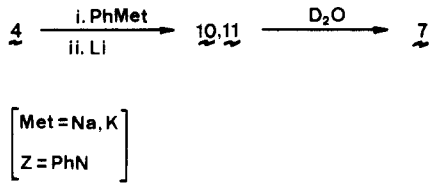
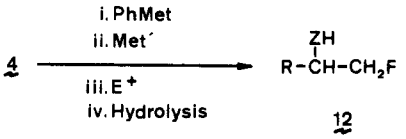
Scheme V



Scheme VI



Met = or ≠ Met' = Li, Na, K
$E^+ = O_2, CO_2$
Z = PhN
R = H, Ph
F = OH, COOH

metal-exchange process to give the more stable β-substituted organolithium compounds[13] **10** and **11** (Scheme IV). (b) The polarity of the Z–Met bond in the β-substituted organoalkali compound is expected to modify the reactivity of the anionic carbon, this being enhanced as the bond becomes more ionic.

In fact, the stability of **10** and **11** decreases in the series Li > Na > K (Scheme V) when **4** (Z = PhN) is treated succesively with a solution of a phenylalkali compound and then with lithium powder at −78 °C. At this temperature, when Met = K, a decomposition of **11** of above a 40% is observed to take place in a period of 8 h. No decomposition of **10** (Met = Na) or of the dilithio dianions[13] is detected under similar conditions.

Dianions **5**, **6**, **8** (**10**), and **9** (**11**) were further characterized upon preparation of a few condensation derivatives **12** by reaction with oxygen and carbon dioxide at low temperature followed by dilute hydrochloric acid hydrolysis (Scheme VI and Table II).

Experimental Section

Preparation and Deuterolysis of 5a. Typical Procedure. To a 250-mL two-necked flask equipped with an argon inlet and a mechanical stirrer were added dry THF (75 mL) and 2-(phenylamino)ethylmercury(II) bromide **4a** (6.0 g, 15 mmol). The resulting solution was cooled to −78 °C, phenylsodium (1.5 g, 15 mmol) was added, and the suspension was stirred for 2 h. The reaction mixture was cooled to −100 °C, then sodium plates (2.07 g, 90 mmol) were added, and the mixture was vigorously stirred. After 30 min deuterium oxide (3 mL) was added and the elemental mercury precipitated was filtered out and weighed (yield 2.55 g, 85%). The resulting solution was neutralized with aqueous hydrochloric acid and extracted with ether and the ether layer washed with water and dried over anhydrous sodium sulfate. Solvents were removed and the residue was distilled under vacuum (15 mmHg) to give the product, yield 1.18 g, 76% relative to Hg precipitated.

Preparation and Deuterolysis of 8a. Typical Procedure. To a 250-mL two-necked flask equipped with an argon inlet and a mechanical stirrer were added dry THF (75 mL) and 2-(phenylamino)ethylmercury(II) bromide **4a** (6.0 g, 15 mmol). The resulting solution was cooled to −78 °C, and a 0.83 N ether solution of phenyllithium (18 mL, 15 mmol) was added in 5 min. Sodium plates (2.07 g, 90 mmol) were added and the mixture was stirred for 2 h. Deuterium oxide (3 mL) was added and the elemental mercury precipitated was filtered out and weighed (yield 2.37 g, 76%). The resulting solution was neutralized with aqueous hydrochloric acid and extracted with ether and the ether layer washed with water and dried over anhydrous sodium sulfate. Solvents were removed and the residue was distilled under vacuum (15 mmHg) to give the product, yield 1.16 g, 80% relative to Hg precipitated.

Reaction of Dianions 5, 6, 8 (10), and 9 (11) with Oxygen and Carbon Dioxide. Obtention of Compounds 12. Dianions **5**, **6**, **8** (**10**), and **9** (**11**) obtained as above described were reacted with a precooled stream of oxygen or solid carbon dioxide, following the procedure previously reported.[14]

Registry No. 4a, 52969-23-0; **4b**, 55552-57-3; **5a**, 76269-88-0; **5b**, 76269-89-1; **6a**, 76269-90-4; **6b**, 76269-91-5; **7a**, 68090-84-6; **7b**, 68090-85-7; **7c**, 68090-86-8; **8a**, 76269-92-6; **8b**, 76269-93-7; **8c**, 76269-94-8; **9a**, 76269-95-9; **9b**, 76269-96-0; **9c**, 76269-97-1; **10a**, 76269-98-2; **10b**, 76269-99-3; **10c**, 76270-00-3; **11a**, 76270-01-4; **11b**, 76270-02-5; **11c**, 76281-99-7; **12a** (F = OH), 122-98-5; **12a** (F = CO_2Et), 62750-11-2; **12b** (F = OH), 13891-02-6; **12b** (F = CO_2Et), 6846-55-5.

Silyl Halides from (Phenylseleno)silanes. Reaction with Oxiranes and Alcohols To Give Hydrolytically Stable Silyl Ethers

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The preparation of (phenylseleno)silanes and their reactions with halogens (Cl_2, Br_2, I_2) to give silyl halides and diphenyl diselenide are described. Highly hindered *tert*-butyldimethyl and *tert*-butyldiphenylsilyl halides were easily prepared. The reaction of silyl bromides and iodides with oxiranes followed by diazabicyclononane treatment gave allylic alcohol silyl ethers. Tertiary alcohols reacted rapidly with silyl iodides to give hydrolytically stable silyl ethers. Treatment of the silyl ethers with tetra-*n*-butylammonium fluoride gave the free alcohols without rearrangement or isomerization.

(Phenylseleno)trimethylsilane (**1**) has emerged as a very useful synthetic reagent for (a) the generation of potassium phenylselenide,[1] (b) the preparation of γ-phenylseleno trimethylsilyl enol ethers,[2,3] *O*-(trimethylsilyl)phenylseleno acetals,[2-4] diseleno acetals,[4] and phenylseleno esters from acid chlorides,[5] (c) the deoxygenation of sulfoxides, selenoxides, and telluroxides,[6] and (d) the in situ preparation of trimethylsilyl iodide.[2] The chemistry and preparation

(1) Detty, M. R. *Tetrahedron Lett.* **1978**, 5087–5090.
(2) Detty, M. R. *Tetrahedron Lett.* **1979**, 4189–4192.
(3) Liotta, D.; Paty, P. B.; Johnston, J.; Zima, G. *Tetrahedron Lett.* **1978**, 5091–5094.
(4) Dumont, W.; Krief, A. *Angew. Chem.* **1977**, *89*, 559–561.
(5) Derkach, N. Y.; Tishchenko, M. P. *Zh. Org. Khim.* **1977**, *13*, 100–103.
(6) Detty, M. R. *J. Org. Chem.* **1979**, *44*, 4528–4531.

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Scheme I

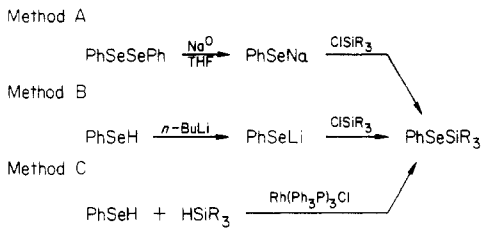


Table I. Preparation of Selenosilanes

compd	method	yield,[a] %	bp (torr) or mp, °C
$PhSeSiMe_3$ (1)	A[b]	68	63-65 (0.9)
	B[c]	63	
	C[d]	55	
$PhSeSiEt_3$ (2)	A	71	81-85 (0.05)
	C	87	
$PhSeSiMe_2$-*t*-Bu (3)	A	63	92-93 (1.2)
	B	62	
$PhSeSiPh_2$-*t*-Bu (4)	A	82	56-58

[a] Isolated yield. [b] Reference 6. [c] Reference 3. [d] Reference 2.

of other (phenylseleno)silanes have not been described. Several general methods are reported herein for the preparation of (phenylseleno)silanes and the reaction of these compounds with halogens to give silyl halides, including silyl bromides and iodides not easily prepared by other procedures. The chemistry of the silyl halides with oxiranes to give allylic alcohols and with alcohols to give silyl ethers is also described. In particular, hydrolytically stable silyl ethers of acid-sensitive allylic and tertiary alcohols are described.

Results and Discussion

Preparation of (Phenylseleno)silanes. The parent (phenylseleno)silane 1 has been prepared by a variety of methods, including the reaction of sodium phenyl selenide[2,7] or lithium phenyl selenide[3] with trimethylsilyl chloride and the oxidative coupling of benzeneselenol and trimethylsilane.[2,8] Reagent 1 has also been prepared by treating benzeneselenol and trimethylsilyl chloride with triethylamine[9] and by treating thallous phenyl selenide with trimethylsilyl chloride.[10]

Although the latter two methods did not work well with other trialkyl- or aryl-substituted silyl chlorides, we used the first three methods (Scheme I) to prepare (phenylseleno)triethylsilane (2), (phenylseleno)-*tert*-butyldimethylsilane (3), and (phenylseleno)-*tert*-butyldiphenylsilane (4). The various methods are compared in Table I.

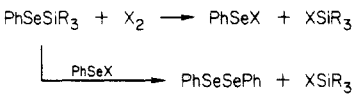
Two trends were apparent as the steric bulk around silicon was increased. The rate of chloride displacement by phenyl selenide anion dramatically decreased, and the hydrolytic stability of the selenosilane increased. Thus 1 reacted quantitatively within seconds at 0 °C with water to give benzeneselenol and hexamethyldisiloxane or with alcohols to give benzeneselenol and trimethylsilyl ethers, but 2 and 3 were hydrolyzed much more slowly by warm water or methanol (50 °C), requiring nearly 1 h for complete hydrolysis. Selenosilane 4 was conveniently recrystallized from warm methanol.

Table II. Preparation of Silyl Halides from Selenosilane and Halogen

compd	yield,[a] %	bp (torr)[f] or mp, °C	lit. bp (torr) or mp, °C
$ClSiMe_3$ (5)	84 (95)	59-61 (atm)	58 (734)[b]
$BrSiMe_3$ (6)	75 (93)	78-80 (atm)	79 (744)[b]
$ISiMe_3$ (7)	98 (96)	103-106 (atm)	106 (734)[b]
$ClSiEt_3$ (8)	96 (96)	144-146 (atm)	144-145[c]
$BrSiEt_3$ (9)	93 (96)	101-105 (125)	78-79 (45)[c]
$ISiEt_3$ (10)	89 (96)	28-31 (0.05)	
$ClSiMe_2$-*t*-Bu (11)	93 (96)	87-89	86-89[d]
$BrSiMe_2$-*t*-Bu (12)	69 (90)	70-79 dec	
$ISiMe_2$-*t*-Bu (13)	53 (93)	53-60 dec	
$ISiPh_2$-*t*-Bu (14)	98 (96)[e]		

[a] Isolated yield; yield of recovered PhSeSePh in parentheses. [b] Reference 12a. [c] Reference 15. [d] Reference 31. [e] Yield of 14 based on ether formed with methanol. [f] Atm indicates atmospheric pressure.

Scheme II

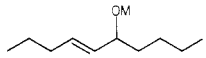
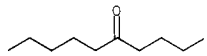
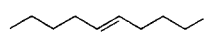
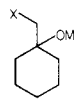


Preparation of Silyl Halides from Selenosilanes. Silyl halides have been prepared by many methods.[11-15] These methods often suffer from low yields and mixtures of products from which the silyl halides are difficult to separate. Recently, acid-free generation of trimethylsilyl iodide from a 1,1-bis(trimethylsilyl)-1,4-dihydrobenzene was described[16] as well as in situ preparations of trimethylsilyl iodide from the silyl chloride and sodium iodide in acetonitrile[17] and from the reaction of hexamethyldisilane with iodine.[17,18] These procedures became impractical with bulkier silyl groups, requiring excessively long reaction times.

We have found that silyl halides can be isolated in excellent yields from the reactions of (phenylseleno)silanes with chlorine, bromine, or iodine (Table II). The byproduct formed in these reactions is diphenyl diselenide,

(7) Miyoshi, N.; Ishii, H.; Kondo, K.; Murai, S.; Sonda, N. *Synthesis* **1979**, 300-301.
(8) Abel, E. W.; Armitage, D. A.; Brady, D. B. *J. Organomet. Chem.* **1966**, *5*, 130-134.
(9) Derkach, N. Y.; Pasmurtseva, N. A.; Levchenko, E. S. *Zh. Org. Khim.* **1971**, *7*, 1543.
(10) Detty, M. R. *J. Org. Chem.* **1980**, *45*, 80-89.
(11) For the direct reaction of halogen with silane, see: Weiderbruch, M.; Peter, W. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 642-643; MacKay, K. M.; Watt, A. E.; Watt, R. *J. Organomet. Chem.* **1968**, *12*, 49-53.
(12) For the reaction of halogen with arylsilanes, see: (a) Pray, B. O.; Sommer, L. H.; Goldberg, G. M.; Kerr, G. J.; DiGiorgio, P. A.; Whitmore, F. C. *J. Am. Chem. Soc.* **1948**, *70*, 433-434; (b) Ho, T.-L.; Olah, G. A. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 774-775.
(13) For the reaction of disiloxanes with aluminum trihalides, see: Schmidbaur, H.; Hussek, H.; Schindler, F. *Chem. Ber.* **1964**, *97*, 255-269.
(14) For the reaction of disiloxanes with halogen and aluminum powder, see: Jung, M. E.; Lyster, M. A. *J. Am. Chem. Soc.* **1977**, *99*, 968-969.
(15) For the reaction of (trialkylamino)silanes with hydrohalic acids, see: Bailey, D. L.; Sommer, L. H.; Whitmore, F. C. *J. Am. Chem. Soc.* **1948**, *70*, 435-436.
(16) Jung, M. E.; Blumenkopf, T. A. *Tetrahedron Lett.* **1978**, 3657-3660.
(17) Olah, G. A.; Narang, S. C.; Gupta, B. G. B.; Malhotra, R. *J. Org. Chem.* **1979**, *44*, 1247-1251.
(18) Sakurai, H.; Shirahata, A.; Sasaki, K.; Hosomi, A. *Synthesis* **1979**, 740-741.

Table III. Conversion of Oxiranes to Allylic Alcohol Silyl Ethers with Silyl Halides and DBN

entry	oxirane	conditions[a]	products (yield, %)[b]
1		13, a, f (48 h)	 (81)
2		14, b, f (27 h)	(78)
3		13, a, f (48 h)	 (90)
4		14, b, f (16 h)	(85)
5		13, a, f (14 h)	 (78)
6		14, b, f (16 h)	(60)
7		13, a, f (12 h)	 (68)
8		14, b, f (12 h)	(75)
9		7, c, f (4 h)	(48)[c]  (7)
10		6, d, f (20 h)	(95)
11		13, a, f (16 h)	 (80)  (2)
12		14, b, f (22 h)	(54) (4)
13		7, c, f (2 h)	(51)[d] (4)  (9)
14		13, a (1 equiv of C_5H_5N)	 (78)
15		14, b (1 equiv of C_5H_5N)	(53)
16		12, e (1 equiv of C_5H_5N)	(48)  (48)
17		13, a, f (2 h)	 (58)  (38) X = I
18		14, b, f (6 h)	(43) (57) X = I
19		12, e, f (16 h)	(31) (69) X = Br
20		13, a, f (1 h)	 (52)  (6)  (23)
21		14, b, f (1 h)	(54) (16) (30)
22		13, a, f (2 h, 25 °C)	 (85)
23		14, b, f (16 h, 25 °C)	(60)

[a] a = CH_3CN, 0 °C, 5 min; b = CH_3CN, 0 °C, 15 min; c = CH_3CN, 0 °C, 5 min; d = CH_3CN, 20 °C, 8 h; e = CH_3CN, 20 °C, 24 h; f = 1.5 equiv of DBN, THF, 65 °C. [b] M = SiR_3. [c] 41% 2-iodocyclooctanol isolated. [d] 10% 6-iodo-5-decanol isolated.

which can be recovered in more than 90% yield and recycled to produce more selenosilane. The reaction of a selenosilane with chlorine was best conducted in a solvent such as carbon tetrachloride or *o*-dichlorobenzene, whereas bromine was added dropwise directly to the selenosilane. Both of these reactions were quite exothermic, and care was exercised during addition. The reaction with iodine was mildly exothermic, allowing iodine to be added directly to the selenosilane in one portion.

As the molecular weight of the silyl halide increased, separation from diphenyl diselenide via sublimation or distillation became more difficult. To avoid the problem of separation, we generated the silyl halides and used them in situ by the addition of halogen to an acetonitrile solution of the selenosilane. Synthetic applications of the in situ generation of silyl halides are described below.

Selenosilanes and halogen presumably react as in Scheme II to give benzeneselenenyl halide and silyl halide. The benzeneselenenyl halide may then react with another molecule of selenosilane to give diphenyl diselenide and silyl halide. The validity of this step of the mechanism was demonstrated by treating 1 with benzeneselenenyl chloride to give diphenyl diselenide and trimethylsilyl chloride and by treating 1 with 1-naphthaleneselenenyl bromide to give phenyl naphthyl diselenide and trimethylsilyl bromide.

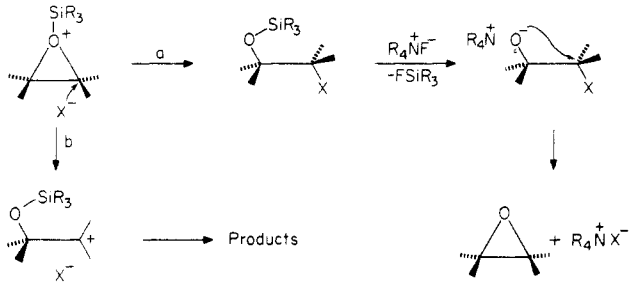
The use of a slight excess of (phenylseleno)silane during the generation of a silyl halide may ensure an acid-free environment, as reagent 1 reacted exothermically with hydrogen chloride gas bubbled into acetonitrile to give benzeneselenol and trimethylsilyl chloride (eq 1). If a similar reaction occurs with other hydrohalic acids, (phenylseleno)silanes would be efficient acid scavengers for acids stronger than benzeneselenol.

$$\underset{\mathbf{1}}{\mathrm{PhSeSiMe_3}} + \mathrm{HCl} \xrightarrow{\mathrm{CH_3CN}} \mathrm{PhSeH} + \underset{\mathbf{5}}{\mathrm{ClSiMe_3}} \quad (1)$$

Reaction of Silyl Halides with Oxiranes To Give Allylic Alcohols.[19] The isomerization of oxiranes to allylic alcohols is a valuable transformation in organic synthesis and has been accomplished by a variety of reagents, including organoselenium compounds,[20] dialkylaluminum amides,[21] dialkylboron trifluoromethanesulfonates,[22] and various dialkylamides.[23] These reagents have their own limitations, including poor yields and failure to react with certain types of oxiranes. Recently, a method was reported for rearranging oxiranes to allylic alcohols with electrophilic ring opening through the use of trimethylsilyl trifluoromethanesulfonate.[24] This me-

(19) For a preliminary report of this work with *tert*-butyldimethylsilyl iodide, see: Detty, M. R. *J. Org. Chem.* **1980**, *45*, 274–276.
(20) Sharpless, K. B.; Lauer, R. F. *J. Am. Chem. Soc.* **1973**, *95*, 2697–2698.
(21) Yasuda, A.; Tanaka, S.; Oshima, K.; Yamamoto, H.; Nozaki, H. *J. Am. Chem. Soc.* **1974**, *96*, 6513–6514. Yamamoto, H.; Nozaki, H. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 169.
(22) Inoue, T.; Uchimara, T.; Mukaiyama, T. *Chem. Lett.* **1977**, 1214.
(23) For example, see the following papers and references cited therein: Whitesell, J. K.; White, P. D. *Synthesis* **1975**, 602; Sheng, M. N.; *Ibid.* **1972**, 194; Kissel, C. L.; Rickborn, B. *J. Org. Chem.* **1972**, *37*, 2060; Rickborn, B.; Thummel, R. P. *Ibid.* **1969**, *34*, 3583; Cope, A. C.; Berchtold, G. A.; Peterson, P. E.; Sharman, S. H. *J. Am. Chem. Soc.* **1960**, *82*, 6370; Corey, E. J.; Marfat, A.; Flack, J. R.; Albright, J. O. *Ibid.* **1980**, *102*, 1433–1435.
(24) Murata, S.; Suzuki, M.; Noyori, R. *J. Am. Chem. Soc.* **1979**, *101*, 2739.

Scheme III



thod fails with cyclooctene oxides and with 2,3-dialkyl- and monoalkyloxiranes.

Silyl bromides **6** and **12** and silyl iodides **7**, **13**, and **14**, in conjunction with 1,5-diazabicyclo[4.3.3]non-5-ene (DBN), reacted with oxiranes to give silylated allylic alcohols in good yields. Silyl chlorides did not effect this transformation. Table III gives examples of the transformation of oxiranes to allylic alcohol silyl ethers.

The isomerization of the oxiranes is initiated apparently by electrophilic attack of silicon on oxygen to give an onium species (Scheme III). This species then undergoes ring-opening displacement by halide to give a trans halohydrin derivative (path a) or cleaves to a tertiary carbenium ion (path b). This ion, in turn, may lose a proton to form the allylic alcohol derivative directly or may trap halide (Scheme III). 2,3-Disubstituted oxiranes (Table III, entries 1–13) gave complete inversion at the carbon undergoing cleavage. The stereochemistry of ring opening was determined by treating the silylated halohydrins with tetra-*n*-butylammonium fluoride in THF to regenerate the starting oxirane. Trisubstituted and 2,2-disubstituted oxiranes gave ring opening preferentially at the more highly substituted carbon, reflecting relative carbenium ion stability. However, the amount of ring opening at the less substituted carbon was slightly increased by using a silyl bromide instead of the silyl iodide (Table III, entries 14–19), perhaps owing to the increased nucleophilicity of bromide relative to iodide in acetonitrile.[25]

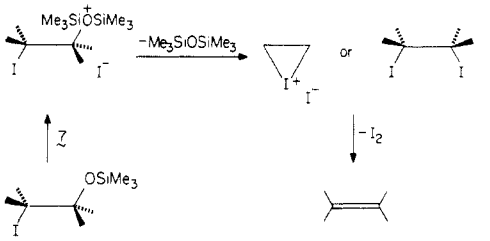
Treatment of the silylated halohydrins with DBN in refluxing THF gave the allylic alcohol silyl ether derivatives. It is interesting to note that very little elimination was observed toward the silyloxy function in 2,3-disubstituted oxiranes. Such elimination complicates the use of trimethylsilyl trifluoromethanesulfonate with 2,3-disubstituted oxiranes.[24]

Addition of DBN to acetonitrile solutions of silylated halohydrins gave the allylic alcohol derivatives directly, but yields were consistently lower than with the two-step procedure described. Treatment of the allylic alcohol silyl ethers with tetra-*n*-butylammonium fluoride in THF gave the free allylic alcohols in nearly quantitative yield.

The present method apparently failed with monosubstituted oxiranes. 2-Butyloxirane upon treatment with **13** opened with preferential cleavage of the less substituted C–O bond to give the 1-iodo derivative, reflecting the ease of nucleophilic attack of iodide on a silylated oxonium intermediate.

The use of trimethylsilyl iodide (**7**) to open the oxirane ring gave substantial amounts of unsilylated iodohydrin and olefin (Table III, entries 9 and 13).[26] The addition of 1 equiv of pyridine did not eliminate the formation of these products, although the relative amount of iodohydrin was reduced.

Scheme IV



The iodohydrin products arise by hydrolysis of the oxirane or silylated iodohydrin by hydriodic acid during reaction or during workup.

The olefinic products may arise as shown in Scheme IV. Attack of a second molecule of **7** on the silylated iodohydrin would give an oxonium species. Loss of hexamethyldisiloxane to give an iodonium species or a vicinal diiodide, followed by loss of iodine, would give olefinic products. Appropriately, small amounts of unreacted oxirane could be recovered from the reaction mixtures when 1 equiv of **7** was used. Alternatively, hydriodic acid could function in the same manner.

The reaction of trimethylsilyl bromide (**6**) with cyclooctene oxide gave, in nearly quantitative yield, the silylated bromohydrin free of isolable amounts of olefinic or alcoholic products. This fact, combined with the smooth elimination of hydrobromic acid with DBN, suggests that **6** is the reagent of choice for forming allylic alcohol trimethylsilyl ethers from oxiranes.[27]

Reaction of Silyl Halides with Alcohols To Give Silyl Ethers. One of the primary functions of silylating agents in synthesis has been the protection of hydroxyl functions. Trimethylsilyl chloride has been the most common reagent, but the trimethylsilyl ether has been of limited value because of extreme reactivity toward acid- and base-catalyzed hydrolysis.[28] Dimethylisopropylsilyl ethers[29,30] and *tert*-butyldimethylsilyl ethers[30,31] are much more stable than trimethylsilyl ethers. However, formation of the ethers from the silyl chloride is sluggish with tertiary and highly hindered secondary alcohols.[32] Similarly, the use of *tert*-butyldiphenylsilyl ethers offers great acid stability,[33] but formation of the ethers from the silyl chloride and tertiary or hindered secondary alcohols is very slow. Silyl perchlorates of *tert*-butyldimethylsilane and di-*tert*-butylmethylsilane have been used to protect tertiary alcohols, but their use introduces the hazards of perchlorate-containing reagents.[32] We have found that *tert*-butyldimethylsilyl iodide (**13**) and *tert*-butyldiphenylsilyl iodide (**14**) react with tertiary alcohols to give silyl ethers that are stable to mild acid and base hydrolysis.

The silyl ethers were prepared at room temperature by treating the alcohol with the silyl iodide (generated in situ)

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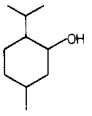
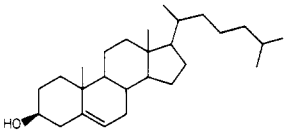
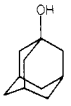
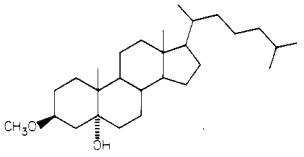
Table IV. Preparation of Silyl Ethers

alcohol	silyl iodide[a]	solvent	reaction time[b]	silyl ether yield,[c] %
$CH_3(CH_2)_{15}OH$	13	CH_3CN/THF	10 min	80
	13	CH_3CN	10 min	96
	13	CH_3CN/THF	10 min	83
Et_3COH	13	CH_3CN	16 h	71
	14	CH_3CN	90 h	77
	13	CH_3CN	16 h	98
	14	CH_3CN	24 h	59
	13	CH_3CN/CH_2Cl_2	16 h	80
	14	CH_3CN/CH_2Cl_2	12 h	65
	13	CH_3CN/CH_2Cl_2	65 h	58

[a] 1.1 equiv of silyl iodide and 2 equiv of pyridine. [b] At 20 °C. [c] Isolated yield; yields are not optimized.

in acetonitrile in the presence of an excess of pyridine. Representative examples of this transformation are listed in Table IV. The silyl ethers of 1-methylcyclohexanol (Table IV) were stable to 1 M sodium methoxide in refluxing methanol, to 1 N hydrochloric acid in refluxing methanol, and to 1/1 (v/v) acetic acid/methanol at reflux. Under more acidic conditions, hydrolysis occurred. The silyl ethers of Table IV were all desilylated with tetra-*n*-butylammonium fluoride in THF[31] to give the free alcohols without elimination or rearrangement.

Silyl bromide **12** reacted rapidly with primary and secondary alcohols but did not react with tertiary alcohols to any appreciable extent after 24 h in refluxing acetonitrile.

No evidence was found for the formation of primary or secondary iodides from the further reaction of the silyl ethers with **13** or **14**.[17,34] However, THF could not be used as a solvent with tertiary alcohols because the longer reaction times allowed ring opening of THF to 4-iodobutylsilyl ethers to become competitive with silyl ether formation from tertiary alcohols.

Conclusions

(Phenylseleno)silanes with various degrees of steric bulk at silicon were easily prepared. These (phenylseleno)silanes reacted with halogens to give silyl halides and diphenyl diselenide, which was recovered and recycled. This technique allowed the high-yield preparation of extremely reactive silyl halides that have not been obtained by other means. The recovery and reuse of diphenyl diselenide lessens the expense associated with the use of selenium reagents. This method of silyl halide preparation avoids contamination by hydrohalic acid.

The silyl halides generated by this procedure were useful for converting oxiranes to allylic alcohols or hydrolytically stable derivatives and for forming hydrolytically stable ethers of alcohols, including tertiary alcohols. The blocking groups were removed with tetra-*n*-butylammonium fluoride without hydrolysis of C–O bonds in the allylic alcohol and tertiary alcohol silyl ethers.

Experimental Section

Melting points were determined on a Thomas-Hoover melting point apparatus and are corrected. Boiling points are uncorrected. ^1H NMR spectra were recorded on a Varian EM 390 instrument. IR spectra were recorded on a Beckman IR 4250 spectrophotometer. Mass spectra were recorded on a Du Pont 21-491 instrument. Microanalyses were performed on a Perkin-Elmer 240 C, H, and N analyzer. Solvents were obtained from Kodak Laboratory Chemicals. Acetonitrile was distilled from phosphorus pentoxide and stored over 3A molecular sieves. Dichloromethane was passed through a column of alumina and stored over 3A molecular sieves. Tetrahydrofuran was distilled from benzophenone ketyl. Pyridine was dried over 3A molecular sieves. Commercially available liquid alcohols were distilled over sodium, and solid alcohols were recrystallized from ligroine/ether. Comercially available oxiranes were distilled. Other oxiranes were prepared by the action of *m*-chloroperbenzoic acid on the corresponding olefin.

Caution. The toxicity of (phenylseleno)silanes is not known. Care should be exercised in their handling.

Preparation of (Phenylseleno)trimethylsilane (2). Method A. Diphenyl diselenide (3.12 g, 10 mmol) in 25 mL of dry THF was added to freshly prepared sodium sand (0.5 g, 22 mmol).[35] The resulting mixture was warmed at reflux for 3 h. Triethylsilyl chloride (3.01 g, 20.2 mmol) was added, and reflux was maintained for 16 h. The reaction mixture was cooled to 0 °C, and 5 mL of methanol was added. The reaction mixture was diluted with 100 mL of ether, washed with several portions of cold water, dried over sodium sulfate, and concentrated. Distillation gave 3.83 g

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(71%) of a pale yellow oil, bp 81–85 °C (0.05 torr).

Method C. A mixture of 0.15 g of tris(triphenylphosphine)-rhodium chloride and 15 mL of triethylsilane was warmed at reflux. Benzeneselenol (4.71 g, 30 mmol) in 5 mL of triethylsilane was added dropwise to the refluxing catalyst slurry, giving an exothermic reaction. As the reaction became less vigorous, 0.15-g portions of catalyst were added. After the addition was complete (~1.5 mol % of catalyst), the reaction mixture was stirred at reflux for 1 h. The catalyst was removed by filtration through Super Celite. Distillation gave 15 mL of triethylsilane and 7.01 g (87%) of **2**: ^{1}H NMR ($CDCl_3$) δ 7.48 (m, 2 H), 7.13 (m, 3 H), 1.1–0.5 (m, 15 H); IR (NaCl, film) 2955, 2876, 1578, 1235, 1070, 1020, 1005, 735, 690 cm^{-1}; mass spectrum, *m/e* 272 ($C_{12}H_{20}SeSi$), 243 (M – C_2H_5).

Anal. Calcd for $C_{12}H_{20}SeSi$: C, 53.1; H, 7.4; Se, 29.1. Found: C, 51.7; H, 7.7; Se, 28.7.

Preparation of (Phenylseleno)-*tert*-butyldimethylsilane (3). Method A. Diphenyl diselenide (15.6 g, 0.05 mol) in 100 mL of dry THF was added to freshly prepared sodium sand (3 g, 0.13 mol).[35] The resulting mixture was warmed at reflux for 4 h. *tert*-Butyldimethylsilyl chloride (15.1 g, 0.1 mol) was added, and the resulting mixture was warmed at reflux for 16 h. Workup as described above and distillation gave 17 g (63%) of a colorless oil, bp 92–93 °C (1.2 torr).

Method B. Benzeneselenol (10.4 g, 0.0662 mol) in 150 mL of dry ether was cooled to 0 °C under argon. *n*-Butyllithium (2.6 M solution, 26 mL, 0.068 mol) was added dropwise, giving a milky white solution. *tert*-Butyldimethylsilyl chloride (10.5 g, 0.0698 mol) in 50 mL of ether was added. The resulting mixture was warmed at reflux for 20 h. The reaction mixture was washed with 100 mL of cold water, dried over sodium sulfate, and concentrated. Distillation gave 11.1 g (62%) of a colorless oil: ^{1}H NMR ($CDCl_3$) δ 7.40 (m, 2 H), 7.10 (m, 3 H), 0.94 (s, 9 H), 0.20 (s, 6 H); IR (NaCl, film) 2950, 2860, 1590, 1480, 1260, 739, 692 cm^{-1}; mass spectrum, *m/e* 272 ($C_{12}H_{20}SeSi$), 215 (M – C_4H_9).

Anal. Calcd for $C_{12}H_{20}SeSi$: C, 53.1; H, 7.4; Se, 29.1. Found: C, 52.7; H, 8.1; Se, 28.6.

Preparation of (Phenylseleno)-*tert*-butyldiphenylsilane (4). Method A. Diphenyl diselenide (15.6 g, 0.05 mol) in 100 mL of dry THF was added to freshly prepared sodium sand (3 g, 0.13 mol).[36] The resulting mixture was warmed at reflux for 3 h. *tert*-Butyldiphenylsilyl chloride (27.5 g, 0.1 mol) was added, and the resulting mixture was warmed at reflux for 20 h. Workup as described above gave a yellow crystalline mass. Recrystallization from methanol gave 32.5 g (82%) of a white solid: mp 56–58 °C; ^{1}H NMR ($CDCl_3$) δ 7.64 (m, 4 H, Ph_2Si), 7.29 (m, 6 H, Ph_2Si), 6.98 (m, 5 H, PhSe), 1.14 (s, 9 H); IR (KBr) 3038, 2910, 2840, 1563, 805, 720, 660 cm^{-1}; mass spectrum, *m/e* 396 ($C_{22}H_{24}SeSi$).

Anal. Calcd for $C_{22}H_{24}SeSi$: C, 66.8; H, 6.1; Se, 20.0. Found: C, 66.6; H, 6.2; Se, 20.3.

Preparation of Trimethylsilyl Chloride (5). (Phenylseleno)trimethylsilane (1; 10 g, 0.0437 mol) was placed in an argon-flushed flask and cooled to 0 °C. Chlorine (1 equiv, 3.1 g, 0.0437 mol) dissolved in *o*-dichlorobenzene was added, giving an exothermic reaction. After the mixture was stirred for 10 min, distillation gave 3.99 g (84%) of trimethylsilyl chloride, bp 59–61 °C. The solvent was distilled at reduced pressure. The pot residue was recrystallized from methanol to give 6.48 g (95%) of diphenyl diselenide, mp 60–62 °C.

Preparation of Trimethylsilyl Bromide (6). Bromine (3.2 g, 0.02 mol) was added dropwise (extremely vigorous reaction) to selenosilane 1 (9.16 g, 0.04 mol) in an argon-flushed flask cooled to 0 °C. The reaction mixture was distilled to give 4.57 g (75%) of **6** as a colorless oil, bp 78–80 °C. The pot residue was recrystallized from methanol to give 5.8 g (93%) of diphenyl diselenide, mp 60–62 °C.

Preparation of Trimethylsilyl Iodide (7). Iodine (5.82 g, 0.023 mol) was added in one portion to selenosilane 1 (10.5 g, 0.0459 mol) in an argon-flushed flask, giving a mildly exothermic reaction. Distillation gave 9 g (98%) of **7** as a colorless oil (bp 103–106 °C) which was stored at 0 °C over copper wire. Recrystallization of the pot residue from methanol gave 6.87 g (96%) of diphenyl diselenide, mp 60–62 °C.

Preparation of Triethylsilyl Chloride (8). A 2.5-mL sample of 1 M chlorine (0.18 g, 2.5 mmol) in carbon tetrachloride was added slowly to selenosilane **2** (1.36 g, 5 mmol; vigorous reaction). Distillation gave 0.72 g (96%) of **8** as a colorless oil, bp 144–146 °C. Recrystallization of the pot residue from methanol gave 0.75 g (96%) of diphenyl diselenide, mp 60–62 °C.

Preparation of Triethylsilyl Bromide (9). Bromine (2.4 g, 0.015 mol) was added dropwise (vigorous reaction) to selenosilane **2** (8.1 g, 0.03 mol) in an argon-flushed flask cooled to 0 °C. Distillation gave 5.5 g (93%) of **9** as a pink oil: bp 101–105 °C (125 torr); ^{1}H NMR ($CDCl_3$) δ 1.0 (m, 15 H). Recrystallization of the pot residue from methanol gave 4.5 g (96%) of diphenyl diselenide, mp 61–62 °C.

Preparation of Triethylsilyl Iodide (10). Iodine (0.38 g, 1.5 mmol) was added in one portion to selenosilane **2** (0.81 g, 3 mmol) in an argon-flushed flask, giving a mildly exothermic reaction. Distillation gave 0.65 g (89%) of **10** as a pink oil: bp 28–31 °C (0.05 torr); ^{1}H NMR ($CDCl_3$) δ 1.00 (s). Recrystallization of the pot residue from methanol gave 0.45 g (96%) of diphenyl diselenide.

Preparation of *tert*-Butyldimethylsilyl Chloride (11). A 2.5-mL sample of 1 M chlorine (0.18 g, 2.5 mmol) in carbon tetrachloride was added slowly (exothermic reaction) to selenosilane **3** (1.36 g, 5 mmol) in an argon-flushed flask. Distillation removed solvent. Sublimation (80 °C, 125 torr) gave 0.70 g of **11** (93%) as a white crystalline solid, mp 86–89 °C. Recrystallization of the pot residue from methanol gave 0.75 g (96%) of diphenyl diselenide.

Preparation of *tert*-Butyldimethylsilyl Bromide (12). Selenosilane **3** (2.91 g, 10.7 mmol) was placed in the bottom of a sublimation apparatus under argon. Bromine (0.91 g, 5.7 mmol) was added slowly, giving an exothermic reaction. Sublimation onto a cold finger (80 °C, 25 torr) gave 1.43 g (69%) of a white solid which decomposed quickly to a red oil. The initial white solid had the following: mp 70–79 °C dec; ^{1}H NMR (CD_3CN) δ 0.96 (s, 9 H), 0.47 (s, 6 H); mass spectrum *m/e* 194 ($C_6H_{15}BrSi$).

Preparation of *tert*-Butyldimethylsilyl Iodide (13). Iodine (3.12 g, 0.0123 mol) was added to selenosilane **3** (7 g, 0.0258 mol) under argon at the bottom of a sublimation apparatus. Sublimation (80 °C, 1.2 torr) gave 3.15 g (53%) of **13** as a white solid that turned to a red oil on being allowed to stand. The initial white solid had the following: mp 53–60 °C dec; ^{1}H NMR (CD_3CN) δ 0.97 (s, 9 H), 0.66 (s, 6 H); mass spectrum, *m/e* 242 ($C_6H_{15}ISi$).

Preparation of *tert*-Butyldiphenylsilyl Iodide (14). A sample of selenosilane **4** (3.96 g, 10.0 mmol) was warmed at 60 °C, and iodine (1.27 g, 5.00 mmol) was added, giving an exothermic reaction and loss of the iodine color. No attempt was made to isolate the silyl iodide. Methanol was added. Chromatography of the reaction mixture (silica, 1/10 ether/hexane) gave 1.5 g (96%) of diphenyl diselenide and 2.65 g (98%) of methoxy-*tert*-butyldiphenylsilane: mp 50.5–51.5 °C; ^{1}H NMR ($CDCl_3$) δ 7.60 (m, 4 H), 7.30 (m, 6 H), 3.48 (s, 3 H), 1.04 (s, 9 H); mass spectrum, *m/e* 270 ($C_{17}H_{22}OSi$).

Anal. Calcd for $C_{17}H_{22}OSi$: C, 75.5; H, 8.2. Found: C, 75.3; H, 8.1.

General Procedure for Conversion of Oxiranes to Allylic Alcohols with *tert*-Butyldimethylsilyl Iodide (13) and *tert*-Butyldiphenylsilyl Iodide (14). A. The apparatus was flame dried and flushed with argon before use. The oxirane was dissolved in enough acetonitrile to make a 2 M solution. One equivalent of the silyl iodide **13** or **14** was prepared by adding 1 equiv of iodine in one portion to a 1 M solution of selenosilane **3** or **4** in acetonitrile in a dropping funnel. The resulting solution was stirred until the iodine color faded. The oxirane solution was cooled to 0 °C, and the silyl halide solution was added dropwise. After the addition was complete, the reaction mixture was stirred for 5 min for **13** or 15 min for **14** at 0 °C. The reaction mixture was poured into saturated sodium bicarbonate solution, and the products were extracted with ether. The combined ether extracts were washed with 10% sodium thiosulfate solution, dried over sodium sulfate, and concentrated. For the examples listed in Table III, chromatography on silica gel eluted with 1/10 ether/hexane separated silylated iodohydrin (high R_f) from diphenyl diselenide (lower R_f).

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B. The silylated iodohydrins were dissolved in THF to give ~0.5 M solutions, and 1.5 equiv of DBN was added. The resulting solutions were warmed at reflux under argon. At the completion of reaction, the reaction mixtures were diluted with ether, washed with cold 10% hydrochloric acid and then with saturated sodium bicarbonate, dried over sodium sulfate, and concentrated. The silyl ethers were purified by chromatography on silica or by distillation. Analytical samples were prepared by molecular distillation.

Reaction of 13 with Cyclopentene Oxide. A. Cyclopentene oxide (0.42 g, 5 mmol) was treated with **3** (1.36 g, 5 mmol) and iodine (0.63 g, 2.5 mmol) as described to give 0.75 g (96%) of diphenyl diselenide and 1.32 g (81%) of *trans*-2-iodocyclopentyl *tert*-butyldimethylsilyl ether as a colorless oil: ^{1}H NMR ($CDCl_3$) δ 4.37 (m, 1 H), 3.98 (m, 1 H), 2.50–1.40 (m, 6 H), 0.90 (s, 9 H), 0.08 (s, 3 H); IR (NaCl, film) 2950, 2920, 2850, 1470, 1462, 1255, 1074, 1035, 832, 773 cm^{-1}; mass spectrum, *m/e* 311 (M – CH_3), 269 (M – C_4H_9).

B. The iodohydrin in 8 mL of THF was treated with DBN (0.74 g, 6 mmol) as described. Distillation gave 0.59 g (100%, 81% overall) of a colorless oil [bp 36–38 °C (1 torr)] identified as cyclopent-2-enyl *tert*-butyldimethylsilyl ether: ^{1}H NMR ($CDCl_3$) δ 5.83 (m, 1 H), 5.65 (m, 1 H), 4.85 (m, 1 H), 2.65–1.90 (m, 3 H), 1.90–1.40 (m, 1 H), 0.90 (s, 9 H), 0.07 (s, 6 H); IR (NaCl, film) 2960, 2933, 2861, 1620 (w), 1475, 1467, 1258, 1071, 838, 776 cm^{-1}; mass spectrum, *m/e* 198 ($C_{11}H_{22}OSi$), 141 (M – C_4H_9).

Anal. Calcd for $C_{11}H_{22}OSi$: C, 66.6; H, 11.2. Found: C, 67.0; H, 11.2.

Reaction of 13 with Cyclohexene Oxide. A. Cyclohexene oxide (0.39 g, 4 mmol) was treated as described with **3** (1.08 g, 4 mmol) and iodine (0.51 g, 2 mmol) to give 0.52 g (84%) of diphenyl diselenide and 1.25 g (92%) of *trans*-2-iodocyclohexyl *tert*-butyldimethylsilyl ether as a pale yellow oil: ^{1}H NMR ($CDCl_3$) δ 4.01 (m, 1 H), 3.73 (m, 1 H), 2.30 (m, 1 H), 2.15–1.60 (m, 3 H), 1.60–1.20 (m, 4 H), 0.93 (s, 9 H), 0.15 (s, 3 H), 0.07 (s, 3 H); IR (NaCl, film) 2930, 2855, 1471, 1260, 1250, 1166, 1107, 873, 835, 775, 773 cm^{-1}; mass spectrum, *m/e* 340 ($C_{12}H_{25}IOSi$), 283 (M – C_4H_9).

B. The silylated iodohydrin was treated with DBN (0.74 g, 6 mmol) as described to give 0.76 g (98%, 90% overall) of a colorless oil [bp 38–40 °C (0.03 torr)] identified as cyclohex-2-enyl *tert*-butyldimethyl silyl ether: ^{1}H NMR ($CDCl_3$) δ 5.63 (m, 2 H), 4.18 (m, 1 H), 2.10–1.30 (m, 6 H), 0.92 (s, 9 H), 0.08 (s, 6 H); IR (NaCl, film) 2921, 2850, 1650 (w), 1470, 1250, 1080, 832, 770 cm^{-1}; mass spectrum, *m/e* 115 (M – C_4H_9).

Anal. Calcd for $C_{12}H_{24}OSi$: C, 67.9; H, 11.4. Found: C, 68.2; H, 11.1.

Reaction of 13 with Cycloheptene Oxide. A. Cycloheptene oxide (0.56 g, 5 mmol) was treated as described with **3** (1.36 g, 5 mmol) and iodine (0.63 g, 2.5 mmol) to give 0.75 g (96%) of diphenyl diselenide and 1.52 g (86%) of *trans*-2-iodocycloheptyl *tert*-butyldimethylsilyl ether as a colorless oil: ^{1}H NMR ($CDCl_3$) δ 4.25 (m, 2 H), 2.25–1.40 (m, 10 H), 0.92 (s, 9 H), 0.12 (s, 3 H), 0.06 (s, 3 H); IR (NaCl, film) 2943, 2922, 2850, 1470, 1460, 1253, 1050, 835, 772 cm^{-1}; mass spectrum, *m/e* 297 (M – C_4H_9), 227 (M – I).

B. The silylated iodohydrin was heated as described with DBN (0.74 g, 6 mmol) to give 0.88 g (91%, 78% overall) of a colorless oil [bp 74–76 °C (1.5 torr)] identified as cyclohept-2-enyl *tert*-butyldimethylsilyl ether: ^{1}H NMR ($CDCl_3$) δ 5.69 (m, 2 H), 4.31 (m, 1 H), 2.20–1.40 (m, 8 H), 0.93 (s, 9 H), 0.08 (s, 6 H); IR (NaCl, film) 2960, 2925, 2855, 1650 (w), 1471, 1462, 1256, 1083, 835, 773 cm^{-1}; mass spectrum, *m/e* 169 (M – C_4H_9).

Desilylation to 2-Cycloheptenol. The cyclohept-2-enyl *tert*-butyldimethylsilyl ether (0.5 g, 2.2 mmol) was dissolved in 5 mL of 1 M tetra-*n*-butylammonium fluoride in THF (Aldrich). The resulting solution was warmed at reflux for 4 h. The reaction mixture was poured into 25 mL of water, and the products were extracted with ether (2 × 25 mL). The combined ether extracts were dried over sodium sulfate and concentrated. Chromatography on silica (1/5 ether/hexane) separated 0.24 g (96%) of 2-cycloheptenol from *tert*-butyldimethylsilyl fluoride.

Desilylation of *trans*-2-Iodocycloheptyl *tert*-Butyldimethylsilyl Ether. The silylated iodohydrin (1 g, 2.82 mmol) was dissolved in 5 mL of 1 M tetra-*n*-butylammonium fluoride in THF. The resulting solution was warmed at reflux for 4 h. The reaction mixture was poured into 25 mL of water, and the products were extracted with ether (3 × 25 mL). The ether extracts were dried over sodium sulfate and concentrated. Chromatography on silica (1/10 ether/hexane) gave 0.31 g (98%) of cycloheptene oxide: bp 146–150 °C; ^{1}H NMR ($CDCl_3$) δ 3.01 (m, 2 H), 1.87 (m, 4 H), 1.50–1.00 (m, 6 H); mass spectrum, *m/e* 112 ($C_7H_{12}O$).

Reaction of Cyclooctene Oxide with 13. A. Cyclooctene oxide (0.63 g, 5 mmol) was treated as described with **3** (1.36 g, 5 mmol) and iodine (0.63 g, 2.5 mmol) to give 0.71 g (91%) of diphenyl diselenide and 1.3 g (71%) of *trans*-2-iodocyclooctyl *tert*-butyldimethylsilyl ether as a colorless oil: ^{1}H NMR ($CDCl_3$) δ 4.32 (m, 1 H), 2.10 (m, 2 H), 1.95–1.20 (m, 10 H), 0.95 (s, 9 H), 0.17 (s, 3 H), 0.09 (s, 3 H); IR (NaCl, film) 2935, 2862, 1478, 1467, 1260, 1087, 840, 778 cm^{-1}; mass spectrum, *m/e* 368 ($C_{14}H_{29}IOSi$), 311 (M – C_4H_9), 241 (M – I).

B. The silylated iodohydrin was treated as described with DBN (0.62 g, 5 mmol) to give 0.82 g (96%, 68% overall) of a colorless oil [bp 81–83 °C (1.5 torr)] identified as cyclooct-2-enyl *tert*-butyldimethylsilyl ether: ^{1}H NMR ($CDCl_3$) δ 5.48 (m, 2 H), 4.55 (m, 1 H), 2.07 (m, 2 H), 1.50 (m, 8 H), 0.91 (s, 9 H), 0.05 (s, 6 H); IR (NaCl, film) 2930, 2860, 1650, 1474, 1464, 1250, 1073, 834, 733 cm^{-1}; mass spectrum, *m/e* 240 ($C_{14}H_{28}OSi$), 183 (M – C_4H_9).

Anal. Calcd for $C_{14}H_{28}OSi$: C, 69.9; H, 11.7. Found: C, 69.9; H, 11.5.

Reaction of *trans*-2,3-Dibutyloxirane with 13. A. *trans*-2,3-Dibutyloxirane (0.78 g, 5 mmol) was treated as described with **3** (1.36 g, 5 mmol) and iodine (0.64 g, 2.5 mmol) to give 0.75 g (96%) of diphenyl diselenide and 1.69 g (85%) of 6-iodo-5-decyl *tert*-butyldimethylsilyl ether as a colorless oil: ^{1}H NMR ($CDCl_3$) δ 4.08 (m, 1 H), 3.22 (m, 1 H), 1.90–1.10 (m, 12 H), 0.92 (s, 9 H), 0.90 (t, 6 H, *J* = 7 Hz), 0.10 (s, 3 H), 0.07 (s, 3 H); IR (NaCl, film) 2958, 2950, 2860, 1464, 1257, 1080, 834, 773 cm^{-1}; mass spectrum, *m/e* 398 ($C_{16}H_{35}IOSi$), 341 (M – C_4H_9).

B. The silylated iodohydrin was treated as described with DBN (0.74 g, 6 mmol) to give 0.65 g (96%, 80% overall) of a colorless oil [bp 88–90 °C (1.5 torr)] that was identified as *trans*-6-decen-5-yl *tert*-butyldimethylsilyl ether contaminated with 2% of 5-decanone: ^{1}H NMR ($CDCl_3$) δ 2.35 (t, *J* = 7.5 Hz); IR (NaCl, film) 1720 cm^{-1}; mass spectrum, *m/e* 156. Chromatography on silica (1/10 ether/hexane) gave pure silyl ether: ^{1}H NMR ($CDCl_3$) δ 5.34 (m, 2 H), 4.00 (m, 1 H), 1.97 (m, 2 H), 1.35 (m, 8 H), 0.90 (s, 9 H), 0.91 (t, 6 H, *J* = 7 Hz), 0.03 (s, 3 H), 0.01 (s, 3 H); IR (NaCl, film) 2960, 2930, 2860, 1670 (w), 1464, 1255, 1070, 833, 733 cm^{-1}; mass spectrum, *m/e* 270 ($C_{16}H_{34}OSi$), 255 (M – CH_3), 213 (M – C_4H_9).

Anal. Calcd for $C_{16}H_{34}OSi$: C, 71.0; H, 12.7. Found: C, 70.8; H, 12.8.

Desilylation of 6-Iododec-5-yl *tert*-Butyldimethylsilyl Ether. The silylated iodohydrin (0.3 g, 0.75 mmol) was dissolved in 2 mL of 1 M tetra-*n*-butylammonium fluoride. The resulting solution was warmed at reflux for 4 h. Workup as described gave 0.10 g (91%) of *trans*-2,3-dibutyloxirane: ^{1}H NMR ($CDCl_3$) δ 2.63 (br t, 2 H, *J* = 4.5 Hz), 1.43 (m, 12 H), 0.93 (t, 6 H, *J* = 7 Hz); IR (NaCl, film) 2960, 2930, 2860, 1466, 1457, 1378 cm^{-1}; mass spectrum, *m/e* 156 ($C_{10}H_{20}O$). This reaction established the erythro stereochemistry for the iodohydrin.

Reaction of 2,2-Dimethyl-3-ethyloxirane with 13. The oxirane (0.30 g, 3.0 mmol) was treated as described with **3** (0.81 g, 3.0 mmol) and iodine (0.19 g, 1.5 mmol). Pyridine (1 equiv) was added before the addition of **13**. Chromatography on silica (1/10 ether/hexane) gave 0.45 g (97%) of diphenyl diselenide and 0.50 g (78%) of a colorless oil [bp 50 °C (1 torr, molecular still)] identified as 2-methylpent-1-en-3-yl *tert*-butyldimethylsilyl ether: ^{1}H NMR ($CDCl_3$) δ 4.80 (m, 1 H), 4.71 (m, 1 H), 3.90 (t, 1 H, *J* = 6 Hz), 1.65 (br s, 3 H), 1.50 (m, 1 H), 1.35 (m, 1 H), 0.90 (s, 9 H), 0.90 (t, 3 H, *J* = 7 Hz), 0.03 (s, 3 H), –0.03 (s, 3 H); IR (NaCl, film) 2960, 2930, 2800, 1650 (w), 1474, 1464, 1258, 1098, 1090, 1067, 1020, 836, 774 cm^{-1}; mass spectrum, *m/e* 214 ($C_{12}H_{26}OSi$).

Anal. Calcd for $C_{12}H_{26}OSi$: C, 67.2; H, 12.2. Found: C, 67.1; H, 12.1.

Reaction of 6-Oxaspiro[5.2]octane with 13. The oxirane (1.2 g, 0.01 mol) was treated as described with **3** (2.71 g, 0.01 mol), iodine (1.27 g, 0.005 mol), and pyridine (0.8 g, 0.01 mol). Chromatography on silica (1/10 ether/hexane) gave two products isolated in 58% and 38% yields. The major component was (cyclohexen-1-yl)methyl *tert*-butyldimethylsilyl ether: ^{1}H NMR

($CDCl_3$) δ 5.62 (m, 1 H), 3.97 (br s, 2 H), 2.15–1.20 (m, 8 H), 0.92 (s, 9 H), 0.13 (s, 3 H), 0.07 (s, 3 H); IR (NaCl, film) 2930, 2858, 1675 (w), 1260, 1070, 837, 776, 738 cm^{-1}; mass spectrum, *m/e* 226 ($C_{13}H_{26}OSi$), 169 (M – C_4H_9).

The minor component was 1-(iodomethyl)cyclohex-1-yl *tert*-butyldimethylsilyl ether: ^1H NMR ($CDCl_3$) δ 3.34 (s, 2 H), 1.85–1.25 (m, 10 H), 0.93 (s, 9 H), 0.15 (s, 6 H); mass spectrum, *m/e* 354 ($C_{13}H_{27}IOSi$), 339 (M – CH_3), 297 (M – C_4H_9), 227 (M – I).

The identity of the minor component was established by treating it with tetra-*n*-butylammonium fluoride as described to give 6-oxaspiro[5.2]octane: bp 140–143 °C; ^1H NMR ($CDCl_3$) δ 2.63 (s, 2 H), 1.62 (m, 10 H); mass spectrum, *m/e* 112 ($C_7H_{12}O$).

Reaction of 1-Methylcyclohexene Oxide with 13. A. 1-Methylcyclohexene oxide (1.12 g, 10.0 mmol) was treated as described with **3** (2.71 g, 10.0 mmol) and iodine (1.27 g, 5.00 mmol) to give 1.5 g (96%) of diphenyl diselenide and an oil that was a mixture of products. Careful chromatography of the mixture on silica (cyclohexane) gave 0.2 g (9%) of 2-methylcyclohex-2-enyl *tert*-butyldimethylsilyl ether [^1H NMR ($CDCl_3$) δ 5.45 (m, 1 H), 4.00 (m, 1 H), 1.90–1.20 (m, 6 H), 1.69 (br s, 3 H), 0.93 (s, 9 H), 0.10 (s, 6 H); IR (NaCl, film) 2930, 2855, 1655, 1250, 835, 771 cm^{-1}; mass spectrum, *m/e* 226 ($C_{13}H_{26}OSi$)], 0.1 g (4%) of 2-methylenecyclohexyl *tert*-butyldimethylsilyl ether [^1H NMR ($CDCl_3$) δ 4.85 (m, 1 H), 4.65 (m, 1 H), 4.00 (m, 1 H), 2.30 (m, 1 H), 2.20–1.50 (m, 7 H), 0.93 (s, 9 H), 0.05 (s, 6 H); IR (NaCl, film) 2930, 2860, 1657, 1250, 1110, 835, 775 cm^{-1}; mass spectrum, *m/e* 226 ($C_{13}H_{26}OSi$)], and 2.48 g (70%) of a 65:35 mixture of two silylated iodohydrins [mass spectrum, *m/e* 354 ($C_{13}H_{27}IOSi$), 339 (M – CH_3), 297 (M – C_4H_9), 227 (M – I)].

The major component was 2-iodo-2-methylcyclohexanol: ^{13}C NMR ($CDCl_3$) δ 76.8 (d, HCOSi), –3.70 (s, IC); ^1H NMR ($CDCl_3$) δ 4.02 (br dd, 1 H, *J* = 1.7, 6.0 Hz), 1.97 (s, 3 H, $ClCH_3$). The peak width at half-height for the δ 4.02 resonance is 10.2 Hz, which agrees quite well with the values determined for *cis*-1-phenyl-1,2-cyclohexanediol derivatives.[36] This comparison suggests cis stereochemistry for this iodohydrin.

The minor component was 2-iodo-1-methylcyclohexyl *tert*-butyldimethylsilyl ether: ^1H NMR ($CDCl_3$) δ 4.20 (dd, 2 H, *J* = 4.5, 9.6 Hz), 1.70–1.20 (m, 8 H), 1.43 (s, 3 H), 0.90 (s, 9 H), 0.13 (s, 6 H).

B. The iodide mixture was treated with 1.24 g (10 mmol) of DBN as described. Careful chromatography on silica (cyclohexane) gave 0.98 g (43%) of 2-methylcyclohex-2-enyl *tert*-butyldimethylsilyl ether, 0.05 g (2%) of the exocyclic olefin, and 0.80 g (23%) of 2-iodo-1-methylcyclohexyl *tert*-butyldimethylsilyl ether. The iodohydrin was assigned trans stereochemistry because treatment with tetra-*n*-butylammonium fluoride as described gave 1-methylcyclohexene oxide: ^1H NMR ($CDCl_3$) δ 2.90 (t, 1 H, *J* = 2.0 Hz), 1.80 (m, 4 H), 1.80–1.10 (m, 4 H), 1.25 (s, 3 H); mass spectrum, *m/e* 112 ($C_7H_{12}O$).

Reaction of Tetramethyloxirane with 13. A. The oxirane (0.5 g, 5 mmol) was treated as described with **3** (1.36 g, 5 mmol) and iodine (0.64 g, 2.5 mmol) to give 0.77 g (99%) of diphenyl diselenide and a mixture of allylic alcohol derivative and silylated iodohydrin.

B. The mixture was treated with DBN (0.62 g, 5 mmol) as described to give 0.91 g (85%) of a colorless oil [bp 41–43 °C (0.03 torr)] that was identified as 2,3-dimethyl-3-buten-2-yl *tert*-butyldimethylsilyl ether: ^1H NMR ($CDCl_3$) δ 4.93 (narrow m, 1 H), 4.67 (narrow m, 1 H), 1.78 (br s, 3 H), 1.35 (s, 6 H), 0.93 (s, 9 H), 0.13 (s, 6 H); mass spectrum, *m/e* 214 ($C_{12}H_{26}OSi$), 157 (M – C_4H_9).

Anal. Calcd for $C_{12}H_{26}OSi$: C, 67.2; H, 12.2. Found: C, 67.6; H, 11.9.

Reaction of Butyloxirane with 13. Butyloxirane (0.1 g, 1 mmol) was treated as described with **3** (0.27 g, 1 mmol) and iodine (0.13 g, 0.5 mmol) to give 0.25 g (74%) of a 5:1 mixture of two silylated iodohydrins. The major component was 1-iodo-2-hexyl *tert*-butyldimethylsilyl ether: ^1H NMR ($CDCl_3$) δ 3.53 (quintet, 1 H, *J* = 6 Hz), 3.18 (d, 2 H, *J* = 6 Hz), 1.55 (m, 2 H), 1.45–1.10 (m, 4 H), 0.93 (s, 9 H), 0.93 (m, 3 H), 0.10 (s, 3 H), 0.70 (s, 3 H); mass spectrum, *m/e* 285 (M – C_4H_9), 215 (M – I).

The major component was assigned the structure 2-iodo-1-hexyl *tert*-butyldimethylsilyl ether: ^1H NMR ($CDCl_3$) δ 4.00 (m, 1 H), 3.81 (d, 1 H, *J* = 4.5 Hz), 3.69 (dd, 1 H, *J* = 1.5, 4.5 Hz).

Reaction of *tert*-Butyldiphenylsilyl Iodide (14) with Oxiranes. The oxiranes of Table III reacted readily with **14** to give diphenyl diselenide in greater than 90% yield in all cases and good yields of silylated iodohydrins. The DBN elimination followed by chromatographic purification gave the allylic alcohol derivatives as glasses (yields given in Table III) that did not crystallize readily or distill without some decomposition. Spectral data for these compounds are as follows.

For *trans*-2-iodocyclopentyl *tert*-butyldiphenylsilyl ether: ^1H NMR ($CDCl_3$) δ 7.57 (m, 4 H), 7.33 (m, 6 H), 4.50 (m, 1 H), 4.00 (m, 1 H), 2.33 (m, 1 H), 2.00 (m, 1 H), 1.90–1.50 (m, 4 H), 1.07 (s, 9 H); IR (NaCl, film) 3065, 2955, 2915, 2853, 1584 (w), 1455, 1422, 1103, 1066, 876, 815, 730, 695 cm^{-1}; mass spectrum, *m/e* 393 (M – C_4H_9).

For cyclopent-2-enyl *tert*-butyldiphenylsilyl ether: ^1H NMR ($CDCl_3$) δ 7.61 (m, 4 H), 7.32 (m, 6 H), 5.77 (m, 1 H), 5.59 (m, 1 H), 4.87 (m, 1 H), 2.60–1.50 (m, 4 H), 1.07 (s, 9 H); IR (NaCl, film) 3063, 2955, 2925, 2853, 1590 (w), 1575 (w), 1475, 1329, 1110, 1050, 732, 696, 685 cm^{-1}; mass spectrum, *m/e* 322, 265 (M – C_4H_9).

For *trans*-2-iodocyclohexyl *tert*-butyldiphenylsilyl ether: ^1H NMR ($CDCl_3$) δ 7.63 (m, 4 H), 7.33 (m, 6 H), 4.10 (m, 1 H), 3.89 (m, 1 H), 2.20 (m, 1 H), 2.05–1.15 (m, 7 H), 1.07 (s, 9 H); IR (NaCl, film) 3034, 2925, 2825, 1590 (w), 1428, 1161, 1107, 735, 695,685 cm^{-1}; mass spectrum, *m/e* 407 (M – C_4H_9), 279 (M – C_4H_{10} – I).

For cyclohex-2-enyl *tert*-butyldiphenylsilyl ether: ^1H NMR ($CDCl_3$) δ 7.60 (m, 4 H), 7.33 (m, 6 H), 5.60 (m, 2 H), 4.18 (m, 1 H), 1.86 (m, 2 H), 1.75–1.40 (m, 4 H), 1.07 (s, 9 H); IR (NaCl, film) 2922, 2850, 1590 (w), 1425, 1107, 1067, 695 cm^{-1}; mass spectrum, *m/e* 336, 279 (M – C_4H_9).

For *trans*-2-iodocycloheptyl *tert*-butyldiphenylsilyl ether: ^1H NMR ($CDCl_3$) δ 7.60 (m, 4 H), 7.33 (m, 6 H), 4.25 (m, 2 H), 2.20–1.35 (m, 10 H), 1.10 (s, 9 H); IR (NaCl, film) 3035, 2925, 2855, 1590 (w), 1428, 1109, 1045, 820, 735, 696 cm^{-1}; mass spectrum, *m/e* 421 (M – C_4H_9).

For cyclohept-2-enyl *tert*-butyldiphenylsilyl ether: ^1H NMR ($CDCl_3$) δ 7.60 (m, 4 H), 7.30 (m, 6 H), 5.77 (dd, 1 H, *J* = 1.5, 10.5 Hz), 5.53 (m, 1 H), 4.35 (m, 1 H), 2.10–1.20 (m, 8 H), 1.07 (s, 9 H); IR (NaCl, film) 3070, 2925, 2855, 1590 (w), 1429, 1105, 1073, 819, 735, 695 cm^{-1}; mass spectrum, *m/e* 350, 293 (M – C_4H_9).

For *trans*-2-iodocyclooctyl *tert*-butyldiphenylsilyl ether: ^1H NMR ($CDCl_3$) δ 7.63 (m, 4 H), 7.30 (m, 4 H), 7.11 (m, 2 H), 4.40 (m, 1 H), 4.18 (m, 1 H), 1.93 (m, 2 H), 1.90–1.20 (m, 10 H), 1.10 (s, 9 h); mass spectrum, *m/e* 492, 435 (M – C_4H_9).

For cyclooct-2-enyl *tert*-butyldiphenylsilyl ether: ^1H NMR ($CDCl_3$) δ 7.60 (m, 4 H), 7.30 (m, 6 H), 5.48 (m, 2 H), 4.15 (m, 1 H), 1.90–1.15 (m, 10 H), 1.07 (s, 9 H); mass spectrum, *m/e* 364, 307 (M – C_4H_9).

For *erythro*-6-iododec-5-yl *tert*-butyldiphenylsilyl ether: ^1H NMR ($CDCl_3$) δ 7.63 (m, 4 H), 7.30 (m, 6 H), 4.00 (m, 1 H), 3.11 (m, 1 H), 1.80–0.95 (m, 12 H), 1.10 (s, 9 H), 0.80 (t, 6 H, *J* = 6 Hz); mass spectrum, *m/e* 522, 465 (M – C_4H_9).

For dec-6-en-5-yl *tert*-butyldiphenylsilyl ether: ^1H NMR ($CDCl_3$) δ 7.60 (m, 4 H), 7.30 (m, 6 H), 5.25 (m, 2 H), 4.05 (m, 1 H), 1.85 (m, 2 H), 1.70–0.95 (m, 8 H), 1.07 (s, 9 H), 0.80 (t, 6 H, *J* = 6 Hz); IR (NaCl, film) 3070, 2960, 2930, 2860, 1590 (w), 1428, 1260, 1109, 817, 695 cm^{-1}; mass spectrum, *m/e* 294, 337 (M – C_4H_9).

For 2-methylpent-1-en-3-yl *tert*-butyldiphenylsilyl ether: ^1H NMR ($CDCl_3$) δ 7.60 (m, 4 H), 7.30 (m, 6 H), 4.80 (br s, 2 H), 4.00 (t, 1 H, *J* = 6 Hz), 1.65 (br s, 3 H), 1.70–1.20 (m, 2 H), 1.07 (s, 9 H), 0.67 (t, 3 H, *J* = 7 Hz); IR (NaCl, film) 3070, 2960, 2925, 2855, 1650 (w), 1590 (w), 1430, 1107, 819, 736, 695 cm^{-1}; mass spectrum, *m/e* 338, 281 (M – C_4H_9).

For (cyclohexen-1-yl)methyl *tert*-butyldiphenylsilyl ether: ^1H NMR ($CDCl_3$) δ 7.63 (m, 4 H), 7.33 (m, 6 H), 5.63 (m, 1 H), 4.00 (br s, 2 H), 1.93 (m, 4 H), 1.57 (m, 4 H), 1.07 (s, 9 H); IR (NaCl, film) 3070, 2960, 2930, 2860, 1675 (w), 1590 (w), 1430, 1260, 1110, 820, 735, 697 cm^{-1}; mass spectrum, *m/e* 350, 293 (M – C_4H_9).

For 1-(iodomethyl)cyclohexyl *tert*-butyldiphenylsilyl ether: ^1H NMR ($CDCl_3$) δ 7.65 (m, 4 H), 7.30 (m, 6 H), 3.25 (s, 2 H), 1.75–1.10 (m, 10 H), 1.07 (s, 9 H); IR (NaCl, film) 2925, 2850, 1590 (w), 1430, 1110, 820, 736, 696 cm^{-1}; mass spectrum, *m/e* 421 (M – C_4H_9).

For 2-methylenecyclohexyl *tert*-butyldiphenylsilyl ether: ^1H NMR ($CDCl_3$) δ 7.63 (m, 4 H), 7.30 (m, 6 H), 4.85 (m, 1 H), 4.65 (m, 1 H), 4.05 (m, 1 H), 1.95–1.20 (m, 8 H), 1.07 (s, 9 H); mass

spectrum, m/e 350, 293 (M – C_4H_9).

For 2-iodo-1-methylcyclohexyl *tert*-butyldiphenylsilyl ether: ^{1}H NMR ($CDCl_3$) δ 7.63 (m, 4 H), 7.30 (m, 6 H), 4.23 (dd, 1 H, J = 4.5, 11 Hz), 1.27 (s, 3 H), 1.80–1.0 (m, 8 H), 1.07 (s, 9 H); mass spectrum, m/e 421 (M – C_4H_9).

For 3-iodo-2,3-dimethyl-2-butyl *tert*-butyldiphenylsilyl ether: ^{1}H NMR ($CDCl_3$) δ 7.70 (m, 4 H), 7.30 (m, 6 H), 2.05 (s, 6 H), 1.22 (s, 6 H), 1.03 (s, 9 H); mass spectrum, m/e 409 (M – C_4H_9), 339 (M – I).

For 2,3-dimethylbut-3-en-2-yl *tert*-butyldiphenylsilyl ether: ^{1}H NMR ($CDCl_3$) δ 7.65 (m, 4 H), 7.30 (m, 6 H), 4.97 (m, 1 H), 4.70 (m, 1 H), 1.82 (br s, 3 H), 1.22 (s, 6 H), 1.03 (s, 9 H); IR (NaCl, film) 3070, 2930, 2860, 1648 (w), 1590 (w), 1430, 1150, 1110, 700 cm^{-1}; mass spectrum, m/e 281 (M – C_4H_9).

Reaction of 2,2-Dimethyl-3-ethyloxirane with *tert*-Butyldimethylsilyl Bromide (12). The oxirane (0.20 g, 2.0 mmol) was treated as described for **13** with **3** (0.54 g, 2.0 mmol), bromine (0.16 g, 1.0 mmol), and pyridine (0.16 g, 2.0 mmol). Reaction required 24 h at 20 °C. An inseparable mixture of two components was isolated (0.49 g, 96%) that appeared to be the methylpentenol and the bromohydrin derivatives in equal amounts. For 3-bromo-2-methylpentan-2-ol: ^{1}H NMR ($CDCl_3$) δ 3.60 (dd, 1 H, J = 3, 6 Hz), 1.73 (s, 3 H), 1.70 (s, 3 H), 1.75–1.20 (m, 2 H), 0.93 (s, 9 H), 0.90 (t, 3 H), 0.03 (s, 6 H); mass spectrum, m/e 294, 296.

Reaction of 6-Oxaspiro[5.2]octane with 12. The oxirane (0.23 g, 2.0 mmol) was treated as described for **13** with **3** (0.54 g, 2.0 mmol) and bromine (0.16 g, 1.0 mmol) for 24 h at 20 °C. (Cyclohexen-1-yl)methyl *tert*-butyldimethylsilyl ether was isolated in 37% yield and 1-(bromomethyl)cyclohexyl *tert*-butyldimethylsilyl ether in 69% yield. For the bromohydrin: ^{1}H NMR ($CDCl_3$) δ 3.40 (s, 2 H), 2.0–1.2 (m, 10 H), 0.93 (s, 9 H), 0.07 (s, 3 H), 0.03 (s, 3 H); mass spectrum, m/e 308, 306, 293, 291 (M – CH_3), 251, 249 (M – C_4H_9), 227 (M – Br).

Reaction of Cyclooctene Oxide with Trimethylsilyl Iodide (7). Trimethylsilyl iodide (0.80 g, 4.0 mmol) was added dropwise via syringe to a solution of cyclooctene oxide (0.50 g, 4.0 mmol) in 8 mL of acetonitrile cooled to 0 °C in an argon-flushed, flame-dried apparatus. The mixture was stirred for 5 min at 0 °C and then poured into cold, saturated sodium bicarbonate solution. The product was extracted with ether (2 × 25 mL), and the combined ether extracts were dried over sodium sulfate and concentrated. Careful chromatography on silica (1/5 ether/hexane) gave 0.03 g (7%) of cyclooctene, 0.64 g (49%) of *trans*-2-iodocyclooctyltrimethylsilyl ether, and 0.42 g (41%) of *trans*-2-iodocyclooctanol.

For the silyl ether: ^{1}H NMR ($CDCl_3$) δ 4.30 (m, 1 H), 4.05 (m, 1 H), 2.07 (m, 2 H), 1.95–1.10 (m, 10 H), 0.19 (s, 9 H); IR (NaCl, film) 2920, 2850, 1463, 1248, 1081, 880, 835, 745 cm^{-1}.

For 2-iodocyclooctanol: ^{1}H NMR ($CDCl_3$) δ 4.43 (m, 1 H), 4.05 (m, 1 H), 2.43 (br s, 1 H), 2.20 (m, 2 H), 2.10–1.20 (m, 10 H); IR (NaCl, film) 3400, 2925, 2860, 1470, 1150 cm^{-1}; mass spectrum, m/e 254.

The silyl ether (0.49 g, 1.5 mmol) was treated with DBN (0.25 g, 2 mmol) as described to give 0.29 g (97%) of a colorless oil [bp 50 °C (0.05 torr, molecular still)] identified as cyclooct-2-enyl trimethylsilyl ether.

Reaction of *trans*-2,3-Dibutyloxirane with 7. The oxirane (0.6 g, 3.8 mmol) was treated as described above with **7** (0.77 g, 3.8 mmol). Chromatography on silica (1/10 ether/hexane) gave 0.05 g (8%) of unreacted oxirane, 0.05 g (9%) of *trans*-decene, 0.69 g (51%) of *erythro*-6-iododec-5-yl trimethylsilyl ether, and 0.16 g (16%) of *erythro*-6-iododecan-5-ol.

For the silyl ether: ^{1}H NMR ($CDCl_3$) δ 4.05 (m, 1 H), 3.37 (m, 1 H), 1.80–1.10 (m, 12 H), 0.90 (m, 6 H), 0.15 (s, 9 H); IR (NaCl, film) 2960, 2930, 2880, 2860, 1470, 1253, 1080, 840, 750 cm^{-1}; mass spectrum, m/e 356, 341 (M – CH_3), 299 (M – C_4H_9), 229 (M – I).

For *erythro*-6-iododecan-5-ol: ^{1}H NMR ($CDCl_3$) δ 4.27 (m, 1 H), 3.30 (m, 1 H), 2.03 (br s), 1.90–1.10 (m, 12 H), 0.93 (m, 6 H); IR (NaCl, film) 3400, 2960, 2930, 2870, 2860, 1468, 1380, 1020 cm^{-1}; mass spectrum, m/e 226 (M – C_4H_{10}), 157 (M – I).

The silyl ether (0.5 g, 1.4 mmol) was treated as described with DBN (0.25 g, 2 mmol) to give 0.31 g (96%) of *trans*-dec-6-en-5-yl trimethylsilyl ether and 0.01 g (4%) of 5-decanone. For dec-6-en-5-yl trimethylsilyl ether: ^{1}H NMR ($CDCl_3$) δ 5.45 (m, 2 H), 4.00 (m, 1 H), 1.96 (m, 2 H), 1.33 (m, 8 H), 0.90 (t, 6 H, J = 7 Hz), 0.10 (s, 9 H); IR (NaCl, film) 2960, 2930, 2870, 1665 (w), 1470, 1250, 965, 836 cm^{-1}; mass spectrum, m/e 228, 213 (M – CH_3), 171 (M – C_4H_9).

Reaction of Cyclooctene Oxide with Trimethylsilyl Bromide (6). Trimethylsilyl bromide (6; 0.49 g, 3.2 mmol) was added dropwise via syringe to a solution of cyclooctene oxide (0.4 g, 3.2 mmol) in 6 mL of acetonitrile at 20 °C. The reaction mixture was stirred at 20 °C for 8 h. Workup as described gave 0.82 g (98%) of *trans*-2-bromocyclooctyl trimethylsilyl ether: ^{1}H NMR ($CDCl_3$) δ 4.07 (m, 2 H), 2.10 (m, 2 H), 1.95–1.10 (m, 10 H), 0.18 (s, 9 H); IR (NaCl, film) 2925, 2850, 1462, 1440, 1248, 1113, 1085, 880, 838 cm^{-1}; mass spectrum, m/e 280, 278, 199 (M – Br).

The silyl ether (0.52 g, 1.9 mmol) was treated with DBN (0.3 g, 2.5 mmol) as described to give 0.36 g (97%) of cyclooct-2-enyl trimethylsilyl ether.

Desilylation of *trans*-2-Bromocyclooctyl Trimethylsilyl Ether. The silyl ether (0.28 g, 1 mmol) was dissolved in 2 mL of 1 M tetra-*n*-butylammonium fluoride. The mixture was stirred at reflux for 1 h, and workup as described gave 0.12 g (96%) of cyclooctene oxide.

General Procedure for the Conversion of Alcohols to Silyl Ethers with *tert*-Butyldimethylsilyl Iodide (13) and *tert*-Butyldiphenylsilyl Iodide (14). The apparatus was flame dried and flushed with argon prior to use. The alcohol was dissolved in enough acetonitrile to make a 1 M solution, and 2 equiv of pyridine was added. Silyl iodide **13** or **14** was then prepared by adding 1 equiv of iodine in one portion to a 1 M solution of selenosilane **3** or **4** in acetonitrile in a dropping funnel. The resulting solution was stirred until the iodine color faded. The silyl iodide solution was added to the alcohol solution, and the resulting mixture was stirred at 20 °C for the required time (Table IV). The reaction mixture was diluted with ether and washed with several portions of water. The ether phase was dried over sodium sulfate and concentrated. Chromatography on silica (1/10 ether/hexane) separated diphenyl diselenide (isolated in greater than 90% yield) from the desired silyl ethers (yields given in Table IV). Spectral and analytical data are as follows.

For 1-hexadecyl *tert*-butyldimethylsilyl ether: mp 5–10 °C; ^{1}H NMR ($CDCl_3$) δ 3.60 (t, 2 H, J = 6 Hz), 1.30 (br s, 30 H), 0.93 (s, 9 H, and buried CH_3, 3 H), 0.08 (s, 6 H); IR (NaCl, film) 2920, 2850, 1470, 1255, 1100, 832, 771 cm^{-1}; mass spectrum, m/e 356.

Anal. Calcd for $C_{22}H_{48}OSi$: C, 74.1; H, 13.6. Found: C, 73.8; H, 13.8.

For (–)-menthyl *tert*-butyldimethylsilyl ether: ^{1}H NMR ($CDCl_3$) δ 3.40 (dt, 1 H, J = 4, 9 Hz), 2.26 (m, 1 H), 1.90 (m, 1 H), 1.75–1.10 (m, 6 H), 0.95 (d, 6 H, J = 7 Hz), 0.94 (s, 9 H), 0.77 (d, 3 H, J = 7 Hz), 0.10 (s, 6 H); IR (NaCl, film) 2950, 2927, 2855, 1465, 1258, 1085, 1070, 874, 835, 775 cm^{-1}; mass spectrum, m/e 270, 225 (M – CH_3), 213 (M – C_4H_9).

For cholesteryl *tert*-butyldimethylsilyl ether: mp 156.6–158.5 °C; ^{1}H NMR ($CDCl_3$) δ 5.28 (m, 1 H), 2.35–0.30 (m), 1.00 (s, 3 H), 0.95 (s, 6 H), 0.90 (s, 9 H), 0.83 (s, 3 H), 0.68 (s, 3 H), 0.05 (s, 6 H); IR (KBr) 2920, 1090, 867, 770 cm^{-1}; mass spectrum, m/e 443 (M – C_4H_9).

Anal. Calcd for $C_{33}H_{60}OSi$: C, 79.1; H, 12.0. Found: C, 78.7; H, 11.6.

For 3-ethyl-3-pentyl *tert*-butyldimethylsilyl ether: ^{1}H NMR ($CDCl_3$) δ 1.45 (q, 6 H, J = 7 Hz), 0.90 (s, 9 H), 0.83 (t, 9 H, J = 7 Hz), 0.09 (s, 6 H); IR (NaCl, film) 2960, 2930, 2860, 1461, 1257, 1155, 1063, 837, 799, 771, 675 cm^{-1}; mass spectrum, m/e 201 (M – C_2H_5), 173 (M – C_4H_9).

For 3-ethyl-3-pentyl *tert*-butyldiphenylsilyl ether: ^{1}H NMR ($CDCl_3$) δ 7.67 (m, 4 H), 7.30 (m, 6 H), 1.40 (m, 6 H), 1.03 (s, 9 H), 0.77 (t, 9 H, J = 7 Hz); IR (NaCl, film) 3070, 2960, 2930, 2860, 1590, 1428, 1145, 1105, 1060, 820, 699 cm^{-1}; mass spectrum, m/e 339 (M – CH_3), 325 (M – C_2H_5), 297 (M – C_4H_9).

For 1-methylcyclohexyl *tert*-butyldimethylsilyl ether: ^{1}H NMR ($CDCl_3$) δ 1.85–1.20 (m, 10 H), 1.23 (s, 3 H), 0.93 (s, 9 H), 0.10 (s, 6 H); IR (NaCl, film) 2950, 2850, 1465, 1255, 1063, 1028, 1005, 832, 770, 680 cm^{-1}; mass spectrum, m/e 228, 171 (M – C_4H_9).

For 1-methylcyclohexyl *tert*-butyldiphenylsilyl ether: ^{1}H NMR ($CDCl_3$) δ 7.67 (m, 4 H), 7.30 (m, 6 H), 1.90–1.10 (m, 10 H), 1.40 (s, 3 H), 1.05 (s, 9 H); IR (NaCl, film) 3070, 2930, 2860, 1590, 1425, 1105, 1058, 1023, 1000, 820, 700 cm^{-1}; mass spectrum, m/e 352, 337 (M – CH_3), 295 (M – C_4H_9).

For 1-adamantyl *tert*-butyldimethylsilyl ether: mp 49–50 °C; ^{1}H NMR ($CDCl_3$) δ 2.15 (br s, 3 H), 1.80 (d, 6 H, J = 1.5 Hz), 1.65

(t, 6 H, J = 1.5 Hz), 0.97 (s, 9 H), 0.15 (s, 6 H); IR (NaCl, film) 2900, 2850, 1355, 1255, 1160, 1094, 1016, 848, 830, 768 cm^{-1}; mass spectrum, m/e 266, 251 (M - CH_3), 209 (M - C_4H_9).

Anal. Calcd for $C_{16}H_{30}OSi$: C, 72.1; H, 11.3. Found: C, 72.2; H, 11.0.

For 1-adamantyl *tert*-butyldiphenylsilyl ether: ^1H NMR ($CDCl_3$) δ 7.67 (m, 4 H), 7.30 (m, 6 H), 2.15 (br s, 3 H), 1.85–1.60 (m, 12 H), 1.07 (s, 9 H); IR (NaCl, film) 3070, 2925, 2900, 2850, 1585, 1423, 1350, 1120, 1013, 735, 700 cm^{-1}; mass spectrum, m/e 390, 333 (M - C_4H_9).

For 3β-methoxy-5α-cholestyl *tert*-butyldimethylsilyl ether: ^1H NMR ($CDCl_3$) δ 3.78 (m, 1 H), 3.40 (s, 3 H), 2.20–0.80 (m), 1.07 (s, 3 H), 0.95 (s, 15 H), 0.90 (s, 3 H), 0.75 (s, 3 H), 0.09 (s, 6 H).

Desilylation of 3β-Methoxy-5α-cholestyl *tert*-Butyldimethylsilyl Ether. A sample of the silyl ether (0.53 g, 1 mmol) was dissolved in 5 mL of 1 M tetra-*n*-butylammonium fluoride. After 4 h at reflux, the reaction mixture was diluted with ether and washed with water. The ether layer was concentrated. Recrystallization from methanol gave 0.4 g (95%) of a white solid (mp 131.5–132 °C) identified as 3β-methoxy-5α-cholestanol: ^1H NMR ($CDCl_3$) δ 3.68 (m, 1 H), 3.41 (s, 3 H), 2.20–0.80 (m), 1.07 (s, 3 H), 1.00 (s, 6 H), 0.93 (s, 3 H), 0.75 (s, 3 H).

Anal. Calcd for $C_{28}H_{50}O_2$: C, 80.5; H, 11.8. Found: C, 80.3; H, 11.9.

Reaction of (Phenylseleno)trimethylsilane (1) with Hydrochloric Acid. Hydrogen chloride gas was bubbled through a solution of 1 (4.58 g, 0.02 mol) in 40 mL of acetonitrile, giving an exothermic reaction. Distillation gave 2.1 g (97%) of trimethylsilyl chloride [bp 59–61 °C (atm)] and 2.93 g (93%) of benzeneselenol, bp 28–30 °C (0.03 torr).

Reaction of (Phenylseleno)trimethylsilane (1) with Benzeneselenenyl Chloride. Benzeneselenenyl chloride (1.91 g, 0.01 mol) was added to a solution of 1 (2.29 g, 0.01 mol) in 10 mL of acetonitrile cooled to 9 °C. Distillation gave 1.05 g (97%) of trimethylsilyl chloride, bp 59-61 °C (atm). Recrystallization of the pot residue from methanol gave 2.98 g (93%) of diphenyl diselenide, mp 61-62 °C.

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Registry No. 1, 33861-17-5; 2, 76358-43-5; 3, 72726-46-6; 4, 76358-44-6; 5, 75-77-4; 6, 2857-97-8; 7, 16029-98-4; 8, 994-30-9; 9, 1112-48-7; 10, 1112-49-8; 11, 18162-48-6; 12, 76358-45-7; 13, 72726-45-5; 14, 76358-46-8; diphenyl diselenide, 1666-13-3; triethylsilane, 617-86-7; benzeneselenol, 645-96-5; *tert*-butyldiphenylsilyl chloride, 58479-61-1; chlorine, 7782-50-5; bromine, 7726-95-6; iodine, 7553-56-2; methoxy-*tert*-butyldiphenylsilane, 76358-47-9; cyclopentene oxide, 285-67-6; *trans*-2-iodocyclopentyl *tert*-butyldimethylsilyl ether, 76358-48-0; cyclopent-2-enyl *tert*-butyldimethylsilyl ether, 68845-73-8; cyclohexene oxide, 286-20-4; *trans*-2-iodocyclohexyl *tert*-butyldimethylsilyl ether, 76358-49-1; cyclohex-2-enyl *tert*-butyldimethylsilyl ether, 72726-49-9; cycloheptene oxide, 286-45-3; *trans*-2-iodocycloheptyl *tert*-butyldimethylsilyl ether, 76358-50-4; cyclohept-2-enyl *tert*-butyldimethylsilyl ether, 72726-50-2; 2-cycloheptenol, 4096-38-2; cyclooctene oxide, 286-62-4; *trans*-2-iodocyclooctyl *tert*-butyldimethylsilyl ether, 76358-51-5; cyclooct-2-enyl *tert*-butyldimethylsilyl ether, 72726-51-3; *trans*-2,3-dibutyloxirane, 2165-61-9; *erythro*-6-iodo-5-decyl *tert*-butyldimethylsilyl ether, 76358-52-6; *trans*-6-decen-5-yl *tert*-butyldimethylsilyl ether, 72726-52-4; 5-decanone, 820-29-1; 2,2-dimethyl-3-ethyloxirane, 1192-22-9; 2-methylpent-1-en-3-yl *tert*-butyldimethylsilyl ether, 72726-53-5; 6-oxaspiro[5.2]octane, 185-70-6; (cyclohexen-1-yl)methyl *tert*-butyldimethylsilyl ether, 76358-53-7; 1-(iodomethyl)cyclohex-1-yl *tert*-butyldimethylsilyl ether, 72726-54-6; 1-methylcyclohexene oxide, 1713-33-3; 2-methylcyclohex-2-enyl *tert*-butyldimethylsilyl ether, 72726-55-7; 2-methylenecyclohexyl *tert*-butyldimethylsilyl ether, 72726-56-8; *cis*-2-iodo-2-methylcyclohexanol, 76358-54-8; *trans*-2-iodo-1-methylcyclohexyl *tert*-butyldimethylsilyl ether, 72726-47-7; tetramethyloxirane, 5076-20-0; 2,3-dimethyl-3-buten-2-yl *tert*-butyldimethylsilyl ether, 72726-57-9; butyloxirane, 1436-34-6; 1-iodo-2-hexyl *tert*-butyldimethylsilyl ether, 76358-55-9; 2-iodo-1-hexyl *tert*-butyldimethylsilyl ether, 76358-56-0; *trans*-2-iodocyclopentyl *tert*-butyldiphenylsilyl ether, 76376-85-7; cyclopent-2-enyl *tert*-butyldiphenylsilyl ether, 76358-57-1; *trans*-2-iodocyclohexyl *tert*-butyldiphenylsilyl ether, 76358-58-2; cyclohex-2-enyl *tert*-butyldiphenylsilyl ether, 76358-59-3; *trans*-2-iodocycloheptyl *tert*-butyldiphenylsilyl ether, 76358-60-6; cyclohept-2-enyl *tert*-butyldiphenylsilyl ether, 76358-61-7; *trans*-2-iodocyclooctyl *tert*-butyldiphenylsilyl ether, 76358-62-8; cyclooct-2-enyl *tert*-butyldiphenylsilyl ether, 76358-63-9; *erythro*-6-iododec-5-yl *tert*-butyldiphenylsilyl ether, 76358-64-0; *trans*-dec-6-en-5-yl *tert*-butyldiphenylsilyl ether, 76358-65-1; 2-methylpent-1-en-3-yl *tert*-butyldiphenylsilyl ether, 76358-66-2; (cyclohexen-1-yl)methyl *tert*-butyldiphenylsilyl ether, 76358-67-3; 1-(iodomethyl)cyclohexyl *tert*-butyldiphenylsilyl ether, 76358-68-4; 2-methylenecyclohexyl *tert*-butyldiphenylsilyl ether, 76358-69-5; *trans*-2-iodo-1-methylcyclohexyl *tert*-butyldiphenylsilyl ether, 76358-70-8; 3-iodo-2,3-dimethyl-2-butyl *tert*-butyldiphenylsilyl ether, 76358-71-9; 2,3-dimethylbut-3-en-2-yl *tert*-butyldiphenylsilyl ether, 76358-72-0; 3-bromo-2-methylpentan-2-ol, 76358-73-1; 1-(bromomethyl)cyclohexyl *tert*-butyldimethylsilyl ether, 76376-86-8; cyclooctene, 931-88-4; *trans*-2-iodocyclooctyl trimethylsilyl ether, 76358-74-2; *trans*-2-iodocyclooctanol, 76358-75-3; *trans*-dec-5-ene, 7433-56-9; *erythro*-6-iododec-5-yl trimethylsilyl ether, 76358-76-4; *erythro*-6-iododecan-5-ol, 76358-77-5; *trans*-dec-6-en-5-yl trimethylsilyl ether, 76358-78-6; *trans*-2-bromocyclooctyl trimethylsilyl ether, 76358-79-7; cyclooct-2-enyl trimethylsilyl ether, 31059-41-3; 1-hexadecyl *tert*-butyldimethylsilyl ether, 76358-80-0; (-)-menthyl *tert*-butyldimethylsilyl ether, 76358-81-1; cholesteryl *tert*-butyltrimethylsilyl ether, 57711-50-9; 3-ethyl-3-pentyl *tert*-butyldimethylsilyl ether, 76376-87-9; 3-ethyl-3-pentyl *tert*-butyldiphenylsilyl ether, 76358-82-2; 1-methylcyclohexyl *tert*-butyldimethylsilyl ether, 76358-83-3; 1-methylcyclohexyl *tert*-butyldiphenylsilyl ether, 76358-84-4; 1-adamantyl *tert*-butyldimethylsilyl ether, 76358-85-5; 1-adamantyl *tert*-butyldiphenylsilyl ether, 76358-86-6; 3β-methoxy-5α-cholestyl *tert*-butyldimethylsilyl ether, 76376-88-0; 1-hexadecanol, 36653-82-4; (-)-menthol, 2216-51-5; cholesterol, 57-88-5; 3-ethyl-3-pentanol, 597-49-9; 1-methylcyclohexanol, 590-67-0; 1-adamantol, 768-95-6; 3β-methoxy-5α-cholesterol, 76376-89-1; hydrochloric acid, 7647-01-0; benzeneselenenyl chloride, 5707-04-0; 3-bromo-2-methylpent-2-yl *tert*-butyldimethylsilyl ether, 76376-90-4; 2-methylcyclohex-2-enyl *tert*-butyldiphenylsilyl ether, 76358-87-7.

(*E*)- and (*Z*)-(1-Iodo-1-alkenyl)silanes. Their Preparation and Their Conversion into (*E*)- and (*Z*)-(1-Lithio-1-alkenyl)silanes[1]

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(*Z*)-(1-Iodo-1-alkenyl)trimethylsilanes can be conveniently obtained by isomerization of the readily available *E* isomers through the intermediacy of (1-lithioalkenyl)silanes formed by addition of catalytic amounts of *tert*-butyllithium. Reaction of (*E*)- and (*Z*)-(1-iodoalkenyl)silanes with 2.1 equiv of *tert*-butyllithium produces the (*E*)- and (*Z*)-(1-lithio-1-alkenyl)silanes. These synthetically important alkenyllithiums have been found to be configurationally stable at -70 °C. However, they isomerize at higher temperatures, reaching an *E*/*Z* equilibrium distribution at 0 °C of 86:14 (±5%) irrespective of the size of the β-alkyl substituent.

Recently we reported that (*E*)-(1-haloalkenyl)silanes 1-X (X = Cl, Br, I) are produced in high isomeric purities and yields by halogenation of the monohydroalumination products derived from the reaction of (1-alkynyl)tri-

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