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Ring Opening of Oxiranes by Trimethylsilyl Trifluoromethanesulfonate†

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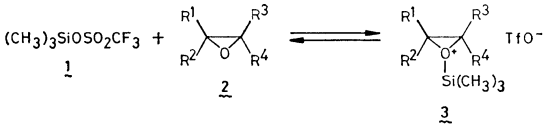
Trimethylsilyl trifluoromethanesulfonate promotes ring opening reactions of oxirane derivatives. The reaction course is highly affected by the structures and substitution pattern of the substrates. Tetra-, tri-, and 2,2-disubstituted oxiranes and simple cycloalkene oxides are converted to the corresponding allylic alcohol trimethylsilyl ethers. The overall transformation is interpreted in terms of trans addition of the silyl trifluoromethanesulfonate to the oxirane ring followed by base-promoted anti elimination of a trifluoromethanesulfonic acid element. 2,3-Dialkyl- or monoalkyloxiranes isomerize to the corresponding ketones and aldehydes, respectively. (*Z*)-Cyclooctene oxide undergoes the transannular reaction to give *endo-cis*-2-trimethylsiloxybicyclo[3.3.0]octane. The reaction of 6-methyl-5-hepten-2-one oxide produces 2,2,6-trimethyl-3-trimethylsiloxy-3,4-dihydro-2*H*-pyran. 1,2-Methyl migration takes place in the reaction of (*E*)-3α-*t*-butyldimethylsiloxy-5α-pregnene 17α,20-oxide to afford 3α-*t*-butyldimethylsiloxy-17β-methyl-17α-[1-(trimethylsiloxy)ethyl]-18-nor-5α-androst-13(14)-ene. α-Pinene oxide gives *trans*-carveol trimethylsilyl ether.

Trimethylsilyl trifluoromethanesulfonate (triflate) (**1**)[1,2] is known as a powerful reagent for the silylation of various active hydrogen compounds such as alcohols, carbonyl compounds, imines, nitriles, *etc.*[3] The efficiency is based on the strong tendency of the trimethylsilyl moiety to coordinate to hetero atoms, particularly an oxygen atom, in the organic substrates. We have been intrigued by the reaction with oxiranes which possess a basic oxygen atom.[4] The strained oxonium salts of type **3**, formed from **1** and oxiranes (**2**), are anticipated to undergo a variety of unique transformations depending on the structures of the substrates and reaction conditions. This paper describes the silyl triflate promoted reactions of a series of oxirane substrates.



1 **2** **3**

Results and Discussion

Conversion of Oxiranes to Allyl Trimethylsilyl Ethers.[5] Certain classes of oxiranes (**4**) were converted smoothly to the allyl trimethylsilyl ethers of type **5** by the treatment with **1** and a nitrogen base in aromatic hydrocarbon media. The trimethylsilyl group of **5** was easily removed by exposure to dilute hydrochloric acid or potassium fluoride in methanol to give the allylic alcohol **6**. Simple cycloalkene oxides were con-

4 **5**, R = $Si(CH_3)_3$; **6**, R = H

verted to the allyl silyl ethers by exposure to a 1:1 mixture of **1** and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) in benzene at ambient temperature (method A). Tetra-, tri-, and 2,2-dialkylated oxiranes are even more reactive and the ring opening reaction has been usually accomplished by the treatment with an equimolar mixture of **1** and 2,6-lutidine in toluene at temperatures as low as −78 °C and then with 1.2—1.3 equiv of DBU at room temperature (method B). Some examples are given in Table 1.

Although ketonic and ester substrates are susceptible to the silylation with **1** in the presence of a nitrogen base,[3] the oxirane ring is much more reactive under these reaction conditions and is cleaved in an ordinary manner, leaving these functions intact. The chemoselective transformations of the bifunctional substrates **17** and **19** illustrate this feature (entries 8 and 9). Oxiranes containing a hydroxyl function were converted to the bis(trimethylsilyl) ethers by using 2 equiv of **1** (entries 10—12).

The overall transformation, **4**→**5**, is accomplished *via* trans addition of **1** to the oxirane ring[6] followed by anti elimination of a TfOH element away from the trimethylsiloxy group. Under the present reaction conditions, trimethylsilylammonium triflates of type **31** or **32** may serve as active species.[7] Triflate,

31 **32**

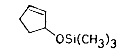
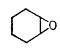
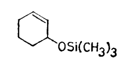
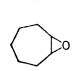
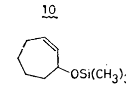
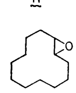
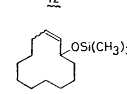
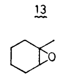
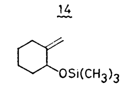
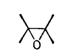
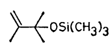
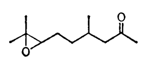
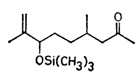
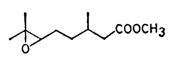
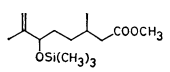
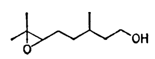
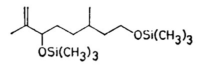
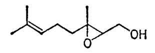
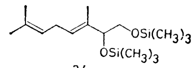
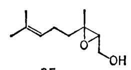
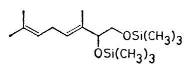
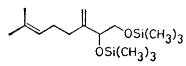
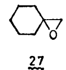
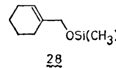
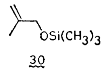
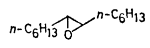
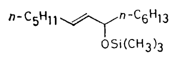
though is a feeble nucleophile, displaces the oxirane ring activated through coordination of a trimethylsilyl group, giving the addition product. When an unsymmetrically alkylated oxirane is used, the triflate displacement takes place preferentially at the more substituted carbon atom. This regioselection is readily understood by considering the electronic properties of the silylated oxirane structure; the alkyl substitution decreases the relative magnitude of electron density at the carbon attached to it and increases the LUMO coefficient of the same carbon, resulting in enhancement of the electrophilic reactivity.[6]

When cyclohexene oxide (**9**) was treated with **1** equiv of **1** and triethylamine in hexane at room temperature, a single, labile product **33** was produced. The ^1H NMR spectrum exhibited Ha and Hb signals at δ 4.46 (ddd) and 3.57 (ddd) with the vicinal coupling constant of 10 Hz, substantiating the trans stereochemistry. Treatment of **33** with DBU led to the olefinic compound **10**. The production of the allyl silyl ether **10** (not an enol silyl ether) is a consequence

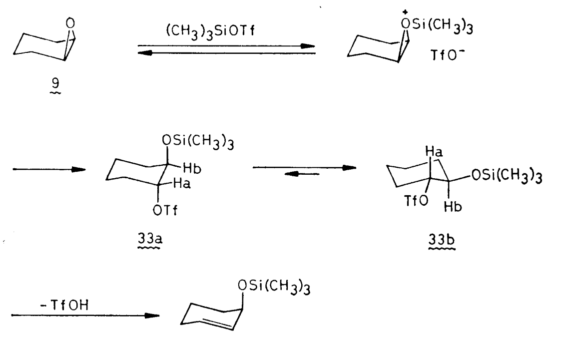
† Dedicated to Professor Hitosi Nozaki on the occasion of his 60th birthday.

of anti elimination of TfOH; the two conformers, **33a** and **33b**, are possible for **33**, but only the less stable conformer **33a** can undergo the E2 elimination reaction.[8)] It is worth noting that such controlling factors display a unique selectivity in the reaction of certain cyclic trisubstituted oxirane derivatives. For instance, the reaction of 1-methylcyclohexene oxide (**34**) with **1** produces the initial adduct **35**. Since the TfO group locates in an equatorial position in the stable conformer, the base-promoted anti elimination of TfOH occurs selectively in such a way to produce **36** which possesses an exocyclic methylene group.[8e,f)] In a like manner, the reaction of the steroidal substrate **37** with **1** and 2,6-di-*t*-butylpyridine afforded after desilylation the alcoholic product **38** exclusively.

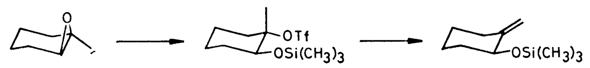
TABLE 1. CONVERSION OF OXIRANES TO ALLYL TRIMETHYLSILYL ETHERS

Entry	Orirane	Method	Product	Yield/%[a)]
1	 7	A	 8	59[b)]
2	 9	A	 10	87
3	 11	A	 12	40, 100[c)]
4	 13	A	 14	38
5		B		80
6	3β-Methyl-5α-cholest-2-ene 2α,3α-oxide	d)	3-Methylene-5α-cholestan-2α-ol trimethylsilyl ether	59,[e)] 95[c)]
7	 15	B	 16	87[b)]
8	 17	B	 18	69
9	 19	B	 20	79
10	 21	B	 22	71
11	 23	B	 24	66
12	 25	B	 24	65
			 26	16
13	 27	B	 28	72
14	 29	B	 30	62[b)]
15	 41	B[f)]	 42	17[g)]

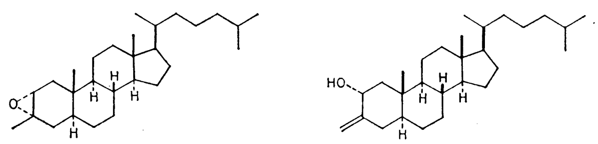
a) Isolated yield. b) Determined by GLPC analysis. c) Based on consumed starting material. d) The reaction was carried out in toluene by using 2,6-di-*t*-butylpyridine as base. e) Isolated yield of desilylated product. f) The reaction was carried at 80 °C. g) A mixture of isomeric enol silyl ethers was obtained in 65% yield.



9 33a 33b 10

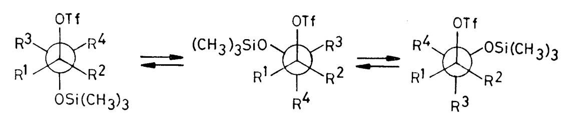


34 35 36



37 38

When a monocyclic oxirane is subjected to the displacement by **1**, a conformationally flexible adduct of type **39a**⇄**39b**⇄**39c** is formed. The E2 elimination reaction occurs from the most stable conformer **39a** in which the dipole repulsion is minimized, resulting in the regioselective formation of the allyl silyl ether. The stereoselective production of *E* dienes from geraniol or nerol 2,3-oxide (**23** and **25**, respectively) is interpreted in terms of the preference of the conformer **40a** over **40b**[8a–d)] (entries 11 and 12).



39a 39b 39c

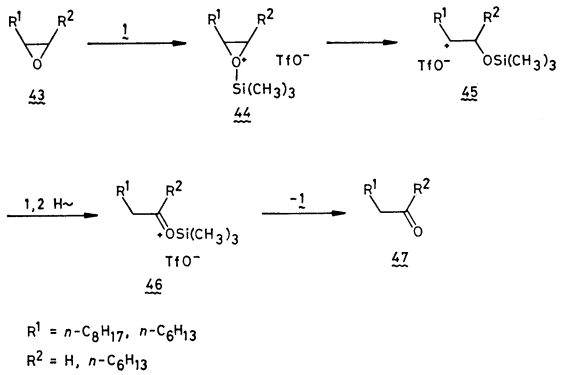
40a 40b

R^1 = $(CH_3)_2C{=}CHCH_2-$

R^2 = $(CH_3)_3SiOCH_2CH(OSi(CH_3)_3)-$

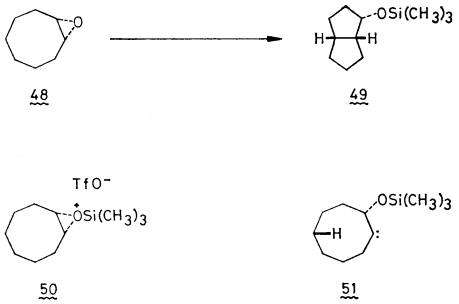
The oxirane to allylic alcohol conversion is an important operation from the synthetic point of view, and a number of effective reagents have been devised for this purpose. Oxiranes derived from five- to seven-membered cyclic olefins can be converted to the corresponding allylic alcohols by strongly basic lithium amide reagents in refluxing solvents.[9] The recently developed dialkylaluminum amides[10] and a dialkylboron triflate[11] are applicable to the reaction of *trans*-2,3-dialkylated or further alkylated oxiranes. These reagents are not utilized for the isomerization of the *cis*-2,3-dialkylated oxiranes, however. A mild, two-step procedure by the use of an organoselenium compound was also elaborated; reaction of oxiranes with sodium benzeneselenolate followed by oxidative deselenation of the addition products gives rise to the allylic alcohols.[12] Here when an unsymmetrically substituted oxirane is used, the ring opening occurs preferentially at the less substituted carbon atom, and the sense of the regioselection is opposite that observed in this work. The present procedure based on the use of the organosilicon compound **1** requires very mild reaction conditions and displays unique stereo-, regio-, and chemoselectivity. As such this method, complementary to the existing recipes, provides a useful tool in organic synthesis. It should be added that silyl iodides[13] and silyl selenides in the presence of a Lewis acid[14] behave in a similar manner in the reaction with oxiranes.

Isomerization of Oxiranes to Carbonyl Compounds. Unlike cycloalkene oxides, simple 2,3-dialkylated and monoalkylated oxiranes were inert to the standard reaction conditions. When these substrates with **1** added amines were subjected to the more forcing conditions, there were obtained the corresponding carbonyl compounds as exclusive or major products. For instance, reaction of 1-decene oxide with **1** and 2,6-lutidine in benzene at 80 °C led to decanal in 89% yield. Likewise, (*Z*)-7-tetradecene oxide was converted to 7-tetradecanone quantitatively. The reaction of the *E* isomer gave some allylic alcohol derivatives. Thus, reaction of (*E*)-7-tetradecene oxide (**41**) with **1** and 2,6-lutidine in benzene at 80 °C followed by treatment with DBU at room temperature afforded (*E*)-8-trimethylsiloxy-6-tetradecene (**42**) (17% yield) in addition to isomeric enol silyl ethers of 7-tetradecanone (65% combined yield) (Table 1, entry 15).[15] The isomerization to carbonyl compounds would proceed *via* carbocation intermediates. The oxonium species



44, generated from a di- or monosubstituted oxirane **43**, is not reactive enough to suffer nucleophilic displacement by triflate anion.[5] When **44** is heated, however, it undergoes unimolecular C–O bond rupture to produce the unstable carbocation **45**,[16] which readily isomerizes to the stable carboxonium intermediate **46** *via* 1,2-hydride transfer. Subsequent desilylation gives rise to the carbonyl product **47**.

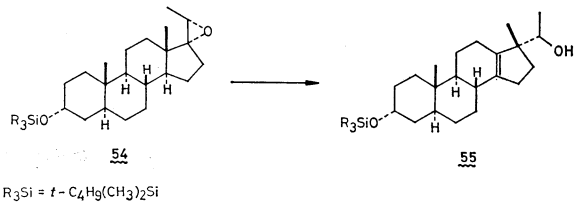
Reaction of Cyclooctene Oxide (48). In the presence of 2,6-lutidine the title reaction proceeded cleanly at room temperature to give the bicyclic compound **49** in quantitative yield. Although the mechanism has not yet been clarified, the carbene species **51** formed by base-aided α-elimination of the trimethylsilylated oxirane **50** seems to be an attractive candidate for the intermediate.[17] The lithium amide-generated carbene is known to undergo the same type of transannular reaction.[18] When reaction of **48** and **1** was conducted in the absence of any added amines, cyclooctanone was formed (87% yield), probably *via* a carbocation mechanism.



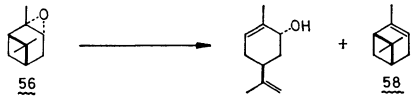
Neighboring Group Participation in the Oxirane Ring Opening. When oxirane substrates contain some nucleophilic atom or bond at a spatially suitable position, the ring opening is facilitated by electron release from such moiety.[19]

The keto oxirane **52** upon sequential treatments by a mixture of **1** and 2,6-lutidine and then by DBU underwent clean cyclization *via* carbonyl group participation to give the dihydropyran derivative **53** in 80% yield.

The carbon-carbon σ bond participation is exemplified by the reaction of the steroidal 17α,20-oxide **54** which affords after removal of the trimethylsilyl group the product **55** in 86% yield. Here the triflate attack on the silylated oxirane species is prevented by screening effect of the adjacent methyl group and, instead, this angular methyl undergoes 1,2-migration to form the rearranged product.[20]

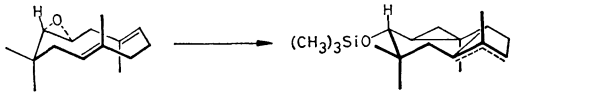


When α-pinene oxide (**55**) was exposed to a mixture of **1** and 2,6-lutidine and then DBU, there was obtained after desilylation *trans*-carveol (**57**) in 72% yield.[21] In addition, α-pinene (**58**), a deoxygenation product, was formed in 6% yield.



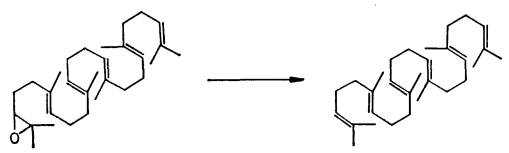
56 57 58

The recently discovered conformationally selective transannular cyclization of humulene 9,10-oxide (**59**) to the tricyclic compounds **60** and **61**[22,23] is an example of the C=C bond participation in the silyl triflate promoted ring cleavage.



59 60 and 61 (two isomers)

Deoxygenation of Oxiranes. With certain oxirane substrates, the deoxygenation becomes a significant pathway. For example, squalene 2,3-oxide (**62**) was converted to squalene (**63**) in 70% yield by the treatment with **1** and 2,6-lutidine at −78 °C. The mechanism is unclear.[24]



62 63

Experimental

*General.*** Melting points and boiling points were uncorrected. IR spectra were recorded on a JASCO IR A-1 spectrometer in a noted phase. ^{1}H NMR spectra were determined on a Varian NV-21 or HA-100 spectrometer. Chemical shifts are reported as δ values in parts per million relative to tetramethylsilane=0. Splitting patterns are indicated as s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet, and br means a broad signal. Mass spectra were determined on a JEOL D-100 spectrometer, operating with an ionization energy of 75 eV. Elemental analyses were performed at Department of Applied Chemistry, Nagoya University. All reactions using trimethylsilyl triflate (**1**) were carried out in a dried vessel under argon atmosphere. Unless otherwise stated, the organic extracts were dried by passing through a short column of anhydrous K_2CO_3. For concentration of solutions, unless otherwise stated, a vacuum (50—100 mmHg) rotary evaporator was used. Bulb-to-bulb short-path distillation was performed by using a Büchi Kugelrohrofen. The cited temperatures for these distillations refer to the maximum temperature attained by the oven during the distillation and are thus not true boiling points.

Chromatography. Silica gel 60 F_{254} precoated plates (E. Merck) at 0.25 mm thickness were used for both analytical and preparative TLC. Analytical plates were visualized by spraying with a solution of 2% $Ce(SO_4)_2$ in 5% H_2SO_4 or 2% *p*-anisaldehyde in 5% ethanolic H_2SO_4 followed by heating on a hot plate, or exposure to I_2 vapor. Column chromatography was conducted by using 70—230 mesh silica gel 60 available from E. Merck. In certain cases silica gel was used after ammonia treatment; silica gel was mixed with about 30% parts of 10% ammonia solution and then heated at 130 °C for 2 h. GLPC analyses were performed on a Hitachi 063 or 163 instrument, using nitrogen or helium as the carrier gas (9.807×10^4 Pa), respectively. A Varian 1700 instrument was used for preparative GLPC, using helium as the carrier gas (1.961×10^5 Pa).

Solvents and Materials. Trimethylsilyl triflate (**1**), prepared from chlorotrimethylsilane and trifluoromethanesulfonic acid,[2c] was distilled twice with *ca.* 1 vol% of triethylamine to remove all protic substances. Commercial oxiranes, **9**, **29**, and **48**, obtained from Tokyo Kasei Kogyo, Wako Junyaku, and Aldrich Chemical Co, respectively, were used without further purification. Oxiranes, **7**, **11**, **19**, **21**, **31**, **36**, **52**, **56**, 1-decene oxide, and (*Z*)- or (*E*)-7-tetradecene oxide were prepared from commercial alkenes by oxidation with 25% acetone solution of peracetic acid or 85% *m*-chloroperbenzoic acid in dichloromethane at 0 °C. The purities (>99%) of these oxiranes were confirmed by the ^{1}H NMR, GLPC, and TLC analises. Other oxiranes, **13**, **23**, **25**, **27**, **39**, **54**, and **62**, were prepared according to the procedures in the literatures.[10c, 25-29] DBU, 2,6-lutidine, and 2,6-di-*t*-butylpyridine were dried by distillation from CaH_2 before use. Benzene, toluene, and hexane were distilled from Na. Dichloromethane was distilled from P_2O_5. Other commercially supplied materials and solvents were used as received.

*Preparation of 4,8-Dimethyl-7-nonen-2-one Oxide (**17**).* To a 1.1 mol dm^{-3} ethereal solution of methylmagnesium bromide (70 ml, 0.077 mol) was added citronellal (10.0 g, 0.065 mol) dissolved in dry ether (50 ml) drop by drop over a period of 30 min at 0 °C. The mixture was stirred at 22 °C for 1 h and at reflux temperature for 3 h. The mixture was cooled to 0 °C and to this was added 1 mol dm^{-3} HCl (100 ml) slowly. The organic layer was separated and the aqueous layer was extracted with ether (50 ml×2). The combined organic layers were dried over anhydrous $MgSO_4$ and concentrated. The residue was dissolved in acetone (300 ml) and to this was added a 3 M CrO_3 solution in 50% H_2SO_4 (150 ml) drop by drop at 0 °C. The mixture was poured into ice water (800 g) and extracted with ether (100 ml×2) and benzene (100 ml×3). The combined extracts were washed with saturated KNO_3, dried over anhydrous $MgSO_4$, and concentrated. Distillation (76—82 °C/3 mmHg) gave 4,8-dimethyl-7-nonen-2-one (7.68 g, 70%) as a colorless oil.

To a mixture of 4,8-dimethyl-7-nonen-2-one (3.00 g, 0.018 mol) thus obtained and anhydrous Na_2CO_3 (3.0 g) in dichloromethane (80 ml) was added in a dropwise manner a 2 mol dm^{-3} acetone solution of peracetic acid (11 ml, 0.022 mol) at 0 °C. After stirring at 0 °C for 4 h, the mixture was poured into water (300 ml). The organic layer was separated and the aqueous layer was extracted with dichloromethane (30 ml×3). The combined organic layers were washed with saturated $NaHCO_3$ and twice with saturated Na_2SO_3, dried, and concentrated. Distillation (80—86 °C/1 mmHg) afforded pure **17** (2.81 g, 85%) as a colorless oil: IR (neat) 1716 cm^{-1} (C=O); NMR (CCl_4) 0.90 (3H, d, J=6.5 Hz, CH_3), 1.20 (3H, s, CH_3), 1.24 (3H, s, CH_3), 1.65—1.25 (5H, m, methylene and methine), 2.04 (3H, s, CH_3C=O), 2.27 (2H, triplet-like, J=7 Hz, CH_2C=O), and 2.51 (1H, t, J=5.2 Hz, CHO). Found:

** 1 mmHg≈133.3 Pa; 1 ml=0.001 dm^3.

C, 71.5; H, 10.7%. Calcd for $C_{11}H_{20}O_2$: C, 71.7; H, 10.9%.

*Reaction of Cyclopentene Oxide (**7**) with **1**.* To a solution of **1** (1.01 g, 4.56 mmol) in benzene (12 ml) was added a mixture of **7** (0.348 g, 4.13 mmol) and DBU (0.8 ml) in benzene (5 ml) drop by drop over a period of 5 min at 32 °C. The mixture was stirred for 19 h and then poured into 0.1 mol dm^{-3} HCl. The mixture was extracted with pentane (20 ml×3). The extracts were dried, concentrated at 200 mmHg, and chromatographed on a column of NH_3-treated silica gel, eluting with a 1:1 mixture of benzene and hexane, to afford pure **8** (0.236 g, 33%) as a colorless oil. GLPC analysis of the extracts on a column of 5% FFAP on Chromosorb W AW (3 mm×2 m) at 60 °C indicated the yield of **8** (t_R=2.3 min) to be 59%: IR (neat) 1251 cm^{-1}; NMR ($CDCl_3$) 0.14 (9H, s, CH_3Si), 2.5—1.4 (4H, m, two methylenes), 4.88 (1H, m, CHO), 5.71 (1H, br d, J=5.7 Hz, CH=), and 5.98 (1H, br d, J=5.7 Hz, CH=).

*Reaction of Cyclohexene Oxide (**9**) with **1**.* A mixture of **1** (2.26 g, 10.2 mmol), **9** (1.06 g, 10.7 mmol), and DBU (2 ml) in benzene (25 ml) was stirred at 22 °C for 20 h. The mixture was poured onto a column of NH_3-treated silica gel (15 g) and eluted by a 2:1 mixture of hexane and ether (300 ml). The eluate was cocentrated at 200 mmHg and distilled. Redistillation of the fraction boiling at 50—60 °C/50 mmHg gave pure **10** (1.51 g, 87%) as a colorless oil; IR (neat) 1250 cm^{-1}; NMR ($CDCl_3$) 0.13 (9H, s, CH_3Si), 2.1—1.2 (6H, m, methylene), 4.19 (1H, m, CHO), and 5.67 (2H, m, CH=).

*Reaction of Cyclohexene Oxide (**9**) with **1** in the Absence of DBU.* A mixture of **1** (0.225 g, 1.15 mmol), triethylamine (0.16 ml), and **9** (0.110 g, 1.12 mmol) in hexane (5 ml) was stirred at 21 °C for 10 h and then the solvent was removed at 1 mmHg. The adduct **35** (0.339 g) was obtained as a pale brown oil: NMR (CCl_4) 0.14 (9H, s, CH_3Si), 2.4—1.2 (8H, m, methylene), 3.57 (1H, ddd, J=10.0, 7.8, and 4.2 Hz, CHOSi), and 4.47 (1H, ddd, J=10.0, 7.8, and 4.0 Hz, CHOTf).

*Treatment of **35** with DBU.* The adduct **35** (0.339 g, 1.13 mmol) was mixed with DBU (0.3 ml) in benzene (5 ml) and the mixture was stirred at 21 °C for 18 h. This was then poured into water and extracted with hexane (5 ml×3). The extracts were dried and concentrated. Column chromatography on NH_3-treated silica gel, eluting with a 1:1 mixture of benzene and hexane, gave pure **10** (0.133 g, 71%).

*Reaction of Cycloheptene Oxide (**11**) with **1**.* A mixture of **1** (1.14 g, 5.01 mmol), **11** (0.506 g, 4.51 mmol), and DBU (1 ml) in benzene (15 ml) was stirred at 22 °C for 14 h. This was then poured into water and extracted with pentane (5 ml×3). The extracts were dried, concentrated, and chromatographed on a column of silica gel, eluting with a 1:1 mixture of benzene and hexane, to give **11** (0.298 g, 59%) and pure **12** (0.317 g, 40%, 100% based on consumed **11**): IR (neat) 1251 cm^{-1}; NMR ($CDCl_3$) 0.12 (9H, s, CH_3Si), 2.2—1.2 (8H, m, four methylenes), 4.38 (1H, m, CHO), and 5.68 (2H, m, CH=).

*Reaction of (E)-Cyclododecene Oxide (**13**) with **1**.* A mixture of **1** (0.502 g, 2.26 mmol), **13** (0.392 g, 2.15 mmol), and DBU (0.4 ml) in benzene (11 ml) was stirred at 27 °C for 40 h, and then to this was added a mixture of hexane (10 ml) and 0.1 mol dm^{-3} HCl (3 ml). The organic layer was separated and the aqueous layer was extracted with pentane (5 ml×6). The combined organic layers were washed with 0.1 mol dm^{-3} HCl and 5% $NaHCO_3$, dried, and concentrated. Column chromatography on silica gel, eluting with a 1:1 mixture of benzene and hexane, gave pure **14** (0.208 g, 38%): IR (neat) 1249 cm^{-1}; NMR (CCl_4) 0.12 (9H, s, CH_3Si), 2.5—1.2 (18H, m, nine methylenes) 3.94 (1H, br, CHO), and 5.28 (2H, m, CH=).

*Reaction of 2,3-Dimethyl-2-butene Oxide (**15**) with **1**.* To a solution of **1** (0.195 g, 0.88 mmol) and 2,6-lutidine (0.10 ml) in toluene (4 ml) was added **15** (0.105 g, 1.10 mmol) dissolved in toluene (1 ml) at −78 °C drop by drop over a period of 5 min. The mixture was stirred at −78 °C for 4 h, and then to this was added DBU (0.15 ml). After stirring at 15 °C for 5 h, a solution of 1-trimethylsiloxycyclohexene (0.158 g, 0.93 mmol) in hexane (2 ml) was added as the internal standard. The mixture was washed with 0.1 mol dm^{-3} HCl and dried. The GLPC analysis on a column of 3% Silicone OV-1 on Chromosorb W AW (3 mm×2 m) at 90 °C indicated the yield of **16** (t_R=4.6 min) to be 87%. Pure **16** was isolated by preparative GLPC, by using a column of 10% Silicone OV-1 on Chromosorb W AW (7 mm×3 m) at 110 °C: IR (neat) 1248 cm^{-1}; NMR (CCl_4) 0.08 (9H, s, CH_3Si), 1.33 (6H, s, CH_3), 1.76 (3H, br s, CH_3C=), 4.68 (1H, m, CH_2=), and 4.87 (1H, m, CH_2C=).

*Reaction of 4,8-Dimethyl-7-nonen-2-one Oxide (**17**) with **1**.* A mixture of **1** (0.545 g, 2.45 mmol), 2.6-lutidine (0.28 ml), and **17** (0.516 g, 2.45 mmol) in toluene (7 ml) was stirred at −78 °C for 4 h, and to this was added DBU (0.35 ml). The mixture was stirred at 20 °C for 30 min and poured into a mixture of hexane (30 ml) and water (10 ml). The mixture was extracted with hexane (5 ml×3). The extracts were washed with 0.1 mol dm^{-3} HCl and 5% $NaHCO_3$, dried, and concentrated. Column chromatography on silica gel, eluting with benzene, gave pure **18** (0.437 g, 69%) as a colorless oil: IR (neat) 1718 (C=O) and 1249 cm^{-1}; NMR (CCl_4) 0.02 (9H, s, CH_3Si), 0.86 (3H, d, J=6.1 Hz, CH_3), 1.62 (3H, br s, CH_3C=), 2.0—1.0 (5H, m, two methylenes and methine), 2.03 (3H, s, CH_3C=O), 2.18 (1H, d, J=6.5 Hz, CH_2C=O), 2.26 (1H, d, J=6.5 Hz, CH_2C=O), 3.91 (1H, t, J=6.0 Hz, CHO), 4.68 (1H, m, CH_2=), and 4.78 (1H, m, CH_2=); Ms *m/e* (rel intensity) 256 (15), 143 (100), and 73 (44). Found: C, 65.8; H, 10.8%. Calcd for $C_{14}H_{28}O_2Si$: C, 65.6; H, 11.0%.

*Reaction of Methyl Citronellate Oxide (**19**) with **1**.* A mixture of **1** (0.346 g, 1.55 mmol), 2,6-lutidine (0.18 ml), and **19** (0.306 g, 1.53 mmol) in toluene (6 ml) was stirred at −78 °C for 4 h. Then to this was added DBU (0.15 ml) at −78 °C. The mixture was stirred at 15 °C for 2 h and diluted by hexane (30 ml). The mixture was washed with 0.1 mol dm^{-3} HCl and saturated $NaHCO_3$, dried, and concentrated. Column chromatography on silica gel, eluting with a 20:1 mixture of benzene and ethyl acetate, gave pure **20** (0.330 g, 79%) as a colorless oil: IR (neat) 1742 (C=O) and 1250 cm^{-1}; NMR (CCl_4) 0.02 (9H, s, CH_3Si), 0.90 (3H, d, J=6.2 Hz, CH_3), 1.64 (3H, br s, CH_3C=), 2.3—1.0 (7H, m, three methylenes and methine), 3.61 (3H, s, CH_3O), 3.92 (1H, t, J=6.0 Hz, CHO), 4.76 (1H, m, CH_2=), and 4.81 (1H, m, CH_2=); Ms *m/e* (rel intensity) 272 (8), 257 (7), 143 (100), 73 (59), and 59 (21). Found: C, 61.7; H, 10.4%. Calcd for $C_{14}H_{28}O_3Si$: C, 61.8; H, 10.3%.

*Reaction of Citronellol Oxide (**21**) with **1**.* To a solution of **1** (0.429 g, 1.93 mmol) and 2,6-lutidine (0.22 ml) in toluene (5 ml) was added in a dropwise manner **21** (0.170 g, 0.99 mmol) dissolved in toluene (3 ml) at −78 °C. The mixture was stirred at −78 °C for 5 h and then to this was added DBU (0.3 ml). The mixture was stirred at 28 °C for 4 h, poured into 0.1 mol dm^{-3} HCl, and extracted with hexane (8 ml×4). The combined extracts were dried and

concentrated. Bulb-to-bulb distillation (120 °C/1 mmHg) gave pure **22** (0.217 g, 71%) as a colorless oil: IR (neat) 1248 cm^{-1}; NMR ($CDCl_3$) 0.10 (18H, s, CH_3Si), 0.83 (3H, d, J=6.2 Hz, CH_3), 1.7—1.0 (7H, m, three methylenes and methine), 1.70 (3H, br s, CH_3C=), 3.62 (2H, t, J=6.5 Hz, CH_2O), 4.20 (1H, t, J=6.5 Hz, CHO), 4.80 (1H, m, CH_2=), and 4.87 (1H, m, CH_2=).

*Reaction of Geraniol 2,3-Oxide (**23**) with **1**.* To a solution of **1** (0.264 g, 1.19 mmol) and 2,6-lutidine (0.14 ml) in toluene (3 ml) was added **23** (0.109 g, 0.64 mmol) dissolved in toluene (2 ml) in a dropwise manner over a period of 5 min at −78 °C. After stirring at −78 °C for 4 h, DBU (0.2 ml) was added. The mixture was stirred at 30 °C for 54 h, poured into 0.1 mol dm^{-3} HCl, and extracted with hexane (5 ml×3). The combined extracts were dried, concentrated, and chromatographed on a column of NH_3-treated silica gel, eluting with a 1:1 mixture of benzene and hexane, to give bis(trimethylsilyl) ether of (*E*)-3,7-dimethyl-3,6-octadiene-1,2-diol[10] (**24**) (0.124 g, 66%) as a colorless oil: IR (neat) 1250 cm^{-1}; NMR ($CDCl_3$) 0.09 (18H, s, CH_3Si), 1.58 (3H, s, CH_3C=), 1.72 (3H, s, CH_3C=), 2.71 (2H, t, J=7.0 Hz, =CCH_2C=), 3.48 (2H, d, J=6.3 Hz, CH_2O), 4.04 (1H, t, J=6.2 Hz, CHO), 5.11 (1H, br t, CH=), and 5.38 (1H, t, J=7.0 Hz, CH=).

*Reaction of Nerol 2,3-Oxide (**25**) with **1**.* To a mixture of **1** (0.330 g, 1.48 mmol) and 2,6-lutidine (0.17 ml) in toluene (4 ml) was added a solution of **25** (0.132 g, 0.78 mmol) in toluene (2 ml) drop by drop over a period of 10 min at −78 °C. After stirring at −78 °C for 3 h, DBU (0.25 ml) was added and the mixture was stirred at 32 °C for an additional 14 h. The reaction was quenched by pouring into 0.1 mol dm^{-3} HCl. The mixture was extracted with hexane (5 ml×3). The extracts were dried and concentrated. Column chromatography on NH_3-treated silica gel, eluting with a 1:2 mixture of benzene and hexane, afforded a 4:1 mixture of **24** and bis(trimethylsilyl) ether of 7-methyl-3-methylene-6-octene-1,2-diol[10d] (**26**) (totally 0.188 g, 81%) as a colorless oil: IR (neat) 1252 cm^{-1}; NMR (CCl_4) 0.07 and 0.09 (totally 18H, two singlets, CH_3Si), 1.55 and 1.72 (totally 8.4H, two broad singlets, CH_3C= of **24** and **26**), 2.04 (0.4H, m, CH_2C= of **26**), 2.72 (1.6H, t, J=7.0 Hz, =CCH_2C= of **24**), 3.45 (2H, m, CH_2O of **24** and **26**), 4.06 (1H, m, CHO of **24** and **26**), 4.83 (0.2H, m, CH_2= of **26**), 5.3—5.0 (1.2H, m, CH_2= of **26** and CH= of **24**), and 5.41 (0.8H, t, J=6.3 Hz, CH= of **24**).

*Reaction of Methylenecyclohexane Oxide (**27**) with **1**.* To a stirred solution of **1** (0.987 g, 4.40 mmol) and 2,6-lutidine (0.52 ml) in toluene (7 ml) was added in a dropwise manner **27** (0.490 g, 4.37 mmol) dissolved in toluene (3 ml) over a period of 5 min at −78 °C. The mixture was stirred at −78 °C for 3 h and to this was added DBU (0.52 ml). The mixture was stirred at 32 °C for 14 h, then poured into 0.1 mol dm^{-3} HCl, and extracted with hexane (5 ml×3). The combined extracts were dried and concentrated. Bulb-to-bulb distillation (150 °C/40 mmHg) gave pure **28** (0.581 g, 72%) as a colorless oil: IR (neat) 1250 cm^{-1}; NMR (CCl_4) 0.11 (9H, s, CH_3Si), 1.60 (4H, m, two methylenes), 1.98 (4H, m, CH_2C=), 3.96 (2H, s, CH_2O), and 5.62 (1H, br, CH=).

*Reaction of 2-Methylpropene Oxide (**29**) with **1**.* To a solution of **1** (0.473 g, 2.13 mmol) in toluene (7 ml) was added 2,6-lutidine (0.25 ml) at 13 °C. The mixture was cooled in a Dry Ice–acetone bath (−78 °C), and to this was added a solution of **29** (0.164 g, 2.27 mmol) in toluene (1 ml). After the mixture was stirred at −78 °C for 10 h, DBU (0.33 ml) was added. Then the cooling bath was removed and the mixture was stirred at 13 °C for 0.5 h. To this was added 1-trimethylsiloxycyclopentene (0.229 g, 1.47 mmol) as the internal standard and poured into water. The mixture was extracted with pentane (10 ml). The GLPC analysis on a column of 5% Apiezone-L on Neopak 1 A (3 mm×2 m) at 70 °C indicated the yield of **30** (t_R= 5.6 min) to be 62%. The product identification was made by coinjection with authentic sample prepared from 2-methyl-2-propen-1-ol and chlorotrimethylsilane.

*Reaction of 1-Methylcyclohexene Oxide (**34**) with **1**.* To a mixture of **1** (0.705 g, 3.17 mmol) and 2,6-lutidine (0.37 ml) in toluene (5 ml) was added **34** (0.368 g, 3.28 mmol) dissolved in toluene (2 ml) drop by drop over a period of 10 min at −78 °C. The mixture was stirred at −78 °C for an additional 2 h, and then to this was added DBU (0.55 ml). The mixture was stirred at 24 °C for 3 h, poured into 0.1 mol dm^{-3} HCl, and extracted with hexane (5 ml× 4). The extracts were washed with water, dried, concentrated, and chromatographed on a column of silica gel, eluting with a 2:3 mixture of benzene and hexane, to afford pure **36** (0.459 g, 80%) as a colorless oil: IR (neat) 1252 cm^{-1}; NMR ($CDCl_3$) 0.11 (9H, s, CH_3Si), 2.6—1.1 (8H, m, four methylenes), 4.04 (1H, m, CHO), 4.69 (1H, m, CH_2=), and 4.86 (1H, m, CH_2=).

*Reaction of 3β-Methyl-5α-cholest-2-ene 2α,3α-Oxide (**37**) with **1**.* A 0.2 M toluene solution of **1** (0.5 ml, 0.1 mmol) was cooled to −78 °C and to this was added 2,6-di-*t*-butylpyridine (0.03 ml) followed by the addition of **37** (0.020 g, 0.05 mmol) dissolved in toluene (1.5 ml). The mixture was stirred at −78 °C for 10 h and quenched by adding methanol (1 ml) and 3 drops of concd HCl. The mixture was stirred at 17 °C for 2 h, poured into water, and extracted with petroleum ether (5 ml×3). The extracts were dried and concentrated. Preparative TLC on a silica gel plate, developing with a 7:1 mixture of petroleum ether and ethyl acetate, gave pure **37** (0.008 g) and pure **38** (0.012 g, 58%, 95% based on consumed **37**) as colorless crystals: mp 112—114 °C (lit,[30] mp 113—114 °C); IR (KBr) 3640—3250 cm^{-1} (OH); NMR (CCl_4) 2.2—0.6 (45H, m, methyl, methylene, and methine), 4.13 (1H, m, CHO), 4.65 (1H, m, CH_2=), and 4.80 (1H, m, CH_2=).

*Reaction of 1-Decene Oxide with **1**.* A mixture of **1** (0.260 g, 1.17 mmol), 2,6-lutidine (0.1 ml), and 1-decene oxide (0.167 g, 1.07 mmol) in benzene (4 ml) was heated at 80 °C for 10 h. After cooling to 18 °C, the mixture was poured into water and extracted with hexane (5 ml×3). The extracts were washed with saturated $NaHCO_3$, dried, and concentrated. Bulb-to-bulb distillation (120 °C/100 mmHg) gave pure decanal (0.148 g, 89%) as a colorless oil. The identification was made by GLPC analysis on a column of 5% DEGS on Neopak 1A (3 mm×2 m) at 110 °C (t_R=6.4 min).

*Reaction of (Z)-7-Tetradecene Oxide with **1**.* A mixture of **1** (0.542 g, 2.44 mmol), 2.6-lutidine (0.19 ml), and (*Z*)-7-tetradecene oxide (0.536 g, 2.53 mmol) in benzene (5 ml) was heated at 80 °C for 10 h. After cooling to 15 °C, the mixture was poured into water and extracted with hexane (5 ml×3). The extracts were washed with saturated $NaHCO_3$, dried, and concentrated. Bulb-to-bulb distillation (100 °C/1 mmHg) gave 7-tetradecanone (0.511 g, 100%) as a colorless oil. The identification was made by GLPC analysis on a column of 5% DEGS on Nepopak 1A (3 mm× 2 m) at 150 °C (t_R=5.1 min).

*Reaction of (E)-7-Tetradecene Oxide (**41**) with **1**.* A mixture of **1** (0.270 g, 1.20 mmol), 2,6-lutidine (0.14 ml), and **41** (0.260 g, 1.22 mmol) in benzene (5 ml) was heated at 80 °C for 8 h in a sealed tube. After cooling to 13 °C, to this was added DBU (0.19 ml). The mixture was stirred

at 13 °C for 2 h and then poured into 0.1 mol dm^{-3} HCl. The mixture was extracted with hexane (10 ml×3), and the extracts were dried and concentrated. Bulb-to-bulb distillation (125 °C/0.5 mmHg) gave a mixture (0.305 g, 89%) of **42** and four isomers of 7-tetradecanone enol silyl ethers as a colorless oil: IR (neat) 1675 (C=C) and 1251 cm^{-1}; NMR (CCl_4) 0.04 (2H, s, CH_3Si), 0.14 (7H, s, CH_3Si), 0.88 (6H, br t, CH_3), 1.28 (16H, br s, eight methylenes), 1.94 (3H, br, CH_2C=), 2.26 (1H, t, CH_2C=), 3.98 (0.2H, m, CHO of **42**), 4.35 (0.2H, t, J=7.4 Hz, CH= of enol silyl ethers trans to OSi),[31] 4.47 (0.6H, t, J=7.0 Hz, CH= of enol silyl ethers cis to OSi),[31] 5.27 (0.2H, m, CH= of **42**), and 5.51 (0.2H, dd, J=14.8 and 6.3 Hz, =CCHO of **42**).

Reaction of Cyclooctene Oxide (48) with 1. To a solution of **1** (0.344 g, 1.55 mmol) and 2,6-lutidine (0.18 ml) in toluene (3 ml) was added **48** (0.205 g, 1.63 mmol) dissolved in toluene (2 ml) drop by drop over a period of 5 min at −50 °C. After 3-h reaction at −50 °C, the mixture was warmed to 26 °C and stood for 40 h. The mixture was poured into water and extracted with hexane (5 ml×4). The combined extracts were dried and concentrated. The crude products consisted of the silyl ether **49** and the desilylated alcohol. This was dissolved in 5% methanolic HCl (10 ml), stirred at 26 °C for 1 h, and concentrated. Bulb-to-bulb distillation (125 °C/20 Torr) gave pure *endo-cis*-bicyclo[3.3.0]octan-2-ol[9r] (0.203 g, 100%): IR (neat) 3650—3300 cm^{-1} (OH); NMR (CCl_4) 1.9—1.2 (10H, m, five methylenes), 2.40 (2H, m, bridgehead CH), 3.2—2.7 (1H, br, OH, exchangeable with D_2O), and 4.11 (1H, m, CHO).

Reaction of Cyclooctene Oxide (48) with 1. Formation of Cyclooctanone: A mixture of **1** (0.919 g, 4.14 mmol) and **48** (0.464 g, 3.68 mmol) in toluene (5 ml) was stirred at 0 °C for 2 h. The mixture was poured into saturated $NaHCO_3$ and extracted with hexane (7 ml×3). The combined extracts were dried and concentrated. Bulb-to-bulb distillation (120 °C/40 mmHg) gave cyclooctanone (0.403 g, 87%) as colorless crystals: mp 39—41 °C.

Reaction of 6-Methyl-5-hepten-2-one Oxide (52) with 1. To a solution of **1** (0.408 g, 1.83 mmol) and 2,6-lutidine (0.22 ml) in toluene (4 ml) was added **52** (0.242 g, 1.83 mmol) dissolved in toluene (2 ml) at −78 °C. After stirring at −78 °C for 3 h, to this was added DBU (0.28 ml), and stirring was continued at 15 °C for 1 h. The mixture was quenched by pouring into water and extracted with hexane (5 ml×3). The extracts were dried, concentrated, and chromatographed on a column of NH_3-treated silica gel, eluting with a 10:1 mixture of pentane and ether, gave pure **53** (0.314 g, 80%) as a colorless oil: IR (neat) 1684 (C=C) and 1245 cm^{-1}; NMR (CCl_4) 0.06 (9H, s, CH_3Si), 1.06 (3H, s, CH_3), 1.19 (3H, s, CH_3), 1.63 (3H, br s, CH_3C=), 1.96 (2H, m, CH_2), 4.53 (1H, dd, J=8.6 and 6.0 Hz, CHO), and 5.22 (1H, t, J=3.6 Hz, CH=). Found: C, 61.6; H, 10.4. Calcd for $C_{11}H_{22}O_2Si$: C, 61.6; H, 10.4.

Reaction of (E)-3α-t-Butyldimethylsiloxy-5α-pregnene Oxide (54) with 1. A mixture of **1** (0.075 g, 0.34 mmol), 2,6-lutidine (0.04 ml), and **54** (0.104 g, 0.24 mmol) in toluene (4 ml) was stirred at −78 °C for 4 h and then at 15 °C for 10 h. The mixture was poured into 0.1 mol dm^{-3} HCl and extracted with hexane (5 ml×3). The combined extracts were washed with saturated $NaHCO_3$, dried, and concentrated. Column chromatography on silica gel, eluting with a 10:1 mixture of benzene and ethyl acetate, gave pure **55** (0.090 g, 86%) as colorless crystals: mp 118—120 °C; IR (CCl_4) 3635 (OH) and 1253 cm^{-1}; NMR (CCl_4) 0.04 (6H, s, CH_3Si), 0.76 (3H, s, CH_3), 0.94 (9H, s, $(CH_3)_3CSi$), 1.04 (3H, s, CH_3), 2.2—1.0 (24H, m, methyl, methylene, and methine), 3.60 (1H, q, J=6.5 Hz, CHO), and 4.01 (1H, m, CHO); Ms *m/e* (rel intensity) 432 (4), 414 (7), 387 (72), 255 (25), and 75 (100). Found: C, 75.1; H, 10.9%. Calcd for $C_{27}H_{48}O_2Si$: C, 74.9; H, 11.2%.

Reaction of α-Pinene Oxide (56) with 1. To a mixture of **1** (0.483 g, 2.17 mmol) and 2,6-lutidine (0.25 ml) in toluene (5 ml) was added a solution of **56** (0.332 g, 2.18 mmol) in toluene (2 ml) at −50 °C. The mixture was stirred at −50 °C for 1 h and then to this was added DBU (0.4 ml) at −50 °C. The mixture was stirred at 26 °C for 10 h, quenched by pouring into 0.1 mol dm^{-3} HCl, and extracted with hexane (7 ml×4). The combined extracts were dried, concentrated, and chromatographed on a silica gel column, eluting with a 5:1 mixture of benzene and ethyl acetate. Careful concentration of the eluates gave α-pinene (**58**) (0.023 g, 6%) and pure **57** (0.240 g, 72%) as a colorless oil. **57**: IR (neat) 3660—3300 (OH) and 1643 cm^{-1} (C=C); NMR (CCl_4) 2.7—1.1 (6H, m, CH_2, CH, and OH, 1H was D_2O exchangeable), 1.73 (6H, br s, CH_3C=), 3.98 (1H, br, CHO), 4.62 (2H, br s, CH_2=), and 5.44 (1H, m, CH=).

Reaction of Squalene Oxide (62) with 1. A mixture of **1** (0.392 g, 1.76 mmol) 2,6-lutidine (0.15 ml), and **62** (0.512 g, 1.20 mmol) in toluene (7 ml) was stirred at −78 °C for 12 h, then poured into 0.1 mol dm^{-3} HCl, and extracted with hexane (10 ml×3). The combined extracts were dried, concentrated, and chromatographed on a silica gel column, eluting with benzene, to give pure squalene (**63**) (0.348 g, 70%) as a colorless oil.

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