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

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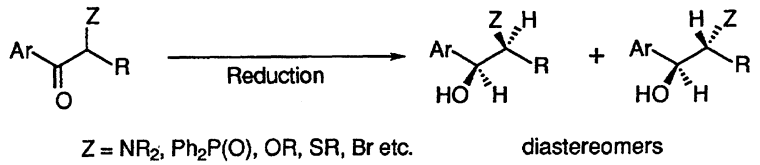
Metal hydride reduction of a variety of α-[phenyl(or methyl)seleno]alkyl aryl ketones gives a mixture of *threo*- and *erythro*-β-aryl-β-hydroxyalkyl phenyl(or methyl)selenides by carbonyl reduction and 1-aryl-1-alkanol by the substitution of a phenyl(or methyl)seleno group with hydrogen. With all metal 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 $Zn(BH_4)_2$ 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 ($Ph_2P(O)$ etc.),[1] oxygen (OH, OR, $OSiR_3$, epoxide etc.),[2—4] sulfur (SR, S(O)R, $S(O)_2R$ etc.),[5,6] and bromine[7] (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.

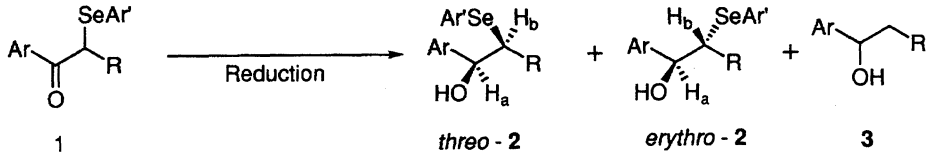
Results and Discussion

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 stereospecific transformation to 1-aryl-1-propenes (*threo*→*cis*, *erythro*→*trans*) according to a literature method[11] or directly by ^{1}H NMR; results from the two methods were consistent. Direct determination by ^{1}H NMR showed the smaller (3.29—3.57 Hz) and larger (8.24—8.79 Hz) coupling constant (J_{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 $Zn(BH_4)_2$, the proportion of the *erythro*-isomer increased, and yet the *threo*-isomer is major, in contrast to the reduction of α-thio ketones with $Zn(BH_4)_2$, where the *erythro*-isomer became major.[5] In the $Zn(BH_4)_2$ reduction of α-thio ketones[5] 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 reported[1] 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_6H_4	Me	Ph
e:	4-PhC_6H_4	Me	Ph
f:	4-$MeOC_6H_4$	Me	Ph
g:	4-FC_6H_4	Me	Ph
h:	Ph	Me	Me

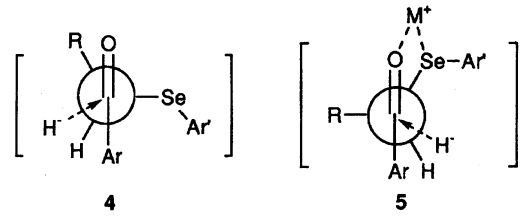
Scheme 2.

Table 1. Reduction of α-Seleno Ketones with Various Reagents[a)]

Ketone	Reducing agent	Solvent	Temp	Time	Products and GLC yield /%		
			°C	h	**2**	(*threo* : *erythro*)[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_2O	0	2	82	(87 : 13)	7
1a	$KBHBu^s{}_3$	THF	0	3	Trace		88
1a	$Bu^i{}_2AlH$	THF	−78→ 0	24	79	(85 : 15)	10
1a	$Zn(BH_4)_2$	Et_2O	0	24	87	(78 : 22)	5
1a	Bu_2SnHCl	THF	0	5	10	(100 : 0)	0[e,f)]
1a[g)]	Bu_2SnHCl	THF	0	5	5	(100 : 0)	0[h,i)]
1a[j)]	Ph_2SiH_2	Et_2O	25	15	0		0[k,l)]
1b	$LiAlH_4$	Et_2O	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_2O	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_2O	0	24	61[m)]	(69 : 31)	13[m)]
1g	$LiAlH_4$	Et_2O	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_2O	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) $CaCl_2$ (1.0 mmol) was added. d) $CeCl_3$ (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 $(PPh_3)_3$ (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 $CaCl_2$, $CeCl_3$, $SmCl_3$, $NiCl_2{\cdot}6H_2O$, $ZnCl_2$, and $CuCl_2$. Thus, a ketone and a metal chloride in MeOH were stirred for 1 h, and then a MeOH solution of $NaBH_4$ was added to this mixture. For all metal chlorides examined, the diastereoselectivity did not change



4 5

Chart 1.

much (*threo*: *erythro*=83—91 : 9—17), but was always *threo*-rich. The addition of $NiCl_2 \cdot 6H_2O$ resulted in a sole formation of **3** (73—85% yield). In the latter case, Ni_2B[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×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 F_{254}, Merck, 20×20 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 $C_{16}H_{16}O_2Se$: 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}=255.3 Hz), and 194.8 (s). (Found: C, 58.80; H, 4.24%. Calcd for $C_{15}H_{13}FOSe$: 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 (3×50 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 $C_{10}H_{12}OSe$: 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}H NMR δ_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}H NMR δ_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}H NMR δ_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}C NMR δ_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}H NMR δ_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 $C_{17}H_{20}OSe$: C, 63.95; H, 6.31%.

1-(4-Methylphenyl)-2-phenylseleno-1-propanol: *threo*-(**2d**), a yellow oil; ^{1}H NMR δ_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}H NMR δ_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}H NMR δ_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}H NMR δ_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}H NMR δ_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}C NMR δ_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}H NMR δ_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 $C_{16}H_{18}O_2Se$: C, 59.82; H, 5.65%.

1-(4-Fluorophenyl)-2-phenylseleno-1-propanol: *threo*-(**2g**), a yellow oil; ^{1}H NMR δ_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}C NMR δ_C=19.1 (q), 49.4 (d), 76.5 (d), 115.2 (d, d_{CF}, J_{CF}=21.2 Hz), 126.4 (s), 128.4 (d, d_{CF}, J_{CF}=7.5 Hz), 128.5 (d), 129.1 (d), 136.1 (d), 136.5 (s, d_{CF}, J_{CF}=2.5 Hz), and 162.4 (s, d_{CF}, J_{CF}=246.6 Hz).

erythro-(**2g**), a yellow oil; ^{1}H NMR δ_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 $C_{15}H_{15}FOSe$: C, 58.26; H, 4.89%.

1-Phenyl-2-methylseleno-1-propanol: *threo*-(**2h**),[17] a yellow oil; ^{1}H NMR δ_H=1.28 (3H, d, J=7.0 Hz), 1.91 (3H, s), 2.9—3.1 (2H, m and bs; O<u>H</u> and MeSeC<u>H</u>CH$_3$), 4.41 (1H, d, J=8.6 Hz; PhC<u>H</u>(OH)–), and 7.2—7.6 (5H, m).

erythro-(**2h**)[17] [obtained as a mixture with *threo*-(**2h**)], ^{1}H NMR δ_H=4.82 (1H, d, J=4.2 Hz; PhC<u>H</u>(OH)–).

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