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Generation of Carbon–Carbon Double Bonds from β-Oxygenated Phenylseleno, Phenylthio, and Iodo Species. A New Use for the Chlorotrimethylsilane–Sodium Iodide Reagent

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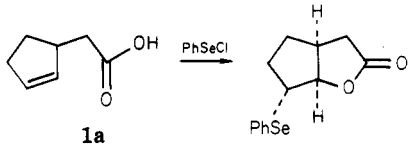
A variety of β-oxygenated selenides, as exemplified by phenylseleno lactones, ethers, and alcohols are converted into olefins by treatment with Me_3SiCl and NaI in MeCN; the reaction is stereospecific and can be extended to iodo and thio species. The conversion of **1**, **3**, and **4** into 2-cyclopentene-1-acetic acid, of **5** into 2-(2-cyclopenten-1-yl)ethanol, and of **9** into (*Z*)-oct-4-ene illustrates the process.

Although synthetic processes based on selenium chemistry have attracted considerable attention,[1] little is known about methods for reversing selenium-based reactions.[2] The transformation of eq 1,[3] for example, is representative



1a **1** (1)

of a large class of cyclofunctionalizations[4] useful for synthesis of lactones,[3] ethers,[4,5] thioethers,[6] and amines.[7] We have found that many of these cyclofunctionalizations can be reversed under mild conditions by the action of Me_3SiCl and NaI in MeCN,[8] so that ring closures such as that shown can be used to protect a double bond and an attached nucleophile.[9]

Each of the compounds listed in the Table I was treated with Me_3SiCl and NaI in MeCN with the results indicated. In a typical experiment, the substrate and NaI were dissolved in anhydrous MeCN under nitrogen to give a solution that was 0.04–0.15 M in substrate. Me_3SiCl was injected and, after the appropriate time (TLC control), the product could be isolated in the yields specified.

Most of our examples are β-oxygenated selenides, which react at room temperature, but the experiments with compounds **3** and **4** establish that the process can be extended to thio and iodo species.[10] The hydroxy selenides **9** and **10** gave the corresponding olefins with little, if any, loss of stereochemistry, and so this reaction differs from that based on lithium–ammonia reduction[2c] in being stereospecific. Hydroxy selenides are available by a variety of carbon–carbon connective routes[1a,11] and so the experiments with **7**–**10** also illustrate a synthesis—as opposed to protection–deprotection—of double bonds.

The compounds we have used are either known compounds or were made (**3**, **4**, **6**, **8**, **9**) according to the general

(1) For reviews of organic selenium chemistry, see: (a) Clive, D. L. J. *Tetrahedron* **1978**, *34*, 1049; (b) *Aldrichimica Acta* **1978**, *11*, 43; (c) Sharpless, K. B.; Gordon, K. M.; Lauer, R. F.; Patrick, D. W.; Singer, S. P.; Young, M. W. *Chem. Scr.* **1975**, *8A*, 9. (d) Reich, H. J. *Acc. Chem. Res.* **1979**, *12*, 22.

(2) (a) Raucher, S.; Koolpe, G. A. *J. Org. Chem.* **1978**, *43*, 3794. (b) Burton, A.; Hevesi, L.; Dumont, W.; Cravador, A.; Krief, A. *Synthesis* **1979**, 877. (c) Nicolaou, K. C.; Sipio, W. J.; Magolda, R. L.; Claremon, D. A. *J. Chem. Soc., Chem. Commun.* **1979**, 83.

(3) (a) Clive, D. L. J.; Chittattu, G. *J. Chem. Soc., Chem. Commun.* **1977**, 484. (b) Clive, D. L. J.; Russell, C. G.; Chittattu, G.; Singh, A. *Tetrahedron* **1980**, *36*, 1399. (c) Full paper: Nicolaou, K. C.; Seitz, S. P.; Sipio, W. J.; Blount, J. F. *J. Am. Chem. Soc.* **1979**, *101*, 3884.

(4) Clive, D. L. J.; Chittattu, G.; Curtis, N. J.; Kiel, W. A.; Wong, C. K. *J. Chem. Soc., Chem. Commun.* **1977**, 725.

(5) (a) Nicolaou, K. C.; Lysenko, Z. *Tetrahedron Lett.* **1977**, 1257. (b) Clive, D. L. J.; Chittattu, G.; Wong, C. K. *Can. J. Chem.* **1977**, *55*, 3894.

(6) Nicolaou, K. C.; Magolda, R. L.; Sipio, W. J.; Barnette, W. E.; Lysenko, Z.; Joullie, M. M. *J. Am. Chem. Soc.* **1980**, *102*, 3784.

(7) Clive, D. L. J.; Farina, V.; Singh, A.; Wong, C. K.; Kiel, W. A.; Menchen, S. M. *J. Org. Chem.* **1980**, *45*, 2120.

(8) Using **1** and **5** as test cases, we found that reaction in CH_2Cl_2 is inconveniently slow. Reaction of **7** with Me_3SiCl and NaCN in refluxing MeCN is also slow [88% (VPC) of 1-decene after 20 h].

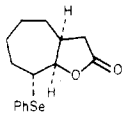
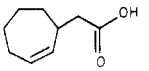
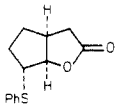
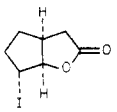
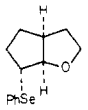
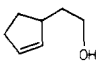
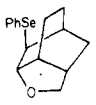
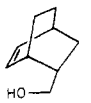
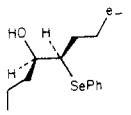
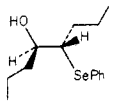
(9) These groups are protected in a manner that also has stereochemical implications.

(10) (a) For methods of reversing iodolactonization, see: Dowle, M. D.; Davies, D. I. *Chem. Soc. Rev.* **1979**, 171. (b) For reaction of epoxides with silicon species, see: Denis, J. N.; Magnane, R.; Van Eenoo, M.; Krief, A. *Nouv. J. Chim.* **1979**, *3*, 705. Detty, M. R. *J. Org. Chem.* **1980**, *45*, 924. Sakurai, H.; Sasaki, K.; Hosomi, A. *Tetrahedron Lett.* **1980**, 2329.

(11) E.g.: Labar, D.; Dumont, W.; Hevesi, L.; Krief, A. *Tetrahedron Lett.* **1978**, 1145.

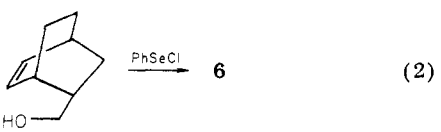
0022-3263/81/1946-0231$01.00/0

Table I[a]

substrate	Me_3SiCl[h]	NaI[h]	t, h	product	yield, %
1	6	6	3	1a	84
 2	4	4	4		83
 3	6	6	17[b]	1a	91[c]
 4	5	5	⩽5	1a	70
 5	2	2	1		75
 6	2	2	1.5		78[d]
$C_8H_{17}CH(OH)C(SePh)H_2$ (7)	2	2	0.3	1-decene	88 (VPC)
$C_9H_{19}C(SePh)HCH_2OH$ (8)	3	3	0.5	1-undecene	83 (VPC)
 9	3.3	3.3	0.67	(Z)-4-octene[f]	>90 (VPC)
 10	2.7	2	0.5	(E)-4-octene[g]	>90 (VPC)

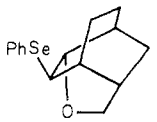
[a] Except where indicated, reactions were run at room temperature, and yields refer to isolated, *distilled* material better than 99% pure as judged by VPC. Isolated products were identified by comparison with authentic samples. Where yields were determined by VPC an internal standard was used, and, in the case of compound 7, a portion of the olefin was isolated and characterized. [b] Reaction run at reflux temperature of MeCN. [c] Better than 98% pure by VPC. [d] Homogeneous by TLC. [e] The 400-MHz NMR spectrum showed ⩽2% erythro isomer. [f] Contains 2% E isomer as judged by VPC analysis on a $AgNO_3$-impregnated column. [g] Contains 1% Z isomer (VPC). [h] Amount given as millimoles per millimole of substrate.

methods described in the Experimental Section. However, some comment is necessary about the preparation (see eq 2) of compound 6. The material isolated (72%) has the



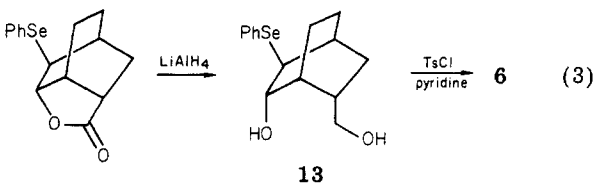
(2)

structure assigned and not the alternative 11. This was



11

established chemically by the experiments summarized in eq 3, the material obtained by the methods of eq 2 and 3 being identical.[12]



(3)

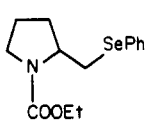
12 13

Of the cases we have studied (cf. Table I) there were two types for which the Me_3SiCl–NaI system is unsuitable.

(12) Lactone 12 is a known substance (see ref 3b); it is recoverable unaltered from boiling toluene but, when treated in boiling toluene with Ph_3SnH, it is converted (see ref 3b) into 4-oxatricyclo[4.3.1.$0^{3,7}$]decan-5-one, which is spectroscopically (e.g., ^{13}C NMR) distinguishable from the isomer 4-oxatricyclo[4.4.0.$0^{3,8}$]decan-5-one.[13]

(13) Davalian, D.; Garratt, P. J.; Riguera, R. *J. Org. Chem.* **1977**, *42*, 368.

The urethane 14[7] appeared (TLC control) to be essentially inert even in refluxing MeCN (32 h),[14] and reaction of the phenol ether 15[4] is not a clean process.



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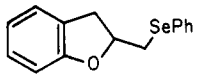

15

The precise nature of the Me_3SiCl–NaI reagent has not been established,[14b,15] and it is appreciated that HI, formed by adventitious hydrolysis, may play a role. Our reaction does work when pyridine is used as the solvent, at least as judged by an experiment with 1, but the process is inefficient (<21% yield after 24 h). Aqueous HI (47% w/v, 5 equiv) in MeCN afforded **1a** in 33% yield after a reaction period of 3.5 h. The yield was 64% when only 2 equiv of HI was used, and we consider the silicon-mediated process to be a better method than deliberate use of strong acid.[16]

Apart from examples **14** and **15**, the reaction with Me_3SiCl–NaI is a general one. It is also efficient and has a predictable stereochemical outcome.

Experimental Section

Except when stated to the contrary, the following particulars apply. Experiments were done with magnetic stirring under a slight static pressure of nitrogen, purified by passage through a column (3.5 × 42 cm) of R-311 catalyst[17] and then through a similar column of Drierite. Inlet and exit needles for nitrogen were passed through a septum on the apparatus, and, after a few minutes (provided no gas was to be generated in the reaction), the exit needle was removed so as to keep the contents of the apparatus under a slight static pressure of nitrogen. Solvents were distilled before use for chromatography. Dry triethylamine, pyridine, and acetonitrile were distilled from CaH_2, dry ether from sodium (benzophenone indicator), and dry ethyl acetate from P_2O_5. Sodium iodide was dried in vacuo. During product isolation, solutions were dried (where necessary) over $MgSO_4$ and evaporated under water-pump vacuum at room temperature. Where compounds were isolated simply by evaporation of their solutions, the residues were kept under oil-pump vacuum and checked for constancy of weight. Isolated products were submitted directly for combustion analysis without the need for additional purification. Yields evaluated by VPC were determined by using an internal standard. Silica gel for column chromatography was Merck type 60 (70–230 mesh). Silica gel for flash chromatography[18] was Merck type 60 (230–400 mesh). Alumina for column chromatography was Camag neutral aluminum oxide of Brockmann activity 3. Commercial TLC plates (Camag DF-B or Merck 60F-254) were used. Mass spectra were run at an ionizing voltage of 70 eV, ^1H NMR spectra at 100 MHz and ^{13}C NMR spectra at 22.628 MHz. Boiling points quoted for products distilled in a Kugelrohr apparatus refer to the oven temperature. The following compounds were prepared by the methods cited: **1**,[3b] **2**,[3b] **5**,[5b] **7**,[19] **10**.[19b]

Typical Procedure for Use of Chlorotrimethylsilane–Sodium Iodide: Conversion of 1 into 2-Cyclopentene-1-acetic Acid. Acetonitrile (20 mL) was injected into a flask containing the lactone **1** (306 mg, 1.09 mmol) and anhydrous NaI (980 mg, 6.54 mmol). The mixture was stirred magnetically for 5 min, and Me_3SiCl (709 mg, 6.52 mmol) was injected. Stirring was continued for 3 h (TLC control), 15% w/v aqueous $Na_2S_2O_3$ (25 mL) was then added, and the mixture was extracted with CH_2Cl_2 (4 × 35 mL), the aqueous phase being saturated with NaCl to crack the resulting emulsion. The organic extract was evaporated, and the residue was dissolved in CH_2Cl_2 (50 mL) and extracted with saturated aqueous $NaHCO_3$ (3 × 20 mL). The aqueous layer was washed with ether (2 × 30 mL), acidified (concentrated HCl), and extracted with CH_2Cl_2 (4 × 35 mL). The extract was dried and evaporated. Kugelrohr distillation of the residue (100–102 °C, 43 mmHg) gave 2-cyclopentene-1-acetic acid (116 mg, 84%) as a colorless liquid of better than 99% purity (VPC) and which was characterized by comparison (VPC, IR, NMR) with an authentic sample.

(3aα,6α,6aα)-Hexahydro-6-(phenylthio)-2*H*-cyclopenta[*b*]furan-2-one (3). Benzenesulfenyl chloride (1.446 g, 9.9 mmol) was injected dropwise into a stirred solution of 2-cyclopentene-1-acetic acid (1.261 g, 10 mmol) in EtOAc (10 mL), and then Et_3N (1.51 g, 14.9 mmol) was added in the same manner. The mixture was stirred overnight and then partitioned between water (50 mL) and ether (150 mL). The organic layer was washed with saturated aqueous Na_2CO_3 (2 × 20 mL). Chromatography over silica gel (45 × 1.5 cm) using 1:9 ethyl acetate–hexane gave **3** (600 mg, 25%) as a homogeneous (TLC, silica gel, 1:9 ethyl acetate–hexane) oil: IR (film) 1772 cm^{-1}; NMR ($CDCl_3$) δ 1.1–3.25 (m, 7 H), 3.69–3.97 (m, 1 H), 4.76 [d (each signal having $W_{1/2}$ = 2.6 Hz), J = 6 Hz, 1 H], 6.8–7.7 (m, 5 H); exact mass, m/e 234.0715 (calcd for $C_{13}H_{14}O_2{}^{32}S$, m/e 234.0715). Anal. Calcd for $C_{13}H_{14}O_2S$: C, 66.64; H, 6.02; S, 13.68. Found: C, 66.50; H, 6.11; S, 13.56. No attempt was made to improve the yield of **3** as a sufficient amount had been made for the present studies, and compounds of the same general class are known[3c] to be available, generally, in good yield.

(3aα,6α,6aα)-Hexahydro-6-iodo-2*H*-cyclopenta[*b*]furan-2-one (4).[20] A solution of iodine (10.1 g, 40 mmol) and KI (20.1 g, 121 mmol) in water (60 mL) was added to a stirred solution of 2-cyclopentene-1-acetic acid (2.5 g, 19.8 mmol) in 0.5 M aqueous $NaHCO_3$ (120 mL). Stirring was continued for 48 h with protection from light. The mixture was decolorized by addition of 15% w/v aqueous $Na_2S_2O_3$ (ca. 20 mL) and extracted with ether (3 × 50 mL). The organic extract was washed successively with 15% w/v aqueous $Na_2S_2O_3$ (30 mL), saturated aqueous Na_2CO_3 (2 × 30 mL), water (2 × 30 mL), and brine (30 mL). It was dried, concentrated, and passed, with ether, through a column (2.5 × 2.5 cm) of alumina. The filtrate was evaporated, and the residue was kept under oil-pump vacuum (protection from light) for 14 h to afford **4** (2.8 g, 56%) as a homogeneous (TLC, silica, 1:3 ethyl acetate–2,2,4-trimethylpentane) oil: IR (film) 1775 cm^{-1}; NMR ($CDCl_3$) δ 1.28–3.4 (m, 6 H), 4.34–4.6 (m, 1 H), 5.18 [d (each signal having $W_{1/2}$ = 2.2 Hz), J = 5.6 Hz, 1 H]; exact mass, m/e 251.9649 (calcd for $C_7H_9O_2I$, m/e 251.9648). Anal. Calcd for $C_7H_9O_2I$: C, 33.36; H, 3.60; I, 50.35; O, 12.70. Found: C, 33.37; H, 3.43; I, 50.65; O, 12.92.

4-Oxa-2-*exo*-(phenylseleno)tricyclo[4.3.1.0^{3,7}]decane (6).[21] Phenylselenenyl chloride (563 mg, 2.94 mmol) in EtOAc (5 mL) was added dropwise over 15 min to a stirred solution of *endo*-2-(hydroxymethyl)bicyclo[2.2.2]oct-5-ene[22] (378 mg, 2.73 mmol) in EtOAc (10 mL). A further portion (5 mL) of EtOAc was used

(14) *cis-N*-Carbethoxy-2-methyl-6-undecylpiperidine also failed to react at a satisfactory rate (~21% conversion after 96 h at reflux): Clive, D. L. J.; Farina, V., unpublished observations. Evidently, ethyl carbamates of secondary amines are not always dealkylated easily. See: (a) Jung, M. E.; Lyster, M. A. *J. Chem. Soc., Chem. Commun.* **1978**, 315; (b) Olah, G. A.; Narang, S. C.; Gupta, B. G. B.; Malhotra, R. *J. Org. Chem.* **1979**, *44*, 1247.

(15) (a) Benkeser, R. A.; Mozdzen, E. C.; Muth, C. L. *J. Org. Chem.* **1979**, *44*, 2185. (b) Morita, T.; Okamoto, Y.; Sakurai, H. *J. Chem. Soc., Chem. Commun.* **1978**, 874. (c) Jung, M. E.; Blumenkopf, T. A. *Tetrahedron Lett.* **1978**, 3657. (d) Olah, G. A.; Narang, S. C.; Gupta, B. G. B. *Synthesis* **1979**, 61. (e) Leading references: Seitz, D. E.; Ferreira, L. *Synth. Commun.* **1979**, *9*, 931.

(16) β-Hydroxy selenides are converted into olefins by the action of strong acid (see ref 1a).

(17) An American supplier of this BASF catalyst is Chemical Dynamics Corp.

(18) Still, W. C.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923.

(19) (a) This known compound [Nicolaou, K. C.; Claremon, D. A.; Barnette, W. E.; Seitz, S. P. *J. Am. Chem. Soc.* **1979**, *101*, 3704] was made from 1,2-epoxydecene by treatment with $PhSe^-$. (b) Sharpless, K. B.; Lauer, R. F. *J. Am. Chem. Soc.* **1973**, *95*, 2697.

(20) Cf.: House, H. O.; Carlson, R. G.; Babad, H. *J. Org. Chem.* **1963**, *28*, 3359.

(21) This is the general method of ref 5b.

(22) (a) Nakazaki, M.; Naemura, K.; Nakahara, S. *J. Org. Chem.* **1978**, *43*, 4745. (b) Whitlock, H. W., Jr.; Siefken, M. W. *J. Am. Chem. Soc.* **1968**, *90*, 4929.

(23) These J values are measured directly from the spectrum by imposing a first-order analysis.

to wash all the phenylselenenyl chloride from the addition syringe into the reaction mixture, and stirring was continued for 24 h. The solution was then evaporated, and chromatography of the residue over silica gel (1.5 × 30 cm) with 1:1.7 ethyl acetate–2,2,4-trimethylpentane gave **6** (580 mg, 72%) as a homogeneous (TLC, silica, 1:4 ethyl acetate–2,2,4-trimethylpentane) oil: NMR (400 MHz, $CDCl_3$) δ 1.0–1.38 (m, 1 H), 1.40–1.49 (br d, J = 13.8 Hz, 1 H), 1.70–1.95 (m, 4 H), 1.95–2.08 (m, 2 H), 2.15–2.25 (m, 1 H), 3.36 (q, J = 3.75, 1.25 Hz, 1 H), 3.49 (d, J = 6.75 Hz,[23] 1 H), 3.74 (q, J = 6.75, 3.5 Hz, 1 H), 4.16 (d, $W_{1/2}$ = 2.5 Hz, J = 5.5 Hz, 1 H), 7.15–7.37 (m, 3 H), 7.45–7.67 (m, 2 H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 15.6, 22.1, 26.9, 34.1, 35.6, 36.0, 51.0, 76.6, 81.4, 126.8, 129.2, 130.4, 132.7; exact mass, m/e 294.0524 [calcd for $C_{15}H_{18}O^{80}Se$, m/e 294.0524]. Anal. Calcd for $C_{15}H_{18}OSe$: C, 61.43; H, 6.19; O, 5.46. Found: C, 61.33; H, 6.21; O, 5.29.

Conversion of 4-Oxa-2-*exo*-(phenylseleno)tricyclo-[4.3.1.0^{3,7}]decan-5-one into 6. The lactone **12**[3b] (215 mg, 0.70 mmol) in ether (15 mL) was injected dropwise over 10 min into a stirred suspension of $LiAlH_4$ (66 mg, 1.74 mmol) in ether (20 mL). A further portion (10 mL) of ether was used as a rinse to complete transfer of all the lactone. After 30 min (TLC control), wet ether and then water were added cautiously to the reaction mixture. Stirring was continued for 10 min, and the mixture was extracted with ether (2 × 50 mL). The extract was washed with water (3 × 30 mL) and brine (30 mL) and then dried. Evaporation afforded the crude diol **13** which was kept 12 h under oil-pump vacuum to remove traces of water: ^{13}C NMR δ 20.1, 26.1, 29.8, 31.2, 36.7, 36.9, 53.8, 65.6, 127.4, 129.1, 134.0; exact mass, m/e 312.0627 (calcd for $C_{15}H_{20}O_2{}^{80}Se$, m/e 312.0628). Anhydrous pyridine (15 mL) was added to the crude diol (200 mg), and the solution was stirred and cooled to −35 °C. *p*-Toluenesulfonyl chloride (147 mg, 0.77 mmol) was added in one lot and stirring was continued at −20 °C for 18 h, then at 0–5 °C for 8 h, and, finally, at room temperature for 5 days. The mixture was diluted with ether (100 mL) and washed with water (3 × 30 mL) and then with brine (2 × 30 mL). The ether solution was dried and evaporated. Flash chromatography of the residue over silica gel (2 × 15 cm) with 1:9 ethyl acetate–hexane gave **6** (100 mg, 52% as a homogeneous (TLC, silica, 1:4 ethyl acetate–2,2,4-trimethylpentane) oil. Comparison of its chromatographic and spectral properties (IR, NMR, ^{13}C NMR, exact mass) with those of material obtained in the previous experiment showed both specimens to have the same structure.

2-(Phenylseleno)undecan-1-ol (8). Phenylselenenyl chloride (1.91 g, 10 mmol) in EtOAc (20 mL) was added from a syringe, with stirring, to undecanal (1.70 g, 10 mmol). A further portion of EtOAc (5 mL) was used as a rinse to transfer all of the phenylselenenyl chloride. Concentrated hydrochloric acid (1 drop) was added to the reaction mixture and stirring was continued for 4 h, by which time the color of the reagent had been discharged. The mixture was diluted with pentane (150 mL) and washed with water (5 × 15 mL) to remove all acid. The pentane layer was dried, and evaporation yielded 2-(phenylseleno)undecanal,[24] which was dissolved in MeOH (20 mL). Sodium borohydride (401 mg, 10.6 mmol) was added in small portions with stirring, and the mixture was immediately extracted with pentane (3 × 50 mL). The organic layer was washed with water (3 × 30 mL), dried, and evaporated. Chromatography of the residue over silica gel (1 × 45 cm) with 1:4 ethyl acetate–2,2,4-trimethylpentane gave **8** (250 mg, 9.8%)[25] as a homogeneous (TLC, silica, 1:4 ethyl acetate–2,2,4-trimethylpentane) oil: NMR ($CDCl_3$) δ 0.62–1.96 (m, 20 H), 3.0–3.8 (m, 3 H), 7.16–7.4 (m, 3 H), 7.4–7.7 (m, 2 H); exact mass, m/e 328.1303 (calcd for $c_{17}H_{28}O^{80}Se$, m/e 328.1305). Anal. Calcd for $C_{17}H_{28}OSe$: C, 62.37; H, 8.62; O, 4.89. Found: C, 62.52; H, 8.71; O, 5.19.

***threo*-5-(Phenylseleno)octan-4-ol (9).** Sodium borohydride (260 mg, 6.87 mmol) was added in portions from a side-arm addition funnel to a stirred solution of diphenyl diselenide (834.6 mg, 2.67 mmol) in absolute EtOH (30 mL). At this stage the reaction mixture was colorless, and (*Z*)-4,5-epoxyoctane[26] (721 mg, 5.62 mmol) was then injected. Stirring at room temperature was continued overnight. The solvent was evaporated and the residue was dissolved in ether (100 mL). The solution was washed with water (2 × 20 mL), dried, and evaporated. Chromatography of the residue over silica gel (1.5 × 60 cm) with 1:4 ethyl acetate–2,2,4-trimethylpentane gave **9** (1.230 g, 80%) as an apparently[27] homogeneous (TLC, silica, 1:9 ethyl acetate–2,2,4-trimethylpentane) oil: NMR (400 MHz, $CDCl_3$) δ 0.78–1.02 (m, 6 H), 1.24–1.82 (m, 9 H), 2.35 (br s, 1 H), 3.06–3.19 (m, 1 H), 3.5–3.62 (m, 1 H), 7.2–7.33 (m, 3 H), 7.5–7.64 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 13.8, 14.0, 19.1, 21.4, 34.7, 37.0, 56.3, 73.1, 127.5, 129.0, 134.8; exact mass, m/e 286.0831 (calcd for $C_{14}H_{22}O^{80}Se$, m/e 286.0836). Anal. Calcd for $C_{14}H_{22}OSe$: C, 58.94; H, 7.77; O, 5.61. Found: C, 58.79; H, 7.88; O, 5.52.

***erythro*-5-(Phenylseleno)octan-4-ol (10).**[19b] This compound had NMR (200 MHz, $CDCl_3$) δ 0.8–1.0 (m, 6 H), 1.4–1.84 (m, 8 H), 2.3 (s, 1 H), 3.23–3.4 (m, 1 H), 3.6–3.72 (m, 1 H), 7.2–7.34 (m, 3 H), 7.52–7.64 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 13.9, 14.0, 19.4, 21.7, 32.6, 35.9, 56.1, 72.7, 127.4, 129.1, 129.5, 134.4.

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Registry No. **1**, 65234-92-6; **1a**, 13668-61-6; **2**, 75250-36-1; **3**, 75600-37-2; **4**, 75658-56-9; **5**, 65539-73-3; **6**, 75600-38-3; **7**, 69814-30-8; **8**, 75600-39-4; **9**, 75600-40-7; **10**, 60221-14-9; **12**, 75250-38-3; **13**, 75600-41-8; benzenesulfenyl chloride, 931-59-9; phenylselenenyl chloride, 5707-04-0; *endo*-2-(hydroxymethyl)bicyclo[2.2.2]oct-5-ene, 15181-03-0; (*Z*)-4,5-epoxyoctane, 1439-06-1; *cis*-*N*-carbethoxy-2-methyl-6-undecylpiperidine, 72845-08-0; 2-cycloheptene-1-acetic acid, 75600-42-9; 2-(2-cyclopentenyl)ethanol, 766-02-9; 1-decene, 872-05-9; 1-undecene, 821-95-4; (*Z*)-4-octene, 7642-15-1; (*E*)-4-octene, 14850-23-8.

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(25) A mixed fraction (200 mg) from the chromatography was not processed further. The phenylselenenylation of aliphatic aldehydes by this route [cf.: Sharpless, K. B.; Lauer, R. F.; Teranishi, A. Y. *J. Am. Chem. Soc.* **1973**, *95*, 6137] sometimes affords poor yields but is very convenient because of its simplicity.

(26) Bissing, D. E.; Speziale, A. J. *J. Am. Chem. Soc.* **1965**, *87*, 2683.

(27) Integration of the region δ 3.2–3.4 in the 400-MHz NMR spectrum revealed the presence of ≤2 mol % erythro isomer.