days before the workup procedure was continued: oil; ^1H NMR δ 1.90 (s, 3 H), 3.58 (m, 2 H), 4.11 (br s, 1 H), 4.56 (d, 1 H, J = 11.7 Hz), 4.65 (d, 1 H, J = 11.7 Hz), 6.67–6.76 (several peaks, 3 H), 7.16 (t, 2 H, J = 7.9 Hz), 7.48 (m, 2 H), 7.61 (m, 1 H), 8.06 (m, 2 H). Anal. Calcd for $C_{17}H_{18}BrNO_2$: C, 58.63; H, 5.21. Found: C, 58.45; H, 5.38.

The addition of bromine (11 μL, 0.21 mmol) to 2-methylallyl N-phenylbenzimidate (0.053 g, 0.21 mmol) was also studied in $CDCl_3$ (3 mL) by ^1H NMR. After 24 h, the spectrum indicated the formation of a cyclofunctionalization product: ^1H NMR δ 2.02 (2, 3 H), 3.72 (d, 1 H J = 12.1 Hz), 4.01 (d, 1 H J = 12.1 Hz), 5.40 (d, 1 H J = 9.5 Hz), 5.84 (d, 1 H, J = 9.5 Hz), 7.37 (t, 2 H), 7.58–7.73 (several peaks, 8 H). At this point the reaction mixture was shaken with $NaHCO_3$ and rapidly dried over $CaCl_2$; then the ^1H NMR spectrum was recorded again. The peaks of the cyclofunctionalization product were now absent, and no peaks corresponding to compound **6a** were observed: ^1H NMR δ 1.53 (s, 3 H), 3.63 (d, 1 H, J = 10.6 Hz), 3.73 (d, 1 H, J = 10.6 Hz), 4.41 (d, 1 H, J = 11.3 Hz), 4.53 (d, 1 H, J = 11.3 Hz), 6.94 (t, 2 H), 7.22 (t, 1 H), 7.43–7.60 (several peaks, 5 H), 8.03 (m, 2 H). A ^1H NMR spectrum of the same sample recorded 32 h later indicated the presence of compound **6a** as the main product of a product mixture.

2-(Benzoyloxy)-3-phenyl-3-(phenylamino)-1-(phenylselenenyl)propane (9a) was prepared as described in the typical procedure above: yield 74%, mp 116 °C. ^1H NMR δ 3.20 (dd, 1 H J = 6.0 and 13.0 Hz), 3.31 (dd, 1 H, J = 6.5 and 13.0 Hz), 4.64 (d, 1 H J = 7.2 Hz), 4.98 (m, 1 H), 5.53 (m, 1 H), 6.55–6.68 (several peaks, 3 H), 7.05–7.59 (several peaks, 15 H), 7.90 (m, 2 H). Anal. Calcd for $C_{28}H_{25}NO_2Se$: C, 69.13; H, 5.18. Found: C, 68.99; H, 5.26.

PhSeBr/PhSeCl/Br_2-Induced Cyclofunctionalization/Hydrolysis of Tertiary Allylic Benzamides. Typical Procedure. 2-(Benzoyloxy)-2-methyl-3-(phenylamino)-1-(phenylselenenyl)propane (12g). To a stirred solution of PhSeCl (0.155 g, 0.81 mmol) in CH_3CN (5 mL) at 0 °C was added dropwise a solution of N-(2-methylallyl)-N-phenylbenzamide (0.20 g, 0.80 mmol) in CH_3CN (1 mL). After 5 min, water (15 mL) was added, and stirring was continued for 30 min. The reaction mixture was then extracted once with CH_2Cl_2 (25 mL). $NaHCO_3$ (0.5 g) was added to the aqueous phase, which was then extracted with another portion of CH_2Cl_2 (25 mL). The combined organic extracts were dried ($CaCl_2$), evaporated, and submitted to flash chromatography (SiO_2; EtOAc/hexanes = 1/9) to give 0.18 g (52%) of compound **12g** as a white solid: mp 80–2 °C (CH_2Cl_2/hexanes). ^1H NMR δ 1.76 (s, 3 H), 3.58–3.77 (several peaks, 4 H), 3.87 (br s, 1 H), 6.62 (d, 2 H, J = 8.5 Hz), 6.71 (t, 1 H, J = 7.3 Hz), 7.12–7.25 (several peaks, 5 H), 7.39 (t, 2 H), 7.51–7.58 (several peaks, 3 H), 7.89 (m, 2 H). Anal. Calcd for $C_{23}H_{23}NO_2Se$: C, 65.09; H, 5.46. Found: C, 64.91; H, 5.37.

Experiments using PhSeBr instead of PhSeCl were carried out as described above. In the bromination experiments, bromine, dissolved in CH_3CN (1 mL), was added dropwise to a stirred solution of the tertiary allylic amide in CH_3CN (5 mL).

In the preparation of selenide **12c**, anhydrous pyridine (1 equiv) was added to a solution of PhSeCl in CH_2Cl_2. The allylic tertiary benzamide was then added in CH_2Cl_2 and the workup procedure carried out after 4 h.

In the preparation of bromide **12f**, workup was carried out after 20 h.

In the preparation of selenide **12a**, $CHCl_3$ was used as a solvent instead of CH_3CN. The workup procedure (involving extraction with water) was carried out 15 min after the addition of the benzamide solution was complete.

The mixture of isomeric bromides **12d/13a** and **12f** could not be separated. Hydrodebromination of the mixture obtained after flash chromatography provided evidence for the assigned structures.

The diastereomers of compound **12e** were not separated. Hydrodeselenation of the isomeric mixture obtained after flash chromatography (vide infra) provided evidence for the assigned structures/isomeric composition of the cyclofunctionalization/hydrolysis products.

Physical, analytical, and ^1H NMR data for compounds **12** and **13** are reported as follows. For solvents, electrophilic reagents used, yields, and isomeric ratios, see Table II.

2-(Benzoyloxy)-3-(phenylamino)-1-(phenylselenenyl)propane (12a): mp 70–1 °C; ^1H NMR δ 3.31 (m, 2 H), 3.51 (m, 2 H), 3.83 (m, 1 H), 5.45 (m, 1 H), 6.63 (d, 2 H), 6.71 (t, 1 H), 7.15 (t, 2 H), 7.21–7.24 (several peaks, 3 H), 7.41 (t, 2 H), 7.53–7.59 (several peaks, 3 H), 7.93 (m, 2 H); IR (cm^{-1}) 3398, 3393, 1703.

2-(Benzoyloxy)-3-(phenylamino)-1-bromopropane (12b): oil; ^1H NMR δ 3.62 (dd, 2 H, J = 1.5 and 6.0 Hz), 3.71 (d, 2 H J = 4.7 Hz), 4.04 (br s, 1 H), 5.43 (m, 1 H), 6.71–6.78 (several peaks, 3 H), 7.20 (t, 2 H), 7.47 (t, 2 H), 7.60 (m, 1 H), 8.06 (m, 2 H). Anal. Calcd for $C_{16}H_{16}BrNO_2$: C, 57.50; H, 4.83. Found: C, 57.23, H, 4.74.

3-(Benzoyloxy)-4-(phenylamino)-2-(phenylselenenyl)butane (12c): mp 82 °C; ^1H NMR δ 1.56 (d, 3 H, J = 7.1 Hz), 3.59 (d, 2 H, J = 5.5 Hz), 3.67 (m, 1 H), 3.88 (br s, 1 H), 5.45 (m, 1 H), 6.60 (d, 2 H), 6.69 (t, 1 H), 7.11–7.24 (several peaks, 5 H), 7.42 (t, 2 H), 7.53–7.59 (several peaks, 3 H), 7.96 (m, 2 H). Anal. Calcd for $C_{23}H_{23}NO_2Se$: C, 65.09; H, 5.46. Found: C, 65.10; H, 5.40.

2-(Benzoyloxy)-4-(phenylamino)-2-bromobutane (12d) and 3-(benzoyloxy)-1-(phenylamino)-2-bromobutane (13a) were inseparable. Doublets at 1.81 and 1.53 ppm in the ^1H NMR spectrum of the mixture were characteristic of the two compounds.

***threo*-2-(Benzoyloxy)-3-(phenylamino)-1-(phenylselenenyl)butane (12e)**: oil, ^1H NMR δ 1.22 (d, 3 H, J = 6.6 Hz), 3.30 (d, 2 H, J = 6.7 Hz), 3.66 (d, 1 H, J = 7.4 Hz), 4.09 (m, 1 H), 5.39 (m, 1 H), 6.67–6.74 (several peaks, 3 H), 7.15–7.20 (several peaks, 5 H), 7.41–7.58 (several peaks, 5 H), 7.98 (m, 2 H). Anal. Calcd for $C_{23}H_{23}NO_2Se$: C, 65.09; H, 5.46. Found: C, 64.91; H, 5.33.

***erythro*-2-(Benzoyloxy)-3-(phenylamino)-1-(phenylselenenyl)butane** was never isolated in pure form. Hydrodeselenation of an 1/1 mixture of erythro and threo isomers provided evidence for its structure.

2-(Benzoyloxy)-3-(phenylamino)-1-bromobutane (12f) was obtained as a mixture of diastereomers after flash chromatography (multiplets at 5.30 and 5.40 ppm in the ^1H NMR spectrum of the mixture were characteristic of the two isomers).

2-(Benzoyloxy)-2-methyl-3-(phenylamino)-1-bromopropane (12h): mp 90 °C. ^1H NMR δ 1.79 (s, 3 H), 3.69 (d, 1 H, J = 13.8 Hz), 3.80 (d, 1 H, J = 13.8 Hz), 3.95–4.05 (several peaks, 3 H), 6.71–6.77 (several peaks, 3 H), 7.19 (t, 2 H), 7.43 (t, 2 H), 7.57 (m, 1 H), 7.98 (m, 2 H). Anal. Calcd for $C_{17}H_{18}BrNO_2$: C, 58.63; H, 5.21. Found: C, 58.47; H, 5.11.

2-(Benzoyloxy)-3-phenyl-3-(phenylamino)-1-(phenylselenenyl)propane (9a) prepared from N-(1-phenylallyl)-N-phenylbenzamide and PhSeBr in $CHCl_3$ with workup after 24 h was identical with compound **9a** prepared as described above.

Hydrodehalogenation and Hydrodeselenation of Cyclofunctionalization/Hydrolysis Products. Typical Procedure. 2-(Benzoyloxy)-1-(phenylamino)propane (15a). 2-(Benzoyloxy)-3-(phenylamino)-1-(phenylselenenyl)propane (0.080 g, 0.195 mmol) and triphenyltin hydride (0.140 g, 0.40 mmol) were heated at reflux in benzene (5 mL) with a small amount of AIBN for 2 h. Evaporation of the solvent and flash chromatography (CH_2CH_2) afforded 0.048 g (96%) of compound **15a**: mp 59 °C (hexanes); ^1H NMR δ 1.45 (d, 2 H J = 6.4 Hz), 3.40 (m, 2 H), 3.96 (br s, 1 H), 5.38 (m, 1 H), 6.64–6.74 (several peaks, 3 H), 7.18 (t, 2 H), 7.44 (t, 2 H), 7.54 (m, 1 H), 8.03 (m, 2 H). Anal. Calcd for $C_{16}H_{17}NO_2$: C, 75.27; H, 6.71. Found: C, 75.16; H, 6.86.

Physical, analytical, and ^1H NMR data for hydrodehalogenation and hydrodeselenation products **14**, **15**, **13b**, **6b**, and **9b** are reported below. For yields see Table III.

1-(Benzoyloxy)-2-(phenylamino)propane (14a): mp 73 °C (lit.[44] 71–2 °C).

1-(Benzoyloxy)-2-(phenylamino)butane (14b): mp 42 °C; ^{1}H NMR δ 1.05 (t, 3 H, J = 7.5 Hz), 1.55–1.85 (several peaks, 2 H), 3.60–3.80 (several peaks, 2 H), 4.28 (dd, 1 H, J = 4.9 and 11.2 Hz), 4.47 (dd, 1 H, J = 4.8 and 11.2 Hz), 6.66–6.74 (several peaks, 3 H), 7.17 (t, 2 H), 7.43 (t, 2 H), 7.56 (m, 1 H), 7.99 (m, 2 H). Anal. Calcd for $C_{17}N_{19}NO_2$: C, 75.81; H, 7.11. Found: C, 75.65; H, 7.18.

***threo*-2-(Benzoyloxy)-3-(phenylamino)butane (14c = 15c)**: oil; ^{1}H NMR δ 1.25 (d, 3 H, J = 6.5 Hz), 1.38 (d, 3 H, J = 6.5 Hz), 3.66 (m, 1 H), 3.79 (m, 1 H), 5.32 (m, 1 H), 6.66–6.72 (several peaks, 3 H), 7.18 (t, 2 H), 7.44 (t, 2 H), 7.57 (m, 1 H), 8.02 (m, 2 H). Anal. Calcd for $C_{17}H_{19}NO_2$: C, 75.81; H, 7.11. Found: C, 75.69; 7.06.

***erythro*-2-(Benzoyloxy)-3-(phenylamino)butane (14c = 15c)**: oil; ^{1}H NMR δ 1.31 (d, 3 H, J = 6.0 Hz), 1.40 (d, 3 H, J = 6.0 Hz), 3.60–3.80 (several peaks, 2 H), 5.24 (m, 1 H), 6.61 (d, 2 H), 6.69 (m, 1 H), 7.15 (t, 2 H), 7.43 (t, 2 H), 7.57 (m, 1 H), 8.01 (m, 2 H). Anal. Calcd for $C_{17}H_{19}NO_2$: C, 75.81; H, 7.11. Found: C, 75.76; H, 7.01.

1-(Benzoyloxy)-2-methyl-2-(phenylamino)propane (14d): mp 99 °C; ^{1}H NMR δ 1.42 (s, 6 H), 3.70 (br s, 1 H), 4.30 (s, 2 H), 6.82–6.86 (several peaks, 3 H), 7.18 (t, 2 H), 7.46 (t, 2 H), 7.59 (m, 1 H), 8.05 (m, 2 H). Anal. Calcd for $C_{17}H_{19}NO_2$: C, 75.81; H, 7.11. Found: C, 75.97; H, 7.08.

2-(Benzoyloxy)-1-(phenylamino)butane (15b): mp 65–6 °C; ^{1}H NMR δ 1.03 (t, 3 H, J = 7.5 Hz), 1.84 (m, 2 H), 3.41 (m, 2 H), 3.95 (br s, 1 H), 5.27 (m, 1 H), 6.63–6.73 (several peaks, 3 H), 7.17 (t, 2 H), 7.44 (m, 2 H), 7.57 (m, 1 H), 8.04 (m, 2 H). Anal. Calcd for $C_{17}H_{19}NO_2$: C, 75.81; H, 7.11. Found: C, 75.89; H, 7.22.

2-(Benzoyloxy)-2-methyl-1-(phenylamino)propane (15d): mp 71–2 °C; ^{1}H NMR δ 1.68 (s, 6 H), 3.50 (d, 2 H, J = 5.6 Hz), 4.05 (br s, 1 H), 6.66–6.74 (several peaks, 3 H), 7.18 (t, 2 H), 7.41 (t, 2 H), 7.54 (m, 1 H), 7.95 (m, 2 H). Anal. Calcd for $C_{17}H_{19}NO_2$: C, 75.81; H, 7.11. Found: C, 75.79; H, 7.09.

2-(Benzoyloxy)-4-(phenylamino)butane (13b): oil; ^{1}H NMR δ 1.40 (d, 3 H, J = 6.3 Hz), 2.00 (m, 2 H), 3.25 (m, 2 H), 3.86 (br s, 1 H), 5.33 (m, 1 H), 6.60 (d, 2 H), 6.69 (t, 1 H), 7.16 (t, 2 H), 7.45 (t, 2 H), 7.57 (m, 1 H), 8.05 (m, 2 H). Anal. Calcd for $C_{17}H_{19}NO_2$: C, 75.81; H, 7.11. Found: C, 75.67; H, 7.00.

1-(Benzoyloxy)-2-methyl-3-(phenylamino)propane (6b): mp 60 °C; ^{1}H NMR δ 1.12 (d, 3 H, J = 6.9 Hz), 2.30 (m, 1 H), 3.05–3.35 (several peaks, 2 H), 3.91 (br s, 1 H), 4.28 (dd, 1 H, J = 5.9 and 11.0 Hz), 4.36 (dd, 1 H, J = 5.4 and 11.0 Hz), 6.62 (d, 2 H), 6.69 (t, 1 H), 7.17 (t, 2 H), 7.46 (t, 2 H), 7.58 (m, 1 H), 8.05 (m, 2 H). Anal. Calcd for $C_{17}H_{19}NO_2$: C, 75.81; H, 7.11. Found: C, 75.71; H, 7.13.

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2-(Benzoyloxy)-1-phenyl-1-(phenylamino)propane (9b): mp 95–6 °C; ^{1}H NMR δ 1.35 (d, 3 H, J = 6.4 Hz), 4.54 (d, 1 H, J = 6.3 Hz), 4.65 (br s, 1 H), 5.45 (m, 1 H), 6.56 (d, 2 H), 6.64 (t, 1 H), 7.08 (t, 2 H), 7.24–7.35 (several peaks, 3 H), 7.40–7.46 (several peaks, 4 H), 7.56 (m, 1 H), 8.00 (m, 2 H). Anal. Calcd for $C_{22}H_{21}NO_2$: C, 79.73; H 6.39. Found: C, 79.64; H, 6.47.

***threo*- and *erythro*-2-(Benzoyloxy)-3-(phenylamino)butane** were hydrolyzed to the corresponding amino alcohol derivatives ***threo*-** and ***erythro*-2-hydroxy-3-(phenylamino)butane** in a refluxing 1:1 mixture of EtOH/NaOH (2 M aqueous). The compounds were identical to authentic samples prepared by phenylaminolysis of *cis*- and *trans*-2,3-epoxybutane according to a literature procedure.[27] ^{1}H NMR data for the amino alcohols are presented below. ***threo*-2-Hydroxy-3-(phenylamino)butane** δ 1.16 (d, 3 H, J = 6.3 Hz), 1.27 (d, 3 H, J = 6.2 Hz), 2.58 (s, 1 H), 3.31–3.39 (several peaks, 2 H), 3.64 (m, 1 H), 6.67–6.77 (several peaks, 3 H), 7.16–7.26 (several peaks, 2 H). ***erythro*-2-Hydroxy-3-(phenylamino)butane**: δ 1.15 (d, 3 H, J = 6.6 Hz), 1.21 (d, 3 H, J = 6.4 Hz), 1.81 (br d, 1 H), 3.50 (m, 1 H). 3.64 (m, 1 H), 3.98 (m, 1 H), 6.64 (d, 2 H), 6.71 (m, 1 H), 7.14–7.21 (several peaks, 2 H).

4,5-Dihydro-1,2-diphenyl-5-[(phenylselenenyl)methyl]-1*H*-imidazole (17a). To a stirred solution of PhSeBr (0.20 g, 0.85 mmol) in $CHCl_3$ (5 mL) was added dropwise a solution of *N*-allyl-*N'*-phenylbenzamidine (0.20 g, 0.85 mmol) in $CHCl_3$ (1 mL). After 24 h, the solution was diluted with CH_2Cl_2 (20 mL) and extracted with $NaHCO_3$ (5% aqueous). Drying, evaporation, and flash chromatography (SiO_2; EtOAc/hexanes = 1/1) afforded 0.29 g (87%) of compound **17a** as an oil: ^{1}H NMR δ 3.14 (dd, 1 H, J = 8.2 and 12.2 Hz), 3.30 (dd, 1 H, J = 2.8 and 12.2 Hz), 3.94 (m, 1 H), 4.25 (several peaks, 2 H), 6.85 (d, 2 H), 7.03–7.34 (several peaks, 10 H), 7.45–7.52 (several peaks, 3 H). Anal. Calcd for $C_{22}H_{20}N_2Se$: C, 67.52; H 5.15. Found: C, 67.48; H, 5.14.

4,5-Dihydro-1,2-diphenyl-5-methyl-5-[(phenylselenenyl)methyl]-1*H*-imidazole (17b) was prepared from compound **16b** using the procedure described for compound **17a**: yield 94%, mp 97–8 °C; ^{1}H NMR δ 1.29 (s, 3 H), 3.11 (d, 1 H, J = 11.9 Hz), 3.38 (d, 1 H, J = 11.9 Hz), 3.91 (d, 1 H, J = 15.0 Hz), 4.28 (d, 1 H, J = 15.0 Hz), 6.99 (d, 1 H), 7.16–7.28 (several peaks, 10 H), 7.41 (d, 2 H), 7.52–7.56 (several peaks, 2 H). Anal. Calcd for $C_{23}H_{22}N_2Se$: C, 68.14; H 5.47. Found: C, 67.90; H, 5.33.

4,5-Dihydro-1,2-diphenyl-5-methyl-1*H*-imidazole (18a) was prepared by treatment of selenide **17a** according to the typical procedure for hydrodeselenation described above: yield 94%, mp 68 °C; ^{1}H NMR δ 1.37 (d, 3 H, J = 5.8 Hz), 3.64 (m, 1 H), 4.13–4.29 (several peaks, 2 H), 6.88 (d, 2 H), 7.05 (m, 1 H), 7.17–7.33 (several peaks, 5 H), 7.47 (m, 2 H). Anal. Calcd for $C_{16}H_{16}N_2$: C, 81.32; H 6.82. Found: C, 81.49; H, 6.98.

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