Amidoselenation of Olefins *via* Hydroxyselenation: Reactions using Nitriles in Reagent Quantity and the Synthesis of β-(Acrylamido)alkyl Phenyl Selenides

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Limitations in a previously reported amidoselenation reaction have been overcome by the use of β-hydroxyalkyl phenyl selenides, (**1**) and (**2**), as starting materials; these when treated with nitriles (1—5 equiv.) in dichloromethane in the presence of trifluoromethanesulphonic acid afforded the β-amidoalkyl phenyl selenides (**3**) or (**4**) in good yield. Further, side reaction brought about by hydrogen chloride have been prevented; thus (**1**) and (**2**) in the presence of acid afforded the β-(acrylamido)alkyl phenyl selenides (**5**) or (**7**), free from side products.

We have already reported that the reaction of olefins with benzeneselenenyl chloride in nitriles in the presence of trifluoromethanesulphonic acid and water, a Ritter-type amide synthesis, affords β-amidoalkyl phenyl selenides in good to excellent yields.[1,2] In this way, mono- and 1,2-di-substituted olefins have been converted into allylic amides or saturated amides by oxidative or reductive elimination of the phenylseleno group from the β-amido selenides thus prepared.[1b,3]

Initially, we had planned to prepare various β-amidoalkyl phenyl selenides bearing haloalkyl or vinyl substituents on the amide carbonyl group by the previously reported amidoselenation method.[1] Problems were however, encountered in that halogenoalkylnitriles are expensive and, moreover, have high boiling points which made them difficult to separate from the products. A further problem encountered in the reaction with acrylonitrile was the formation of a considerable quantity of side product, formed *via* a secondary reaction of the desired product with hydrogen chloride. To overcome these difficulties we used instead the β-hydroxyalkyl phenyl selenides (**1**) or (**2**) as starting materials (instead of olefin and benzeneselenenyl chloride) and obtained satisfactory results.[4]

We report herein that the reaction of (**1**) or (**2**) with trifluoromethanesulphonic acid in acrylonitrile affords the desired β-(acrylamido)alkyl phenyl selenides free from the side product. It is also reported that (**1**) and (**2**) are converted into β-amido selenides smoothly by using only 1—5 equiv. of halogenoalkanonitriles in dichloromethane in the presence of trifluoromethanesulphonic acid.

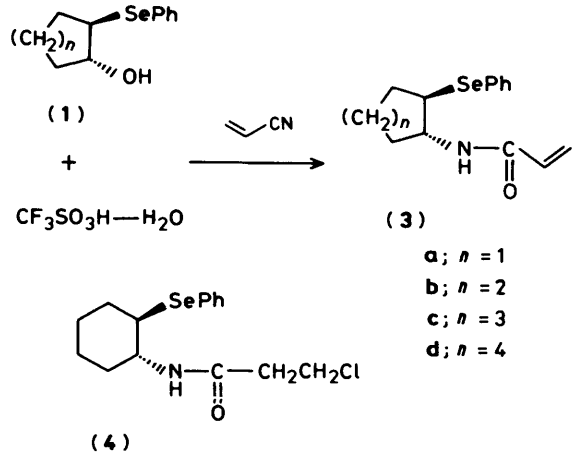
Results and Discussion

Synthesis of β-(Acrylamido)alkyl Phenyl Selenides.—The reaction of cyclohexene with benzeneselenenyl chloride in acrylonitrile in the presence of trifluoromethanesulphonic acid and water (the previously reported conditions for amidoselenation of olefins[1]), gave 1-(3-chloropropanamido)-2-(phenylseleno)cyclohexane (**4**) (22%), in addition to the desired acrylamide derivative (**3b**) (64%). We confirmed separately that (**4**) was produced by the reaction of (**3b**) with hydrogen chloride. Since the separation of (**3b**) from (**4**) required repeated column chromatography, selective formation of (**3b**) was wanted. We realised that carrying out the reaction in the absence of hydrogen chloride would prevent the side reaction, and so we used a β-hydroxy selenide as the starting material. Reaction of the β-hydroxy selenide (**1b**) with 1 equiv. of trifluoromethanesulphonic acid and water in acrylonitrile at ambient temperature for 3 h gave 1-(acrylamido)-2-(phenylseleno)cyclohexane (**3b**) (95%) (Scheme 1). The reaction conditions were briefly examined and the results are summarised in Table 1. As shown in this Table, the addition of water is unnecessary (entries 1 and 4), the hydroxy group contained in the starting material being utilised effectively in the addition to the carbon atom of the nitrile to afford the amide. The role of acid is catalytic, 0.2 equiv. being sufficient to ensure complete conversion of (**1b**) into (**3b**) in 72 h. The use of a 1:1 mixture of trifluoromethanesulphonic acid and water is, however, attractive it being easier to handle than pure, fuming, trifluoromethanesulphonic acid. Thus 1 equiv. of such a mixture was used in the transformation of the β-hydroxy selenides (**1a—d**, **2a—c**) into the corresponding amides and the results are shown in Table 2. The β-(acrylamido)alkyl phenyl selenides (**3**) and (**5**) were produced in excellent yields from the β-hydroxy selenides derived from mono- and 1,2-disubstituted olefins. Only in the case of the cyclo-octene derivative was the yield of (**3d**) unsatisfactory, and several attempts to improve it failed.

Table 1. Reaction conditions for conversion of (**1b**) into (**3b**)[a]

Entry	CF_3SO_3H (mmol)	H_2O (mmol)	Temp. (°C)	Time (h)	(**3b**; yield[b] (%)
1	5		20	1	91
2	5		76	1	83
3	1		20	72	90
4	5	5	20	3	95

[a] Carried out using (**1b**) (5 mmol) in acrylonitrile (15 ml). [b] Isolated yield by column chromatography.

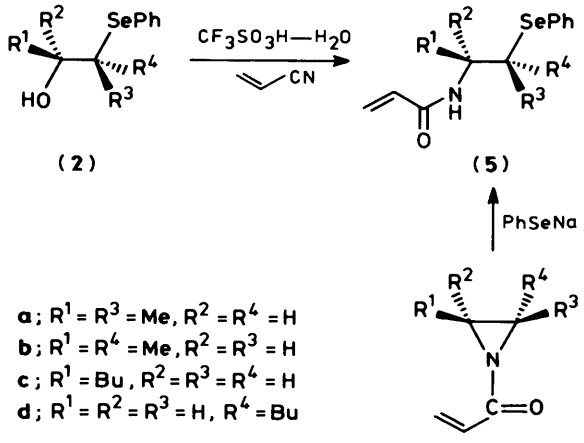


Scheme 1.

Table 2. Reactions of various β-hydroxy selenides in acrylonitrile[a]

Entry	β-Hydroxy selenide	Time (h)	Product(s)	Yield[b] (ratio)[c] (%)
1	(**1a**)	8	(**3a**)	92
2	(**1b**)	3	(**3b**)	95
3	(**1c**)	8	(**3c**)	88
4	(**1d**)	24	(**3d**)	39
5	(**2a**)	24	(**5a**)	89
6	(**2b**)	24	(**5b**)	85
7	(**2c**)	24	(**5c**) + (**5d**)	95 (91:9)

[a] Carried out using β-hydroxy selenide (2 mmol), trifluoromethanesulphonic acid (2 mmol), and water (2 mmol) in acrylonitrile (6 ml). [b] Isolated yield by column chromatography. [c] Determined by h.p.l.c. analysis.



Scheme 2.

There was retention of stereochemistry during the course of the reaction. Thus, the *threo*- and *erythro*-β-hydroxy selenides (**2a**) and (**2b**) afforded the *threo*- and *erythro*-β-(acrylamido)-selenides (**5a**) and (**5b**), respectively (Scheme 2).

The stereochemistry of (**5a**) and (**5b**) was confirmed by comparison (spectral data and mixed m.p.) with authentic samples prepared from *cis*- and *trans*-*N*-acryloyl-2,3-dimethylaziridine[5] by reaction with sodium benzeneselenolate (see Scheme 2). From β-hydroxy selenide derived from the unsymmetrical olefin (**2c**) (pure isomer was used[6]), a 91:9 mixture of regioisomers was produced, the Markovnikov type adduct (**5c**) predominating. These results indicate that the acid-catalysed carbon–oxygen bond fission is assisted by the participation of a phenylseleno group to form an episelenonium ion intermediate which is then attacked by acrylonitrile to give the product.

The Use of Nitriles in Reagent Quantity.—Although 1-(chloroacetamido)-2-(phenylseleno)cyclohexane (**6b**; R = $ClCH_2$) was formed by the reaction of the benzeneselenenyl chloride adduct of cyclohexene with 5 equiv. of chloroacetonitrile in dichloromethane in the presence of trifluoromethanesulphonic acid–water (1:1 equiv.) (20 °C, 24 h), the yield was poor (40%). It was increased to 98% by changing the starting material from the β-chloro selenide to the β-hydroxy selenide (**1b**). Since β-hydroxy selenides are readily prepared in almost quantitative yields from olefins and benzeneselenenyl chloride [acetonitrile-water (5:1) as the solvent[6]], it is clear that the amidoselenation of olefins by way of hydroxyselenation is a better procedure.

As a first step for optimisation of the reaction conditions 2-(phenylseleno)cyclopentan-1-ol (**1a**) and chloroacetonitrile (2.5 equiv.) were allowed to react in a variety of solvents at ambient temperature for 24 h in the presence of 1 equiv. of trifluoromethanesulphonic acid–water (1:1). The yields of (**6a**; R = $ClCH_2$) in various solvents were 72% in dichloromethane, 59% in chloroform, 55% in benzene, 50% in nitromethane, >24% in tetrahydrofuran, and 0% in *N*,*N*-dimethylformamide. Changes in the other reaction conditions were examined and the results are summarised in Table 3. As shown, the yield of (**6a**; R = $ClCH_2$) was poor with a stoicheiometric quantity of chloroacetonitrile, but improved when 2.5 equiv. were employed (entries 1 and 2); 5 equiv. resulted in a slight improvement in the yield (entry 4). Reactions performed at reflux temperature or 0 °C (entries 3 and 6) failed to give good results. The conditions of entry 4 in Table 3 were, therefore, used for the preparation of the amides (**6**) and (**7**) from the corresponding β-hydroxy selenides (**1**) and (**2**) (Scheme 3). The results are listed in Table 4.

The reactions were monitored by t.l.c. and were discontinued when there was no further increase in the amount of products. Various β-(chloroacetamido) selenides (**6**; R = $ClCH_2$) and (**7**) were produced in good to excellent yields. For the cyclohexane derivative (**1b**), the yield of (**6b**; R = $ClCH_2$) was almost quantitative when 5 equiv. of chloroacetonitrile were used (entry 2) and still excellent with only 1 equiv. (entry 3). It is noteworthy that chloroacetonitrile can serve as a nucleophile under the reaction conditions employed to afford the amides (**6**) and (**7**) in good yields, in spite of the presence of an electron-withdrawing group on the α-carbon which reduces the nucleo-

Table 3. Reaction conditions for conversion of (**1a**) into (**6a**; R = $ClCH_2$)[a]

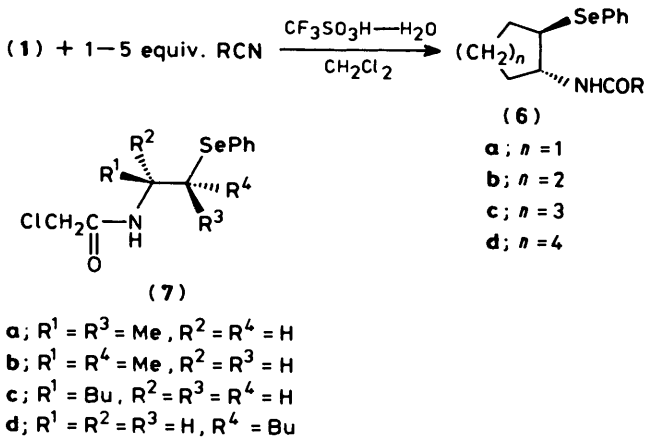
Entry	$ClCH_2CN$ (mmol)	Temp (°C)	Time (h)	(**6a**; R = $ClCH_2$) yield[b] (%)
1	2	20	24	40
2	5	20	24	72
3	5	40	1	50
4	10	20	24	77
5	10	20	1	73
6	10	0	24	40

[a] Carried out by using (**1a**) (2 mmol), trifluoromethanesulphonic acid (2 mmol), and water (2 mmol) in dichloromethane (2 ml). [b] Isolated yield by column chromatography.

Table 4. Reactions of various β-hydroxy selenides with reagent quantities of nitriles[a]

Entry	β-Hydroxy selenide	Nitrile R	Time (h)	Product(s)	Yield[b] (%) (ratio)[c]
1	(**1a**)	$ClCH_2$	24	(**6a**; R = $ClCH_2$)	77
2	(**1b**)	$ClCH_2$	3	(**6b**; R = $ClCH_2$)	99
3	(**1b**)	$ClCH_2$[d]	24	(**6b**; R = $ClCH_2$)	83
4	(**1b**)	$BrCH_2$[d]	24	(**6b**; R = $BrCH_2$)	63
5	(**1b**)	$BrCH_2CH_2$[d]	25	(**6b**; R = $BrCH_2CH_2$)	97
6	(**1c**)	$ClCH_2$	2	(**6c**; R = $ClCH_2$)	52
7	(**1d**)	$ClCH_2$	56	(**6d**; R = $ClCH_2$)	24
8	(**2a**)	$ClCH_2$	1	(**7a**)	89
9	(**2b**)	$ClCH_2$	1	(**7b**)	84
10	(**2c**)	$ClCH_2$	24	(**7c**) + (**7d**)	89 (95:5)

[a] Carried out using β-hydroxy selenide (2 mmol), nitrile (10 mmol), trifluoromethanesulphonic acid (2 mmol), and water (2 mmol) in dichloromethane (2 ml) at 20 °C. [b] Isolated yield by column chromatography. [c] Determined by h.p.l.c. analysis. [d] The amount of nitrile was 2 mmol.



Scheme 3.

philicity of the cyano group.[7] The results of the reaction of (**1b**) with other nitriles such as bromoacetonitrile and 3-bromopropionitrile to afford (**6b**; R = $BrCH_2$ and $BrCH_2CH_2$) are also included in Table 4 (entries 4 and 5); good to excellent yields were obtained by the use of 1 equiv. of the nitriles.

The present methodology was, unfortunately, ineffective in overcoming a further limitation of the amidoselenation reaction in that it was not practicable to employ electron- rich tri- or tetra-substituted olefins.[8] Thus, the β-hydroxy selenides derived from styrene, 1-methylcyclohexene, and 2,3-dimethylbut-2-ene failed to react.

Experimental

I.r. spectra were recorded with a JASCO IR-810 spectrophotometer. ^1H N.m.r. spectra were obtained with JEOLCO JNM-FX-100 (100 MHz) and JEOLCO JNM-GX-400 (400 MHz) instruments for solutions in $CDCl_3$ with Me_4Si as internal standard. M.p.s were determined with a Shimadzu MM-2 micro melting point determination apparatus and are uncorrected. Liquid chromatographic analyses were carried out with a Waters h.p.l.c. system equipped with a 6 000 A solvent delivery system, a Model 440 absorbance detector (at 254 nm), and a μ-Porasil (3.9 mm × 0.3 m) column.

threo- *and* erythro-2-(*Acrylamido*)-3-(*phenylseleno*)*butane* (**5a**) *and* (**5b**).—*cis*-2,3-Dimethylaziridine [prepared by a reported method[5] using *threo*-2-azido-3-iodobutane (4.7 g, 21 mmol)] was acrylated with acryloyl chloride in a reported procedure[1b] to give *N*-acryloyl-*cis*-2,3-dimethylaziridine (0.62 g, 4.9 mmol by column chromatography). Ethanol (30 ml) was added under a nitrogen atmosphere to diphenyl diselenide (0.79 g, 2.5 mmol) and sodium borohydride (0.21 g, 5.5 mmol); the aziridine in ethanol (15 ml) was then added and the resulting pale yellow solution was stirred at ambient temperature for 3 h. The reaction mixture was poured into aqueous hydrogen chloride (0.2M; 85 ml) and the products were extracted with ether (3 × 70 ml). The combined extracts were washed with saturated aqueous sodium hydrogen carbonate, dried, and evaporated to leave a pale yellow oil. Flash column chromatography[9] of this on silica gel (300 mesh) with hexane–ethyl acetate (1:1) as eluant afforded (**5a**); white needles (0.21 g, 0.74 mmol, 15%), m.p. 70.5—71.0 °C (from hexane) (Found: C, 55.0; H, 6.0; N, 4.95%. $C_{13}H_{17}NOSe$ requires C, 55.3; H, 6.1; N, 5.0%); $\nu_{max.}$ (KBr disc) 3 250, 1 652, 1 623, 1 550, 741, and 692 cm^{-1}; δ_H (100 MHz) 1.22 (3 H, d, *J* 6.8 Hz), 1.41 (3 H, d, *J* 7.3 Hz), 3.53 (1 H, dq, *J* 3.9 and 7.3 Hz), 4.30 (1 H, ddq, *J* 8.8, 3.9, and 6.8 Hz), 5.62 (1 H, dd, *J* 9.3 and 2.5 Hz), 5.8 (1 H, br s), 6.06 (1 H, dd, *J* 16.6 and 9.3 Hz), 6.26 (1 H, dd, *J* 16.6 and 2.5 Hz), 7.24—7.34 (3 H, m), and 7.52—7.67 (2 H, m). The same procedure using *trans*-2,3-dimethylaziridine afforded (**5b**); white needles, m.p. 60—61 °C (from hexane) (Found: C, 55.2; H, 6.0; N, 5.0. $C_{13}H_{17}NOSe$ requires C, 55.3; H, 6.1; N, 5.0%); $\nu_{max.}$ (KBr disc) 3 250, 1 652, 1 623, 1 548, 740, and 691 cm^{-1}; δ_H (100 MHz) 1.22 (3 H, d, *J* 6.8 Hz), 1.50 (3 H, d, *J* 7.3 Hz), 3.58 (1 H, dq, *J* 3.4 and 7.3 Hz), 4.27 (1 H, ddq, *J* 8.8, 3.4, and 6.8 Hz), 5.55 (1 H, dd, *J* 9.8 and 2.4 Hz), 5.8 (1 H, br s), 5.89 (1 H, dd, *J* 16.6 and 9.8 Hz), 6.16 (1 H, dd, *J* 16.6 and 2.4 Hz), 7.22—7.32 (3 H, m), and 7.47—7.60 (2 H, m).

β-Hydroxyalkyl phenyl selenides (**1**) and (**2**) were prepared by a reported procedure.[6] All other organic and inorganic materials were commercial products and were used without purification.

Preparation of trans-1-(*Acrylamido*)-2-(*phenylseleno*)*cyclopentane* (**3a**); *General Procedure*.—To a stirred solution of 2-hydroxycyclopentyl phenyl selenide (**1a**) (0.48 g, 2.0 mmol) in acrylonitrile (6 ml) was added a 1:1 (molar ratio) mixture of trifluoromethanesulphonic acid–water (0.34 g, 2.0 mmol) and the resulting solution was stirred at ambient temperature for 24 h. The solution was poured into saturated aqueous sodium hydrogen carbonate (50 ml) and extracted with dichloromethane (3 × 20 ml). The extract was washed with brine, dried, and evaporated to leave a pale yellow oil. Column chromatography of this on silica gel with hexane–ethyl acetate (1:1) as eluant yielded (**3a**) (0.54 g, 1.83 mmol, 92%); pale orange semisolid (Found: C, 57.0; H, 5.5; N, 4.9. $C_{14}H_{17}NOSe$ requires C, 57.2; H, 5.8; N, 4.8%); $\nu_{max.}$ (KBr disc) 3 300, 1 655, 1 624, 1 540, 747, and 695 cm^{-1}; δ_H (100 MHz) 1.2—2.0 (4 H, m), 2.0—2.5 (2 H, m), 3.36 (1 H, q, *J* 7.3 Hz), 4.21 (1 H, quint, *J* 7.3 Hz), 5.58 (1 H, dd, *J* 9.5 and 2.4 Hz), 5.7—5.9 (1 H, m), 6.01 (1 H, dd, *J* 17.1 and 9.5 Hz), 6.22 (1 H, dd, *J* 17.1 and 2.4 Hz), 7.1—7.3 (3 H, m), and 7.5—7.7 (2 H, m).

Spectral as well as combustion analytical data of other β-(acrylamido)alkyl phenyl selenides are as follows.

trans-1-(*Acrylamido*)-2-(*phenylseleno*)*cyclohexane* (**3b**); white needles, m.p. 126—127 °C [from hexane–ethyl acetate (1:1)] (Found: C, 58.5; H, 6.1; N, 4.6. $C_{15}H_{19}NOSe$ requires C, 58.4; H, 6.2; N, 4.5%); $\nu_{max.}$ (KBr disc) 3 300, 1 657, 1 625, 1 550, 736, and 691 cm^{-1}; δ_H (100 MHz) 1.0—1.9 (6 H, m), 2.0—2.4 (2 H, m), 3.06 (1 H, dt, *J* 3.9 and 10.7 Hz), 3.7—4.1 (1 H, m), 5.61 (1 H, dd, *J* 9.6 and 2.4 Hz), 5.73 (1 H, br s), 6.01 (1 H, dd, *J* 16.6 and 9.6 Hz), 6.25 (1 H, dd, *J* 16.6 and 2.4 Hz), 7.1—7.3 (3 H, m), and 7.4—7.6 (2 H, m).

trans-1-(*Acrylamido*)-2-(*phenylseleno*)*cycloheptane* (**3c**); white needles, m.p. 74—75 °C (from hexane) (Found: C, 59.5; H, 6.5; N, 4.3. $C_{16}H_{21}NOSe$ requires C, 59.6; H, 6.6; N, 4.35%); $\nu_{max.}$ (KBr disc) 3 290, 1 655, 1 625, 1 540, 740, and 697 cm^{-1}; δ_H (100 MHz) 1.2—2.3 (10 H, m), 3.29 (1 H, ddd, *J* 9.8, 7.8, and 3.4 Hz), 3.9—4.3 (1 H, m), 5.60 (1 H, dd, *J* 9.3 and 2.4 Hz), 5.70 (1 H, br s), 6.03 (1 H, dd, *J* 16.6 and 9.3 Hz), 6.26 (1 H, dd, *J* 16.6 and 2.4 Hz), 7.1—7.3 (3 H, m), and 7.4—7.6 (2 H, m).

trans-1-(*Acrylamido*)-2-(*phenylseleno*)*cyclo-octane* (**3d**); white plates, m.p. 77—78 °C [from hexane–ethyl acetate (1:1)] (Found: C, 60.7; H, 6.9; N, 4.05. $C_{17}H_{23}NOSe$ requires C, 60.7; H, 6.9; N, 4.2%); $\nu_{max.}$ (KBr disc) 3 310, 1 652, 1 624, 1 535, 735, and 691 cm^{-1}; δ_H (100 MHz) 1.1—2.4 (12 H, m), 3.41 (1 H, ddd, *J* 10.7, 6.8, and 2.9 Hz), 4.1—4.4 (1 H, m), 5.58 (1 H, dd, *J* 9.8 and 2.2 Hz), 5.5—5.8 (1 H, m), 5.96 (1 H, dd, *J* 16.6 and 9.8 Hz), 6.23 (1 H, dd, *J* 16.6 and 2.2 Hz), 7.1—7.4 (3 H, m), and 7.4—7.6 (2 H, m).

1-(*Phenylseleno*)-2-(*acrylamido*)*hexane* (**5c**); white needles, m.p. 77.5—78 °C (from hexane) (Found: C, 58.0; H, 6.7; N, 4.55. $C_{15}H_{21}NOSe$ requires C, 58.1; H, 6.8; N, 4.5%); $\nu_{max.}$ (KBr disc) 3 250, 1 669, 1 652, 1 620, 1 560, 737, and 691 cm^{-1}; δ_H (100

MHz) 0.84 (3 H, t, *J* 7 Hz), 1.1—1.4 (4 H, m), 1.4—1.8 (2 H, m), 3.15 (2 H, d, *J* 5.4 Hz), 4.1—4.4 (1 H, m), 5.57 (1 H, dd, *J* 9.8 and 2.4 Hz), 5.71 (1 H, br s), 5.95 (1 H, dd, *J* 16.6 and 9.8 Hz), 6.20 (1 H, dd, *J* 16.6 and 2.4 Hz), 7.1—7.3 (3 H, m), and 7.3—7.6 (2 H, m).

The Reaction of (**3b**) *with Hydrogen Chloride.*—Dry hydrogen chloride was introduced into a solution of (**3b**) (0.15 g, 0.5 mmol) in acetonitrile (15 ml) until saturation, and the resulting solution was stirred at ambient temperature for 24 h. After work up as described above, column chromatography on silica gel with hexane–ethyl acetate (1:1) as eluant afforded 1-(3-*chloropropanamido*)-2-(*phenylseleno*)*cyclohexane* (**4**) (0.12 g, 0.35 mmol, 70%) and a mixture of (**4**) and (**3b**) (0.02 g); (**4**), white needles, m.p. 88.5—89 °C [from hexane–ethyl acetate (10:1)] (Found: C, 52.3; H, 5.7; N, 4.1. $C_{15}H_{20}ClNOSe$ requires C, 52.3; H, 5.85; N, 4.1%); $\nu_{max.}$ (KBr disc) 3 330, 1 640, 1 543, 752, and 700 cm^{-1}; δ_H (400 MHz) 1.2—1.4 (3 H, m), 1.45—1.6 (1 H, m), 1.65—1.75 (2 H, m), 2.1—2.25 (2 H, m), 2.51 (1 H, ddd, *J* 15.1, 7.6, and 6.4 Hz), 2.57 (1 H, dt, *J* 15.1 and 6.4 Hz), 3.04 (1 H, dt, *J* 3.9 and 11.2 Hz), 3.76 (1 H, dt, *J* 11.2 and 6.4 Hz), 3.8—3.9 (2 H, m), 5.72 (1 H, br s), 7.25—7.35 (3 H, m), and 7.55—7.6 (2 H, m).

Preparation of trans-1-(*Chloroacetamido*)-2-(*phenylseleno*)*cyclohexane* (**6b**; R = $ClCH_2$): *General Procedure.*—To a stirred solution of 2-hydroxycyclohexyl phenyl selenide (**1b**) (0.51 g, 2.0 mmol) and chloroacetonitrile (0.77 g, 10 mmol) in dichloromethane (2 ml) was added a 1:1 (molar ratio) mixture of trifluoromethanesulphonic acid–water (0.34 g, 2.0 mmol) and the resulting yellow solution was stirred at ambient temperature for 3 h. Dichloromethane (20 ml) was added and the solution was washed with saturated aqueous sodium hydrogen carbonate (30 ml). The washing was extracted once with dichloromethane (20 ml) and the combined organic layers were washed with brine, dried, and evaporated to leave a pale yellow oil. Column chromatography on silica gel with hexane–ethyl acetate (2:1) as eluant yielded (**6b**; R = $ClCH_2$) (0.65 g, 1.98 mmol, 99%); white needles, m.p. 86—86.5 °C (from hexane) (Found: C, 50.6; H, 5.4; N, 4.15. $C_{14}H_{18}ClNOSe$ requires C, 50.8; H, 5.5; N, 4.2%); $\nu_{max.}$ (KBr disc) 3 310, 1 660, 1 544, 751, and 698 cm^{-1}; δ_H (400 MHz) 1.2—1.4 (3 H, m), 1.55 (1 H, ddt, *J* 13.7, 3.4, and 11.7 Hz), 1.65—1.75 (2 H, m), 2.1—2.25 (2 H, m), 3.07 (1 H, dt, *J* 3.9 and 10.7 Hz), 3.82 (1 H, ddt, *J* 8.3, 3.9, and 10.7 Hz), 3.98 (2 H, s), 6.59 (1 H, br d, *J* 8.3 Hz), 7.25—7.3 (3 H, m), and 7.55—7.6 (2 H, m).

Spectral as well as combustion analytical data of other β-(halogenoacetamido)alkyl phenyl selenides are as follows.

trans-1-(*Chloroacetamido*)-2-(*phenylseleno*)*cyclopentane* (**6a**; R = $ClCH_2$); pale orange semisolid (Found: C, 49.45; H, 5.1; N, 4.3. $C_{13}H_{16}ClNOSe$ requires C, 49.3; H, 5.1; N, 4.4%); $\nu_{max.}$ (KBr disc) 3 320, 1 645, 1 528, 740, and 696 cm^{-1}; δ_H (400 MHz) 1.49 (1 H, ddd, *J* 9.0; 7.6, and 2.7 Hz), 1.7—1.8 (3 H, m), 2.15—2.25 (2 H, m), 3.36 (1 H, q, *J* 7.8 Hz), 3.91 (1 H, d, *J* 15.1 Hz), 3.94 (1 H, d, *J* 15.1 Hz), 4.19 (1 H, quint, *J* 7.8 Hz), 6.43 (1 H, br s), 7.2—7.3 (3 H, m), and 7.55—7.65 (2 H, m).

trans-1-(*Bromoacetamido*)-2-(*phenylseleno*)*cyclohexane* (**6b**; R = $BrCH_2$); white needles, m.p. 84.5—86 °C (from hexane) (Found: C, 45.0; H, 4.8; N, 3.6. $C_{14}H_{18}BrNOSe$ requires C, 44.8; H, 4.8; N, 3.7%); $\nu_{max.}$ (KBr disc) 3 280, 1 653, 1 537, 752, and 697 cm^{-1}; δ_H (100 MHz) 1.0—1.9 (6 H, m), 2.0—2.4 (2 H, m), 3.06 (1 H, dt, *J* 3.9 and 10.7 Hz), 3.6—4.0 (1 H, m), 3.81 (2 H, s), 6.4—6.6 (1 H, m), 7.2—7.4 (3 H, m), and 7.5—7.7 (2 H, m).

trans-1-(3-*Bromopropanamido*)-2-(*phenylseleno*)*cyclohexane* (**6b**; R = $BrCH_2CH_2$); white needles, m.p. 83—84 °C (from hexane) (Found: C, 46.5; H, 5.2; N, 3.6. $C_{15}H_{20}BrNOSe$ requires C, 46.3; H, 5.2; N, 3.6%); $\nu_{max.}$ (KBr disc) 3 310, 1 650, 1 540, 752, and 698 cm^{-1}; δ_H (400 MHz) 1.15—1.4 (3 H, m), 1.45—1.6 (1 H, m), 1.65—1.8 (2 H, m), 2.1—2.25 (2 H, m), 2.61 (1 H, ddd, *J* 15.2, 7.4, and 6.4 Hz), 2.69 (1 H, dt, *J* 15.2 and 6.4 Hz), 3.04 (1 H, dt, *J* 3.9 and 10.7 Hz), 3.60 (1 H, dt, *J* 10.3 and 6.4 Hz), 3.64 (1 H, ddd, *J* 10.3, 7.4, and 6.4 Hz), 3.83 (1 H, ddt, *J* 7.8, 3.9, and 10.7 Hz), 5.62 (1 H, d, *J* 7.8 Hz), 7.25—7.35 (3 H, m), and 7.55—7.60 (2 H, m).

trans-1-(*Chloroacetamido*)-2-(*phenylseleno*)*cycloheptane* (**6c**); white needles, m.p. 87—88 °C (from hexane) (Found: C, 52.3; H, 5.8; N, 4.1. $C_{15}H_{20}ClNOSe$ requires C, 52.3; H, 5.85; N, 4.1%); $\nu_{max.}$ (KBr disc) 3 300, 1 643, 1 542, 750, and 698 cm^{-1}; δ_H (400 MHz) 1.4—1.65 (4 H, m), 1.65—1.8 (3 H, m), 1.8—1.9 (1 H, m), 1.9—2.0 (1 H, m), 2.08—2.17 (1 H, m), 3.28 (1 H, dt, *J* 3.4 and 8.8 Hz), 3.97 (2 H, s), 4.10 (1 H, dq, *J* 3.4 and 8.8 Hz), 6.70 (1 H, br d, *J* 7.8 Hz), 7.2—7.3 (3 H, m), and 7.5—7.6 (2 H, m).

trans-1-(*Chloroacetamido*)-2-(*phenylseleno*)*cyclo-octane* (**6d**); white needles, m.p. 91—92 °C (from hexane) (Found: C, 53.5; H, 6.1; N, 4.0. $C_{16}H_{22}ClNOSe$ requires C, 53.6; H, 6.2; N, 3.9%); $\nu_{max.}$ (KBr disc) 3 320, 1 648, 1 538, 749, and 700 cm^{-1}; δ_H (400 MHz) 1.4—1.55 (3 H, m), 1.55—1.75 (4 H, m), 1.75—1.95 (4 H, m), 2.21 (1 H, dddd, *J* 15.1, 8.8, 3.4, and 2.4 Hz), 3.41 (1 H, ddd, 10.7, 7.3, and 2.4 Hz), 3.93 (2 H, s), 4.17 (1 H, dddd, *J* 10.7, 7.8, 7.3, and 2.4 Hz), 6.66 (1 H, br d, *J* 7.3 Hz), 7.2—7.3 (3 H, m), and 7.5—7.6 (2 H, m).

threo-2-(*Chloroacetamido*)-3-(*phenylseleno*)*butane* (**7a**); white needles, m.p. 68—69 °C (from hexane) (Found: C, 47.6; H, 5.35; N, 4.6. $C_{12}H_{16}ClNOSe$ requires C, 47.3; H, 5.3; N, 4.6%); $\nu_{max.}$ (KBr disc) 3 270, 1 657, 1 558, 742, and 693 cm^{-1}; δ_H (400 MHz), 1.23 (3 H, d, *J* 6.8 Hz), 1.40 (3 H, d, *J* 6.8 Hz), 3.50 (1 H, dq, *J* 3.9 and 6.8 Hz), 4.03 (2 H, s), 4.21 (1 H, ddq, *J* 8.8, 3.9, and 6.8 Hz), 6.65—6.75 (1 H, m), 7.25—7.35 (3 H, m), and 7.55—7.65 (2 H, m).

erythro-2-(*Chloroacetamido*)-3-(*phenylseleno*)*butane* (**7b**); white needles, m.p. 45.5—46.5 °C (from hexane) (Found: C, 47.2; H, 5.2; N, 4.6. $C_{12}H_{16}ClNOSe$ requires C, 47.3; H, 5.3; N, 4.6%); $\nu_{max.}$ (KBr disc) 3 355, 1 676, 1 541, 753, and 707 cm^{-1}; δ_H (400 MHz) 1.23 (3 H, d, *J* 6.8 Hz), 1.51 (3 H, d, *J* 7.3 Hz), 3.53 (1 H, dq, *J* 3.7 and 7.3 Hz), 3.76 (1 H, d, *J* 15.1 Hz), 3.91 (1 H, d, *J* 15.1 Hz), 4.16 (1 H, ddq, *J* 8.5, 3.7, and 6.8 Hz), 6.75—6.85 (1 H, m), 7.2—7.3 (3 H, m), and 7.5—7.6 (2 H, m).

2-(*Chloroacetamido*)-1-(*phenylseleno*)*hexane* (**7c**); white needles, m.p. 58—59 °C (from hexane) (Found: C, 50.6; H, 6.0; N, 4.1. $C_{14}H_{20}ClNOSe$ requires C, 50.5; H, 6.1; N, 4.2%); $\nu_{max.}$ (KBr disc) 3 195, 1 665, 1 540, 735, and 688 cm^{-1}; δ_H (400 MHz) 0.87 (3 H, t, *J* 6.8 Hz), 1.2—1.35 (4 H, m), 1.5—1.7 (2 H, m), 3.13 (1 H, dd, *J* 13.2 and 4.9 Hz), 3.15 (1 H, dd, *J* 13.2 and 4.9 Hz), 3.82 (1 H, d, *J* 15.1 Hz), 3.93 (1 H, d, *J* 15.1 Hz), 4.17 (1 H, dtt, *J* 8.3, 5.4, and 4.8 Hz), 6.56 (1 H, d, *J* 8.3 Hz), 7.2—7.3 (3 H, m), and 7.5—7.6 (2 H, m).

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