

Stereo- and Chemo-Selectivity in Reduction of α -[Phenyl(or Methyl)seleno]alkyl Aryl Ketones with Metal Hydrides

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Metal hydride reduction of a variety of α -[phenyl(or methyl)seleno]alkyl aryl ketones gives a mixture of *threo*- and *erythro*- β -aryl- β -hydroxyalkyl phenyl(or methyl)selenides by carbonyl reduction and 1-aryl-1-alkanol by the substitution of a phenyl(or methyl)seleno group with hydrogen. With all metal hydrides examined the formation of the *threo*-isomer always predominated. The addition of various metal chlorides in the reduction system did not affect the diastereoselectivity much, in a sharp contrast to the so-far known reduction of various α -heteroatom (N, P, O, S)-substituted ketones.

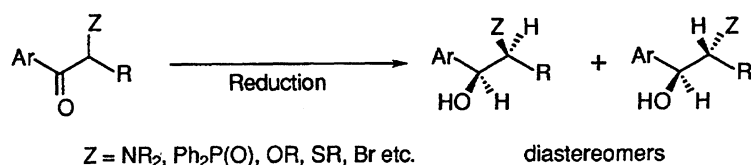
Studies on the diastereoselectivity in the metal hydride reduction of α -heteroatom-substituted acyclic ketones are of current interest.¹⁾ The usual *threo*-rich alcohol formation shifted to *erythro*-rich one by the use of $\text{Zn}(\text{BH}_4)_2$ or by addition of various metal halides, due to chelation of the metal between a heteroatom and a carbonyl oxygen. So-far studied heteroatoms (Z) are nitrogen (NR_2 , NHR , triazolyl etc.),¹⁾ phosphorus ($\text{Ph}_2\text{P}(\text{O})$ etc.),¹⁾ oxygen (OH , OR , OSiR_3 , epoxide etc.),^{2–4)} sulfur (SR , $\text{S}(\text{O})\text{R}$, $\text{S}(\text{O})_2\text{R}$ etc.),^{5,6)} and bromine⁷⁾ (Scheme 1). Recently, one of us reported that the reduction of 1-(biphenyl-4-yl)-2-phenylseleno-1-propanone with some reducing agents produced the corresponding 2-phenylseleno-1-propanol as the intermediate for the pharmaceutically important 2-arylpropanoic acids; the alcohol consisted of a *threo*-rich diastereomeric mixture.⁸⁾ Since there are no detailed and general data available on the diastereoselectivity of the reduction of α -selenium-substituted ketones,⁹⁾ we studied the metal hydride reduction in detail using various α -[phenyl(or methyl)seleno]propiophenones as substrates.

Results and Discussion

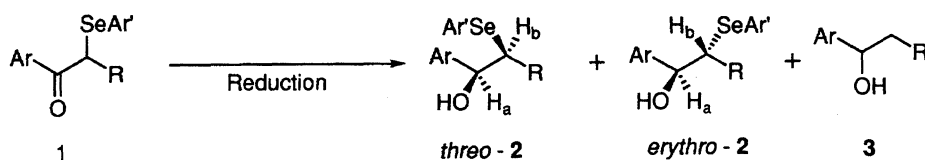
The α -(phenylseleno)alkyl aryl ketones (**1a–1g**) were prepared by treatment of alkyl aryl ketones with benzeneselenenyl chloride in ethyl acetate in 40–84% isolated yields by the reported method.¹⁰⁾ The α -(methylseleno)propiophenone (**1h**) was prepared by treatment of α -lithiopropiophenone with methaneselenenyl bromide in 62% isolated yield (See Experimental). Reduction of **1** with various metal hydrides afforded a mixture of *threo*- and *erythro*- β -aryl- β -hydroxyalkyl phenyl (or methyl) selenides (**2**) and 1-aryl-1-alkanol (**3**) (Scheme 2; Table 1). The diastereoselectivity of **2** was determined either by their stereospe-

cific transformation to 1-aryl-1-propenes (*threo*→*cis*, *erythro*→*trans*) according to a literature method¹¹⁾ or directly by ¹H NMR; results from the two methods were consistent. Direct determination by ¹H NMR showed the smaller (3.29–3.57 Hz) and larger (8.24–8.79 Hz) coupling constant ($J_{\text{Ha-Hb}}$) in **2**; these can be assigned to *erythro*- and *threo*-alcohol, respectively, as has been generally accepted in similar sulfur compounds.^{5,12)} In all cases, the *threo*-isomer was produced predominantly. With $\text{Zn}(\text{BH}_4)_2$, the proportion of the *erythro*-isomer increased, and yet the *threo*-isomer is major, in contrast to the reduction of α -thio ketones with $\text{Zn}(\text{BH}_4)_2$, where the *erythro*-isomer became major.⁵⁾ In the $\text{Zn}(\text{BH}_4)_2$ reduction of α -thio ketones⁵⁾ and the Bu_2SnClH reduction of α -hydroxy ketones,^{4a)} diastereoselectivity depended much on the bulkiness of α -heteroatom-substituent, a smaller one favoring the formation of *erythro*-isomer. However, in our case, almost no change was observed in *threo*-rich diastereoselectivity with **1a–1g**(PhSe) and **1h**(MeSe). The compound **3**, produced by substitution of a phenyl(or methyl)seleno group by a hydrogen, is always present as a side product, except the case of K-selectride (KBHBu^s_3) where **3** became the sole or main product. In order to know whether K-selectride works as a general deselenizing reagent,¹³⁾ we attempted deselenation of 1-(phenylseleno)dodecane and 2-(phenylseleno)octane, prepared separately,¹⁴⁾ with K-selectride. Deselenation, however, did not occur at all, showing that the replacement with K-selectride is very substrate-dependent.

Since it has been reported¹⁾ that, in the reduction of various α -heteroatom-substituted ketones, the diastereoselectivity changed enormously by addition of some metal chlorides via chelation with a heteroatom and a carbonyl oxygen, we carried out the NaBH_4



Scheme 1.



	Ar	R	Ar'
a:	Ph	Me	Ph
b:	Ph	Et	Ph
c:	Ph	Pr ⁿ	Ph
d:	4-MeC ₆ H ₄	Me	Ph
e:	4-PhC ₆ H ₄	Me	Ph
f:	4-MeOC ₆ H ₄	Me	Ph
g:	4-FC ₆ H ₄	Me	Ph
h:	Ph	Me	Me

Scheme 2.

Table 1. Reduction of α -Seleno Ketones with Various Reagents^{a)}

Ketone	Reducing agent	Solvent	Temp	Time	Products and GLC yield /%		
			°C	h	2	(<i>threo</i> : <i>erythro</i>) ^{b)}	3
1a	NaBH ₄	MeOH	0	1	62	(86 : 14)	23
1a^{c)}	NaBH ₄	MeOH	0	1	41	(91 : 9)	30
1a^{d)}	NaBH ₄	MeOH	0	1	78	(87 : 13)	14
1a	NaBH ₄	MeOH	-78	1	66	(99 : 1)	18
1a	LiAlH ₄	Et ₂ O	0	2	82	(87 : 13)	7
1a	KBHBU ^s ₃	THF	0	3	Trace		88
1a	Bu ⁱ ₂ AlH	THF	-78→0	24	79	(85 : 15)	10
1a	Zn(BH ₄) ₂	Et ₂ O	0	24	87	(78 : 22)	5
1a	Bu ₂ SnHCl	THF	0	5	10	(100 : 0)	0 ^{e,f)}
1a^{g)}	Bu ₂ SnHCl	THF	0	5	5	(100 : 0)	0 ^{h,i)}
1a^{j)}	Ph ₂ SiH ₂	Et ₂ O	25	15	0		0 ^{k,l)}
1b	LiAlH ₄	Et ₂ O	0	2	89	(93 : 7)	8
1b	NaBH ₄	MeOH	0	1	79	(87 : 13)	17
1c^{d)}	NaBH ₄	MeOH	0	1	76	(86 : 14)	10
1c	Zn(BH ₄) ₂	Et ₂ O	0	24	85	(76 : 24)	Trace
1d	KBHBU ^s ₃	THF	0	3	16 ^{m)}	(96 : 4)	45 ^{m)}
1e	NaBH ₄	MeOH	0	1	70 ^{m)}	(92 : 8)	23 ^{m)}
1f	Zn(BH ₄) ₂	Et ₂ O	0	24	61 ^{m)}	(69 : 31)	13 ^{m)}
1g	LiAlH ₄	Et ₂ O	0	2	85 ^{m)}	(90 : 10)	14 ^{m)}
1h	NaBH ₄	MeOH	0	1	14	(100 : 0)	61
1h^{c)}	NaBH ₄	MeOH	0	1	23	(100 : 0)	56
1h	Zn(BH ₄) ₂	Et ₂ O	0	24	82	(85 : 15)	8

a) Ketone (0.5 mmol), reducing agent (0.7—1.0 mmol), and solvent (3—6 ml) were used. b) Isomer ratio was determined by GLC after stereospecific transformation to alkenes (see Experimental part). c) CaCl₂ (1.0 mmol) was added. d) CeCl₃ (1.0 mmol) was added. e) Recovered **1a**: 32%. f) Other product: propiophenone, 58%. g) *p*-Dinitrobenzene (0.05 mmol) was added. h) Recovered **1a**: 91%. i) Other product: propiophenone, 4%. j) RhCl(PPh₃)₃ (5 mol%) was used as a catalyst. k) Recovered **1a**: 50%. l) Other product: propiophenone, 50%. m) Isolated yield.

reduction in the presence of various metal chlorides, such as CaCl₂, CeCl₃, SmCl₃, NiCl₂·6H₂O, ZnCl₂, and CuCl₂. Thus, a ketone and a metal chloride in MeOH

were stirred for 1 h, and then a MeOH solution of NaBH₄ was added to this mixture. For all metal chlorides examined, the diastereoselectivity did not change

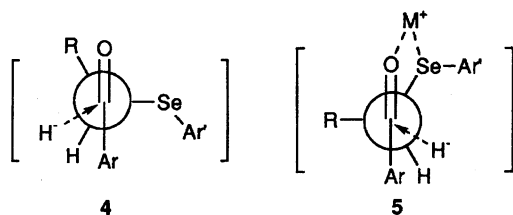


Chart 1.

much (*threo*:*erythro*=83—91:9—17), but was always *threo*-rich. The addition of $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ resulted in a sole formation of **3** (73—85% yield). In the latter case, $\text{Ni}_2\text{B}^{15)}$ which was formed in situ worked as a reducing agent.

As shown in Chart 1, the *threo*-isomer may be formed by a hydride attack from the less hindered site of the more stable conformer **4** of Felkin model.^{1,16)} The conformer **5** is not favored because of the repulsive interaction between a carbonyl group and a bulky phenyl(or methyl)seleno group. Experimental results showed that chelation of various examined metals with a selenium and a carbonyl oxygen (conformer **5**) did not occur appreciably. Unfavorable coordination with those metals is due to the intrinsic nature of a selenium atom.

Experimental

^1H (270 MHz) and ^{13}C (67.8 MHz) NMR spectra were recorded with a JEOL GSX-270 spectrometer on solutions in CDCl_3 ; Me_4Si was used as an internal standard. Chemical shifts are reported in δ units downfield from Me_4Si . GLC analyses were carried out with a Shimadzu GC-14A instrument with flame ionization detectors equipped with a CBP10-S25-050 column (Shimadzu, fused silica capillary column, 0.33 mm $\times$ 25 m, 0.5 μm film thickness) using nitrogen as carrier gas. GLC yields were determined using anthracene as an internal standard. Melting points were determined with a Yanaco MP-S3 micro melting point determination apparatus and were uncorrected. The isolation of pure products was carried out with column chromatography on SiO_2 (Wakogel C-200, 100—200 mesh, Wako Pure Chem. Ind. Ltd.) or with preparative thin-layer chromatography (Kieselgel 60 F₂₅₄, Merck, 20 $\times$ 20 cm silica gel plates).

Commercially available compounds were used without further purification except for the solvent, which was distilled by standard methods before use.

Preparation of α -[Phenyl(or Methyl)seleno]alkyl Aryl Ketones (1a—1h). α -(Phenylseleno)alkyl aryl ketones were prepared by benzeneselenenylation of alkyl aryl ketones according to the literature methods,^{8,10)} while α -(methylseleno)propiophenone (**1h**) was prepared from α -lithiopropiophenone and methaneselenenyl bromide. The compounds **1f**, **1g**, and **1h** are new.

1-Phenyl-2-phenylseleno-1-propanone (1a): A yellow oil, 71% isolated yield; ^1H NMR δ_{H} =1.63 (3H, d, J =6.6 Hz), 4.67 (1H, q, J =6.6 Hz), and 6.9—7.7 (10H, m).

1-Phenyl-2-phenylseleno-1-butanone (1b): A yellow solid, mp 47 °C, 64% isolated yield; ^1H NMR δ_{H} =1.05 (3H, t, J =7.2 Hz), 1.7—2.3 (2H, m), 4.30 (1H, t, J =7.2 Hz), and 7.2—8.0 (10H, m).

1-Phenyl-2-phenylseleno-1-pentanone (1c): A

yellow solid, mp 55 °C, 61% isolated yield; ^1H NMR δ_{H} =0.93 (3H, t, J =7.1 Hz), 1.4—2.1 (4H, m), 4.51 (1H, t, J =7.1 Hz), and 7.2—7.9 (10H, m).

1-(4-Methylphenyl)-2-phenylseleno-1-propanone (1d): A yellow oil, 71% isolated yield; ^1H NMR δ_{H} =1.54 (3H, d, J =6.9 Hz), 2.32 (3H, s), 4.59 (1H, q, J =6.9 Hz), and 7.1—7.8 (9H, m).

1-(Biphenyl-4-yl)-2-phenylseleno-1-propanone (1e): A white solid, (recrystallized from hexane- CHCl_3 (3:1)), mp 123 °C, 84% isolated yield; ^1H NMR δ_{H} =1.67 (3H, d, J =6.9 Hz), 4.72 (1H, q, J =6.9 Hz), and 7.2—8.1 (14H, m).

1-(4-Methoxyphenyl)-2-phenylseleno-1-propanone (1f): A yellow solid, mp 52 °C, 40% isolated yield; ^1H NMR δ_{H} =1.63 (3H, d, J =6.9 Hz), 3.87 (3H, s), 4.66 (1H, q, J =6.9 Hz), and 6.9—7.9 (9H, m); ^{13}C NMR δ_{C} =17.5 (q), 39.6 (d), 55.5 (q), 113.7 (d), 127.3 (s), 128.5 (s), 128.8 (d), 129.0 (d), 130.1 (d), 136.5 (d), 163.4 (s), and 195.3 (s). (Found: C, 60.04; H, 5.13%. Calcd for $\text{C}_{16}\text{H}_{16}\text{O}_2\text{Se}$: C, 60.19; H, 5.05%).

1-(4-Fluorophenyl)-2-phenylseleno-1-propanone (1g): A yellow oil, 64% isolated yield; ^1H NMR δ_{H} =1.64 (3H, d, J =6.9 Hz), 4.63 (1H, q, J =6.9 Hz), and 7.0—7.9 (9H, m); ^{13}C NMR δ_{C} =17.2 (q), 39.6 (d), 115.5 (d, d_{CF} , J_{CF} =21.1 Hz), 126.9 (s), 129.1 (d), 131.0 (d, d_{CF} , J_{CF} =10.0 Hz), 132.2 (s, d_{CF} , J_{CF} =3.7 Hz), 136.6 (d), 165.5 (s, d_{CF} , J_{CF} =25.3 Hz), and 194.8 (s). (Found: C, 58.80; H, 4.24%. Calcd for $\text{C}_{15}\text{H}_{13}\text{FOSe}$: C, 58.64; H, 4.27%).

1-Phenyl-2-methylseleno-1-propanone (1h): To a solution of dimethyl diselenide (496 mg, 2.64 mmol) in benzene (5 ml) was added bromine (422 mg, 2.64 mmol) at 0 °C under N_2 . Separately, propiophenone (690 mg, 5.14 mmol) was dissolved in 5 ml tetrahydrofuran (THF) (distilled on LiAlH_4 under N_2) at -78 °C and a THF solution of lithium diisopropylamide (LDA) (5.09 mmol) was then added slowly at -78 °C; the resulting solution was stirred for 30 min. The above benzene solution of methaneselenenyl bromide was added slowly to this THF solution at -78 °C with a syringe, and then the mixture was warmed up to 0 °C and stirred for 1 h. It was treated with brine (200 ml) and extracted with CH_2Cl_2 (3 $\times$ 50 ml), and then the extract was dried over MgSO_4 . Removal of the solvent under reduced pressure left a yellow residue, which was subjected to column chromatography on SiO_2 (hexane, then 1% EtOAc/hexane), providing **1h** as a yellow oil (720 mg, 3.16 mmol, 62%); ^1H NMR δ_{H} =1.65 (3H, d, J =6.8 Hz), 1.91 (3H, s), 4.46 (1H, q, J =6.8 Hz), 7.40—7.55 (3H, m), and 7.95—7.99 (2H, m); ^{13}C NMR δ_{C} =2.1 (q), 15.9 (q), 33.2 (d), 128.2 (d), 128.4 (d), 132.7 (d), 135.6 (s), and 195.0 (s). (Found: C, 52.56; H, 5.31%. Calcd for $\text{C}_{10}\text{H}_{12}\text{OSe}$: C, 52.87; H, 5.32%).

Reduction of 1 with Various Reducing Agents.

Reduction was carried out as described before. The products were isolated by preparative thin-layer chromatography;⁸⁾ among them, the compounds **2c**, **2f**, and **2g** are new.

***threo*-1-Phenyl-2-phenylseleno-1-propanol (2a):** ^1H NMR δ_{H} =1.21 (3H, d, J =7.1 Hz), 3.21 (1H, d, J =2.2 Hz), 3.41 (1H, dq, J =8.8 and 7.1 Hz), 4.39 (1H, dd, J =8.8 and 2.2 Hz), and 7.2—7.6 (10H, m).

***erythro*-Alcohol (2a):** ^1H NMR δ_{H} =1.24 (3H, d, J =7.2 Hz), 2.68 (1H, bs), 3.63 (1H, qd, J =7.2 and 3.3 Hz), 4.78 (1H, d, J =3.3 Hz), and 7.2—7.6 (10H, m).

1-Phenyl-2-phenylseleno-1-butanol: *threo*-(**2b**), a

yellow oil; $^1\text{H NMR}$ $\delta_{\text{H}}=1.02$ (3H, t, $J=7.1$ Hz), 1.3–1.6 (2H, m), 3.19 (1H, ddd, $J=9.2$, 8.5, and 4.1 Hz), 3.36 (1H, bs), 4.46 (1H, d, $J=8.5$ Hz), and 7.2–7.6 (10H, m).

erythro-(**2b**), a yellow oil; $^1\text{H NMR}$ $\delta_{\text{H}}=1.01$ (3H, t, $J=7.1$ Hz), 1.3–1.6 (2H, m), 2.76 (1H, bs), 3.42 (1H, dt, $J=9.9$ and 3.6 Hz), 4.81 (1H, d, $J=3.6$ Hz), and 7.2–7.6 (10H, m).

1-Phenyl-2-phenylseleno-1-pentanol: *threo*-(**2c**), a yellow oil; $^1\text{H NMR}$ $\delta_{\text{H}}=0.77$ (3H, t, $J=7.1$ Hz), 1.3–1.7 (4H, m), 3.20–3.29 (1H, m), 3.40 (1H, bs), 4.44 (1H, d, $J=8.2$ Hz), and 7.2–7.5 (10H, m); $^{13}\text{C NMR}$ $\delta_{\text{C}}=13.8$ (q), 21.4 (t), 33.9 (t), 58.3 (d), 76.0 (d), 126.1 (s), 127.0 (d), 127.9 (d), 128.0 (d), 128.3 (d), 129.0 (d), 135.6 (d), and 141.3 (s).

erythro-(**2c**), a yellow oil; $^1\text{H NMR}$ $\delta_{\text{H}}=0.77$ (3H, t), 1.3–1.7 (4H, m), 2.76 (1H, bs), 3.47 (1H, m), 4.78 (1H, d, $J=3.1$ Hz), and 7.2–7.5 (10H, m).

Elemental analysis of a mixture of *threo*- and *erythro*-**2c**. Found: C, 63.66; H, 6.34%. Calcd for $\text{C}_{17}\text{H}_{20}\text{OSe}$: C, 63.95; H, 6.31%.

1-(4-Methylphenyl)-2-phenylseleno-1-propanol: *threo*-(**2d**), a yellow oil; $^1\text{H NMR}$ $\delta_{\text{H}}=1.19$ (3H, d, $J=7.2$ Hz), 2.32 (3H, s), 3.17 (1H, bs), 3.40 (1H, dq, $J=8.8$ and 7.2 Hz), 4.36 (1H, d, $J=8.8$ Hz), and 7.1–7.6 (9H, m).

erythro-(**2d**), a yellow oil; $^1\text{H NMR}$ $\delta_{\text{H}}=1.24$ (3H, d, $J=7.2$ Hz), 2.33 (3H, s), 2.65 (1H, bs), 3.60 (1H, qd, $J=7.2$ and 3.3 Hz), 4.74 (1H, d, $J=3.3$ Hz), and 7.1–7.6 (9H, m).

1-(Biphenyl-4-yl)-2-phenylseleno-1-propanol: *threo*-(**2e**), a yellow oil; $^1\text{H NMR}$ $\delta_{\text{H}}=1.26$ (3H, d, $J=7.1$ Hz), 3.24 (1H, bs), 3.45 (1H, dq, $J=8.6$ and 7.1 Hz), 4.44 (1H, d, $J=8.6$ Hz), and 7.2–7.6 (14H, m).

erythro-(**2e**), a yellow oil; $^1\text{H NMR}$ $\delta_{\text{H}}=1.29$ (3H, d, $J=7.1$ Hz), 2.78 (1H, bs), 3.66 (1H, qd, $J=7.1$ and 3.3 Hz), 4.81 (1H, d, $J=3.3$ Hz), and 7.2–7.6 (14H, m).

1-(4-Methoxyphenyl)-2-phenylseleno-1-propanol: *threo*-(**2f**), a yellow oil; $^1\text{H NMR}$ $\delta_{\text{H}}=1.19$ (3H, d, $J=7.1$ Hz), 3.16 (1H, bs), 3.39 (1H, dq, $J=8.8$ and 7.1 Hz), 3.79 (3H, s), 4.36 (1H, d, $J=8.8$ Hz), and 6.8–7.6 (9H, m); $^{13}\text{C NMR}$ $\delta_{\text{C}}=19.2$ (q), 49.4 (d), 55.2 (q), 76.8 (d), 113.7 (d), 126.8 (s), 127.2 (d), 128.0 (d), 129.0 (d), 133.0 (s), 136.0 (d), and 159.4 (s).

erythro-(**2f**), a yellow oil; $^1\text{H NMR}$ $\delta_{\text{H}}=1.26$ (3H, d, $J=7.1$ Hz), 2.59 (1H, bs), 3.59 (1H, qd, $J=7.1$ and 3.6 Hz), 3.80 (3H, s), 4.74 (1H, d, $J=3.6$ Hz), and 6.8–7.6 (9H, m).

Elemental analysis of a mixture of *threo*- and *erythro*-**2f**. Found: C, 59.89; H, 5.62%. Calcd for $\text{C}_{16}\text{H}_{18}\text{O}_2\text{Se}$: C, 59.82; H, 5.65%.

1-(4-Fluorophenyl)-2-phenylseleno-1-propanol: *threo*-(**2g**), a yellow oil; $^1\text{H NMR}$ $\delta_{\text{H}}=1.21$ (3H, d, $J=7.1$ Hz), 3.26 (1H, bs), 3.35 (1H, dq, $J=8.8$ and 7.1 Hz), 4.37 (1H, d, $J=8.8$ Hz), and 6.9–7.6 (9H, m); $^{13}\text{C NMR}$ $\delta_{\text{C}}=19.1$ (q), 49.4 (d), 76.5 (d), 115.2 (d, d_{CF} , $J_{\text{CF}}=21.2$ Hz), 126.4 (s), 128.4 (d, d_{CF} , $J_{\text{CF}}=7.5$ Hz), 128.5 (d), 129.1 (d), 136.1 (d), 136.5 (s, d_{CF} , $J_{\text{CF}}=2.5$ Hz), and 162.4 (s, d_{CF} , $J_{\text{CF}}=246.6$ Hz).

erythro-(**2g**), a yellow oil; $^1\text{H NMR}$ $\delta_{\text{H}}=1.22$ (3H, d, $J=7.1$ Hz), 2.68 (1H, bs), 3.58 (1H, qd, $J=7.1$ and 3.3 Hz), 4.73 (1H, d, $J=3.3$ Hz), and 7.0–7.6 (9H, m).

Elemental analysis of a mixture of *threo*- and *erythro*-**2g**. Found: C, 58.01; H, 4.89%. Calcd for $\text{C}_{15}\text{H}_{15}\text{FOSe}$: C, 58.26; H, 4.89%.

1-Phenyl-2-methylseleno-1-propanol: *threo*-(**2h**),¹⁷⁾ a yellow oil; $^1\text{H NMR}$ $\delta_{\text{H}}=1.28$ (3H, d, $J=7.0$ Hz), 1.91 (3H, s), 2.9–3.1 (2H, m and bs; OH and MeSeCHCH_3), 4.41 (1H, d, $J=8.6$ Hz; PhCH(OH)-), and 7.2–7.6 (5H, m). *erythro*-(**2h**)¹⁷⁾ [obtained as a mixture with *threo*-(**2h**)], $^1\text{H NMR}$ $\delta_{\text{H}}=4.82$ (1H, d, $J=4.2$ Hz; PhCH(OH)-).

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