Highly Regio- and Diastereoselective One-Pot Synthesis of Silyl Epoxy Alcohols and Vinylsilanes by Direct Hydroxy-Epoxidation

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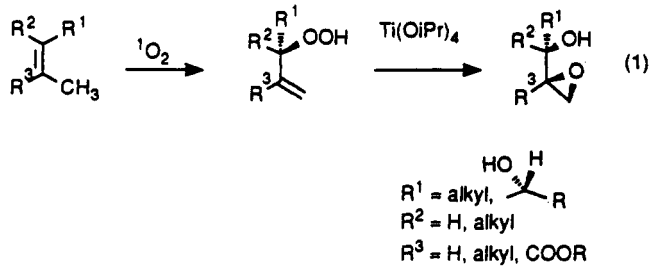
A direct synthesis of silyl epoxy alcohols from vinylsilanes is described. It consists of the regioselective ene reaction of the vinylsilanes with singlet oxygen, which proceeds with predominant hydrogen abstraction at the position *geminal* to the silyl group. The resulting silyl allylic hydroperoxides were treated, without isolation, subsequently with $Ti(O\text{-}i\text{-}Pr)_4$ to afford the silyl epoxy alcohols in good yields and very high diastereomeric ratios, which ranged from 93:7 to greater than 97:3. Alternatively, the vinylsilanes were photooxygenated directly in the presence of the titanium catalyst and the silyl epoxy alcohols obtained in good yields. The method was applied to di- and trisubstituted acyclic vinylsilanes with a methyl group *geminal* to silicon and cyclic derivatives all give consistently good results. In this novel hydroxy-epoxidation, the regioselectivity of the singlet oxygen ene reaction as well as the diastereoselectivity of the oxygen transfer can be controlled by the steering effects of the silyl group.

Introduction

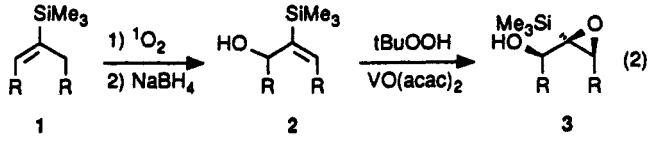
The photooxygenation of alkenes in the presence of transition-metal catalysts, the hydroxy-epoxidation reaction,[1] constitutes a valuable method for the synthesis of stereochemically defined epoxy alcohols (eq 1). It consists



(1)

of the ene reaction of the alkene with photosensitized singlet oxygen ($^1O_2$) to produce an allylic hydroperoxide, which subsequently undergoes intermolecular oxygen transfer by typical epoxidation catalysts such as $Ti(O\text{-}i\text{-}Pr)_4$, $VO(acac)_2$, or $MoO_2(acac)_2$ to afford the epoxy alcohol. If the starting olefin contains a chirality center, additional stereocontrol can be achieved. For example, in the case of allylic alcohols, both the singlet oxygen ene reaction and the titanium-catalyzed oxygen transfer proceed highly diastereoselectively and allow the introduction of up to four oxy-functionalized chirality centers with defined stereochemistry.[2]

Unfortunately, the low regioselectivity of the $^1O_2$ ene reaction[3] for simple alkenes leads to mixtures of regioisomeric epoxy alcohols, and additionally, their oxygen-transfer reaction does not always proceed with high diastereoselectivity.[1] To overcome these drawbacks, we have employed with success vinylsilanes as substrates for the singlet oxygen ene reaction and subsequent hydroxy-epoxidation.[4] The following advantages of this methodology are worth noting: (a) the photooxygenation of vinylsilanes proceeds regioselectively with preferred hydrogen abstraction at the position *geminal* to the silyl group[5] (eq 2) and (b) metal-catalyzed epoxidation of β-silyl



(2)

allylic alcohols yields the silyl epoxy alcohols in high diastereoselectivity due to the steric bulk of the silyl group.[6] Since such silyl epoxy alcohols can be desilylated with complete retention of stereochemistry,[7] regio- and diastereomerically pure epoxy alcohols derived from simple olefins become conveniently available by this pathway. Furthermore, the Me_3Si group at the epoxide provides additional opportunities for further synthetic transformations.[8] Herein we report in detail the scope of this novel synthetic concept for the direct hydroxy-epoxidation of silyl-substituted alkenes.

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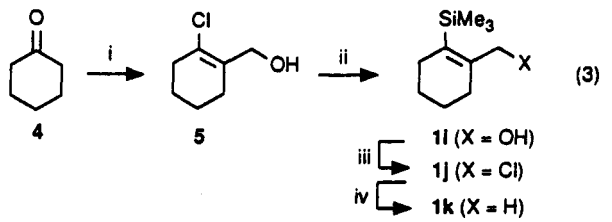
Results

The acyclic vinylsilanes **1a–d** were prepared either by lithiation of 2-bromo-2-butene and subsequent reaction with the appropriate chlorosilane[9] or by carbocupration of (trimethylsilyl)acetylene and subsequent coupling with methyl iodide, for which the published procedure with minor modifications was used.[10] The trisubstituted vinylsilane **1e** was obtained by reductive lithiation of the corresponding vinyl thioether.[11] The cyclic derivatives **1f–h** were synthesized by Wurtz–Fittig reaction from the corresponding vinyl halides,[12] which were prepared from the ketones by reaction with PCl_5 or from cyclooctene by bromination/dehydrobromination.

Since for cyclic trisubstituted vinylsilanes no straightforward synthesis was available in the literature,[13] the sequence shown in eq 3 was developed. Vilsmeier reaction

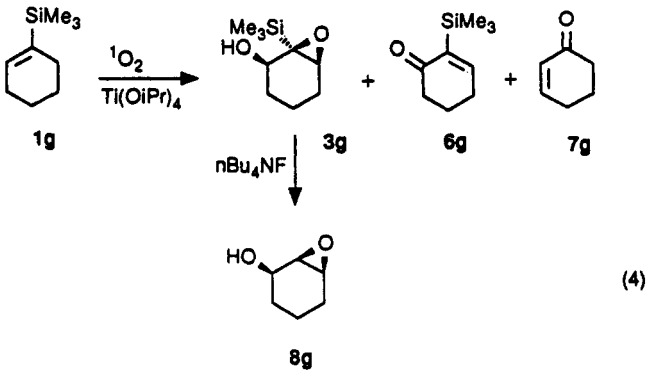


(3)

Reagents: (i) $POCl_3$, DMF; $NaBH_4$; (ii) $NH(SiMe_3)_2$, $ClSiMe_3$; Na, $ClSiMe_3$; 1N HCl, THF, H_2O; (iii) PPh_3, CCl_4; (iv) $LiAlH_4$.

on cyclohexanone followed by immediate reduction of the crude aldehyde,[14] to avoid decomposition during purification, gave the chloro alcohol **5**.[15] In analogy to acyclic derivatives,[16] chloro alcohol **5** was protected as silyl ether, C-silylated and deprotected, again without purification of the intermediate products. The CH_2OH functionality was then transformed by standard methods[17,18] to the chloromethyl and the methyl[13b] derivatives. While this synthesis requires several steps, it is more useful than existing ones in that the reactions are easy to perform, even on large scale, and the yields are high throughout.

Photooxygenation of the vinylsilanes in the presence of Ti(O-*i*-Pr)$_4$ was studied in detail for the silane **1g** (eq 4). Irradiation of a solution of **1g** in dichloromethane in the presence of oxygen, tetraphenylporphine (TPP) as sensitizer, molecular sieves, and 25 mol % Ti(O-*i*-Pr)$_4$ required 19 h for complete conversion of the starting silane. The



(4)

^{1}H NMR spectrum of the crude product mixture after removal of catalyst and solvent showed mainly signals consistent with the epoxy alcohol **3g**, but small amounts of 2-cyclohexenone (7%), the product of the regioisomeric $^1O_2$ ene reaction,[4] and 2-(trimethylsilyl)cyclohexenone[19] (4%) were also detected. Comparison with an authentic sample of a 75:25 mixture of diastereomers, prepared by epoxidation of the corresponding allylic alcohol **2g**[5b] with *m*-CPBA, revealed that only a single diastereomer was present in the crude product. Epoxy alcohol **3g** was isolated from the hydroxy–epoxidation reaction in 70% yield by column chromatography. On a larger scale (40 mmol), purification by distillation proved to be more convenient, and the yield was only slightly decreased. Its diastereoselective[7] desilylation with *n*-Bu_4NF to the known epoxy alcohol **8g**[1a] (eq 4) confirmed the *cis* relationship of the epoxy alcohol functionality.

The results obtained for the other vinylsilanes are shown in Table 1. For the more reactive acyclic vinylsilanes **1a–e**, it proved to be more convenient to conduct the photooxygenation and the oxygen-transfer reactions in separate steps but as a one-pot procedure since the isolation of the intermediary hydroperoxides was not necessary. Only with the cyclic six- and eight-membered ring vinylsilanes **1g–k**, which react only slowly with singlet oxygen, was photooxygenation in the presence of Ti(O-*i*-Pr)$_4$ necessary to avoid decomposition of the formed hydroperoxide during the prolonged photooxygenation. In general, the only side products were the corresponding enones derived from regioisomeric photooxygenation.[4] These are, however, easily separated from the epoxy alcohol products.

Except for **3a,b**, all epoxy alcohols were obtained as single diastereomers, i.e. only one isomer could be detected by high-field (250-MHz) NMR. Authentic samples of diastereomeric mixtures of **3a,b,g**, prepared by epoxidation of the corresponding allylic alcohols, were at hand for comparison. The configurations of the acyclic epoxy alcohols **3b,d** were assigned in analogy to the known[6] products **3a,c**. This assignment was further substantiated by the good agreement of the ^{1}H NMR data of the diastereomeric mixtures of **3a,b** with comparable epoxy alcohols from the literature,[1a] in which the silyl group is replaced by an alkyl group. In all cases the hydrogen α to the OH group for the *erythro* isomer (the designation *erythro* refers to the relative stereochemistry of the hydroxy and the epoxy functionalities) occurs at lower field than the *threo* isomer (cf. Experimental Section). Additionally, the epoxy protons constitute a well-separated set of doublets for the *erythro* but a narrow set for the *threo* isomer.

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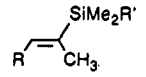
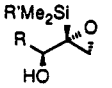
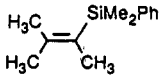
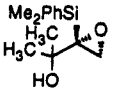
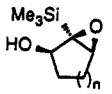
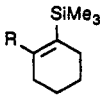
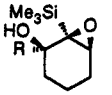
Table 1. Direct Hydroxy-Epoxidation of Vinylsilanes

vinylsilane 1			method[a]	reaction time (h) $t(^1O_2)$[b]	reaction time (h) t[TiO*i*-Pr)$_4$][c]	silyl epoxy alcohol 3	yield (%)[d]	dr[e]
	**1a**[f](R = Me, R′ = Me)		A	6	6		65	93:7
	1b[g](R = Me, R′ = Ph)		A	7	4		66	97:3
	1c(R = *n*-Bu, R′ = Me)		A	4	7		59	>97:3
	**1d** (R = c-C_6H_{11}, R′ = Me)		A	6	8		56	>97:3
	1e		A	2.5	6		70	
	1f	*n* = 1	A	4.5	4		70	>97:3
	**1g**	*n* = 2	B	20[h]			70	>97:3
	1h	*n* = 4	B	16[h]			72	>97:3
	1j	R = CH_2Cl	B	8			58	>97:3
	**1k**	R = CH_3	B	6			43	>97:3

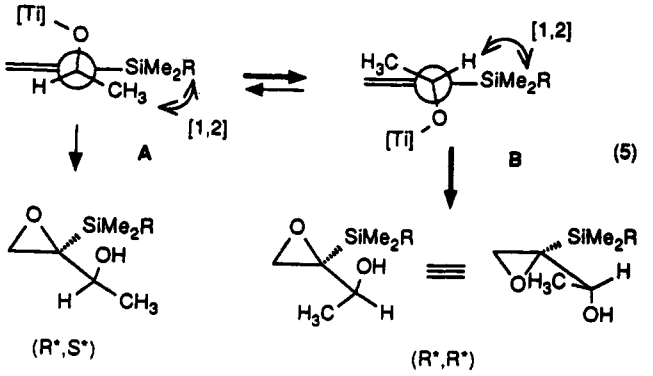
[a] A, photooxygenation and subsequent reaction with Ti(O*i*-Pr)$_4$; B, photooxygenation in the presence of Ti(O*i*-Pr)$_4$. [b] Photooxygenation. [c] Epoxidation with Ti(O*i*-Pr)$_4$. [d] Yield of purified product. [e] Determined by ^{1}H NMR, error ±5%. [f] A 65:35 (*E*/*Z*) mixture was employed. [g] A 67:33 (*E*/*Z*) mixture was employed. [h] An immersion lamp apparatus was used.

The cyclic epoxy alcohols **3f–k** have all been assigned the *cis* configuration. This is based, on one hand, on their transformation to the known corresponding desilylated products (eq 4), e.g. **3g** to *cis*-2,3-epoxy-1-cyclohexanol (**8g**) and **3h** to *cis*-2,3-epoxy-1-cyclooctanol (**8h**).[20] On the other hand, the derivatives **3g,k** showed intramolecular hydrogen bonding[21] between the hydroxy group and the epoxy oxygen in the IR spectrum for dilute CCl_4 solutions.

Discussion

For the direct hydroxy-epoxidation of alkenes, the required vinylsilanes should be readily available. In the present case the vinylsilanes were prepared in no more than one or two steps from commercially available compounds and therewith the prerequisite of ready availability is fulfilled.

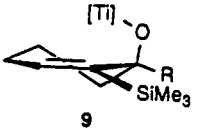
The high diastereomeric ratios obtained in the oxygen-transfer reaction are in good agreement with the general accepted mechanism of metal-catalyzed epoxidation of allylic alcohols.[6,22] The slightly lower diastereoselectivities for the derivatives **1a,b** compared to those reported for the vanadium-catalyzed epoxidation of allylic alcohols[6] reflects the lower *erythro* selectivity observed earlier with Ti(O-*i*-Pr)$_4$.[23] For the later, the diastereoselectivity in the epoxidation is accounted for in terms of a dihedral angle O—C—C=C[1d] of 100°, which is in agreement with most experimental data obtained so far with Ti(O-*i*-Pr)$_4$.[6,24] Inspection of the two possible conformers (eq 5) reveals that the lower 1,2-allylic strain between the silyl group and the substituent at the carbinol center determines the preference for conformer **B** and thus explains the preferred formation of the *erythro* or *R**,*R** isomer.



(5)

Comparison of the diastereoselectivities of the epoxy alcohols **3a** and **3b** illustrates that an increase in size of the silyl group improves the diastereoselectivity significantly. Therefore, by employing a large silyl substituent, which serves as temporary stereochemical directing group, high diastereoselectivities can be achieved also in those cases in which the all-carbon substrate shows poor stereocontrol in the oxygen transfer.

In cyclohexene derivatives, the above-mentioned dihedral angle of 100° corresponds to a *pseudo*-axial arrangement of the C–O bond. Inspection of the reactive complex **9** for the tertiary epoxy alcohols **3j,k** shows that severe



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steric interaction builds up between the silyl group and the substituent α to the hydroxy group. Nevertheless, the hydroxy-epoxidation of the trisubstituted, cyclic vinylsilanes **1j,k** proceeds as well as with the acyclic ones (Table 1). This means that for the present case the

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mechanistic model used above is too simple to account for the observed experimental facts. Apparently the Ti(O-*i*-Pr)$_4$/ROOH system is conformationally more flexible than previously assumed and also sterically encumbered epoxy alcohols such as **3e,j,k** are readily formed. The comparatively low yield for **3k** is due to the decreased regioselectivity of the $^1O_2$ ene reaction compared to the other cyclic vinylsilanes.[25]

In summary, the above results show that the one-pot hydroxy-epoxidation reaction of vinylsilanes is a useful method for the synthesis of silylated epoxy alcohols. The required starting materials are readily available, and the reaction is easily carried out and performs in excellent diastereoselectivities and good yields. Considering the numerous synthetic transformations that the silyl epoxy alcohols offer,[8] the present methodology should constitute a valuable route to such building blocks for organic synthesis.

Experimental Section

General Methods. For instrumentation used in this work, see ref 26. Photooxygenations were performed in test tubes of 1-cm diameter, equipped with a gas inlet tube for the passage of a slow stream of dried ($CaCl_2$, P_2O_5) oxygen gas. In the photooxygenations in the presence of Ti(O-*i*-Pr)$_4$, gas inlet tubes of at least 3 mm in diameter were used in order to avoid plugging by TiO_2, which is formed inevitablely by hydrolysis of Ti(O-*i*-Pr)$_4$. The test tube was placed in a cooling bath connected to a cryostat and irradiated by two 150-W sodium lamps. The photooxygenations with the immersion lamp were run as published,[27] but without the external cooling bath and reflux condenser. THF was distilled from potassium under argon immediatedly prior to use. Ti(O-*i*-Pr)$_4$ was distilled and stored under argon. CuBr (Fluka) and LiBr were dried at 120 °C and 0.1 Torr for 2 h and stored under argon.

Vinylsilanes. *E,Z* mixtures of vinylsilanes **1a,b**[9] were prepared from 2-bromo-2-butene in 79 and 65% yield by reaction with lithium metal, followed by treatment with the corresponding chlorosilane. Silanes **1e**[11] and **1f–h**[12] were prepared according to literature procedures.

(*E*)-(1-Methyl-1-hexenyl)trimethylsilane (1c). A suspension of 720 mg (5.00 mmol) of CuBr and 434 mg (5.00 mmol) of LiBr in 20 mL of dry THF was cooled to –60 °C and 13.5 mL of a solution of *n*-BuMgBr (0.74 M, 10.0 mmol) was added. After 1.5 h of stirring at –60 to –70 °C, 0.70 mL (4.95 mmol) of (trimethylsilyl)acetylene was added, the reaction mixture was stirred for 4.5 h at 0 °C and cooled to –60 °C, and 0.47 mL (7.50 mmol) of methyl iodide was introduced. The mixture was allowed to warm up overnight to room temperature, 10 mL of a saturated, aqueous NH_4Cl solution and 20 mL of a 10% $Na_2S_2O_3 \cdot 5H_2O$ solution were added, and the biphasic mixture was stirred until the solids had dissolved (15 min) and extracted with petroleum ether (bp 30–50 °C, 3 × 50 mL). The combined organic layers were washed with a saturated, aqueous NH_4Cl solution (10 mL) and brine (10 mL), dried ($MgSO_4$), and concentrated (20 °C/20 Torr). Kugelrohr distillation of the residue afforded 564 mg (68%) of **1c** as colorless liquid: oven temperature (ot) 50 °C/3.0 Torr (lit.[28] ot 66–68 °C/7 Torr); ^{1}H NMR (250 MHz, $CDCl_3$) δ 0.05 (s, 9H), 0.91 (t, *J* = 7.0 Hz, 3H), 1.25–1.43 (m, 4H), 1.67 (m, 3H), 2.09 (br q, *J* = 6.8 Hz, 2H), 5.72 (tq, *J* = 6.7, 1.7 Hz, 1H); ^{13}C NMR (63 MHz, $CDCl_3$) δ –1.9 (q), 14.0 (q), 14.3 (q), 22.5 (t), 28.1 (t), 31.6 (t), 135.6 (s), 139.5 (d); IR (neat) ν 1605 cm^{-1}.

(*E*)-(1-Methyl-2-cyclohexylethenyl)trimethylsilane (1d). A suspension of 1.30 g (15.0 mmol) of LiBr and 2.15 g (15.0 mmol) of CuBr in 30 mL of dry THF was cooled to –60 °C and 25 mL of a solution of cyclohexylmagnesium chloride in THF (0.6 M, 15.0 mmol) was added. After 30 min of stirring at –60 °C, 2.12 mL (15.0 mmol) of (trimethylsilyl)acetylene was added and the reaction mixture was stirred for 1.5 h at 0 °C and cooled again to –60 °C. After addition of 1.00 mL (17.5 mmol) of methyl iodide, the mixture was allowed to warm up overnight to room temperature. Workup was performed as for **1c** to yield, after Kugelrohr disillation, 2.08 g (71%) of **1d** as colorless liquid: ot 120 °C/18 Torr (lit.[29] ot 110 °C/14 Torr); ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.03 (s, 9H), 0.92–1.40 (m, 5H), 1.52–1.80 (m, 5H), 1.67 (d, *J* = 1.7 Hz, 3H), 2.24–2.45 (m, 1H), 5.51 (dq, *J* = 8.6, 1.7 Hz, 1H); ^{13}C NMR (63 MHz, $CDCl_3$) δ –2.0 (q), 14.3 (q), 26.0 (t), 26.1 (t), 32.8 (t), 37.0 (d), 133.5 (s), 145.2 (d); IR (neat) ν 1610 cm^{-1}.

(2-Chloro-1-cyclohexen-1-yl)methanol (5). To a solution of 31.0 g (424 mmol) of dimethylformamide in 80 mL trichloroethylene was added 46.0 g (300 mmol) of $POCl_3$ within 1 h, and the temperature was kept below 10 °C. The mixture was allowed to warm up to room temperature and a solution of 33.0 mL (326 mmol) of cyclohexanone in 80 mL of trichloroethylene was added within 45 min. After stirring for 3 h at 55–70 °C, the mixture was cooled by ice water and treated with a solution of 200 g of $NaOAc \cdot 3H_2O$ in 280 mL of water. The solution was kept at room temperature overnight, the layers were separated, the aqueous layer was extracted with trichloroethylene (3 × 50 mL), and the combined organic layers were washed with water (100 mL) and brine (2 × 100 mL) and dried (Na_2SO_4). On addition of 2 g of NaOAc, the solvent was removed by distillation at 45 °C and 100 Torr. The residue was dissolved in 100 mL of methanol, the pH was adjusted to 8–9 by using 10% aqueous NaOH, and 11.3 g (300 mmol) of $NaBH_4$ was added in small portions within 2 h while the mixture was cooled by means of an ice bath. The mixture was stirred overnight at room temperature, treated with water (400 mL), and extracted with ethyl acetate (3 × 100 mL), and the combined organic layers were washed with brine (50 mL), dried ($MgSO_4$), and evaporated (30 °C, 20 Torr). Distillation of the residue yielded 34.0 g (77%) of a colorless liquid: bp 61–62 °C/0.075 Torr (lit.[15] bp 83–84 °C/1.8 Torr); ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.55–1.80 (m, 4H), 2.10–2.25 (m, 3H), 2.25–2.40 (m, 2H), 4.21 (s, 2H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 22.1 (t), 23.7 (t), 28.0 (t), 33.8 (t), 63.1 (t), 128.9 (s), 132.5 (s); IR (neat) ν 3600–3050, 1660 cm^{-1}.

(2-(Trimethylsilyl)-1-cyclohexen-1-yl)methanol (1i). A mixture of 14.6 g (100 mmol) of **5**, 11.6 mL (55.0 mmol) of hexamethyldisilazane, and 2 drops of chlorotrimethylsilane was heated gradually to 140 °C until the gas evolution had ceased (4 h). After the solution was cooled to room temperature, the residual ammonia was removed at 20 °C and 20 Torr within 15 min and the crude silyl ether was kept under argon until needed.

To a mixture of 5.75 g (250 mmol) of sodium metal and 100 mL of dry toluene was added 19.0 mL (150 mmol) of chlorotrimethylsilane, and the mixture was stirred for 15 min. The above crude silyl ether was transfered into a dropping funnel by using 30 mL of dry toluene, and this solution was introduced within 20 min. The mixture was heated to reflux for 2 min under vigorous stirring and a lively reaction ensued. The heat source was removed and the reaction mixture was allowed to reach room temperature within 90 min. The solution was filtered over Celite, the deep blue residue was washed with toluene (3 × 20 mL) and methyl *tert*-butyl ether (20 mL), and the filtate was concentrated (50 °C/20 Torr). The residue was dissolved in 100 mL of THF, 100 mL of 1 M HCl was added, and the mixture was stirred for 8 h at room temperature. The layers were separated, the aqueous layer was extracted with methyl *tert*-butyl ether (3 × 50 mL), and the combined organic layers were washed with a saturated, aqueous $NaHCO_3$ solution (50 mL) and brine (50 mL), dried ($MgSO_4$), and concentrated (20 °C/20 Torr). Distillation of the residual liquid on a 10-cm Vigreux column afforded 13.9 g (76%) of a colorless oil: bp 64–65 °C/0.01 Torr; ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.13 (s, 9H), 1.30 (br s, 1H), 1.45–1.70 (m, 4H), 2.00–2.20 (m, 4H), 4.07 (s, 2H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 0.3 (q), 22.5 (t), 22.9 (t), 28.5 (t), 29.3 (t), 66.7 (t), 135.4 (s), 146.2 (s); IR (neat) ν 3620–3100, 1630 cm^{-1}. Anal. Calcd for $C_{10}H_{20}OSi$ (184.35): C, 65.15; H, 10.93. Found: C, 65.14; H, 11.22.

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(2-(Chloromethyl)-1-cyclohexen-1-yl)trimethylsilane (1j). In 3 mL of dry CCl_4 were dissolved 370 mg (2.00 mmol) of **1i** and 682 mg (2.60 mmol) of triphenylphosphine, and the solution was heated at reflux for 1 h. After the solution was cooled to room temperature, 10 mL of pentane was added, the precipitate was removed by filtration and washed with pentane (3 × 10 mL), and the filtrate was concentrated (20 °C/20 Torr). The residue was filtered over 5 g of silica gel (63–200 μm) by using pentane as eluant to yield 331 mg (82%) of a colorless liquid: ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.17 (s, 9H), 1.45–1.70 (m, 4H), 2.05–2.20 (m, 4H), 4.08 (s, 2H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 0.0 (q), 22.3 (t), 22.7 (t), 28.7 (t), 29.6 (t), 49.3 (t), 138.5 (s), 142.6 (s); IR (neat) ν 2950, 1625 cm^{-1}. Anal. Calcd for $C_{10}H_{19}ClSi$ (202.80): C, 59.23; H, 9.44. Found: C, 59.46; H, 9.92.

(2-Methyl-1-cyclohexen-1-yl)trimethylsilane (1k). A sample of 500 mg (13.2 mmol) of $LiAlH_4$ was suspended in 40 mL of dry THF and a solution of 2.22 g (11.0 mmol) of **1j** in 10 mL of dry THF was added dropwise within 30 min. The reaction mixture was stirred overnight at room temperature, methyl acetate (5 mL) and water (20 mL) were cautiously added, and the mixture was filtered over Celite under suction. The residue was washed with pentane (2 × 20 mL), the layers of the filtrate were separated, the aqueous layer was extracted with pentane (2 × 20 mL), and the combined organic layers were washed with water (20 mL) and brine (20 mL), dried ($MgSO_4$), and concentrated (20 °C/20 Torr). Kugelrohr distillation of the residue yielded 1.42 g (71%) of a colorless liquid: ot 120 °C/40 Torr (lit.[13b] ot 69 °C/9 Torr); ^{1}H NMR (250 MHz, $CDCl_3$) δ 0.11 (s, 9H), 1.42–1.62 (m, 4H), 1.72 (br s, 3H), 1.90–2.20 (m, 4H); ^{13}C NMR (63 MHz, $CDCl_3$): δ 0.0 (q), 22.9 (t), 23.0 (t). 23.9 (q), 29.0 (t), 33.1 (t), 128.9 (s), 143.3 (s). IR (neat) ν 1605 cm^{-1}.

Hydroxy-Epoxidation of Vinylsilanes. General Procedure A for Two-Step Operation. A solution of the vinylsilane (2–15 mmol) in 5–15 mL of dichloromethane, ca. 5 × 10^{-4} M in TPP, was photooxygenated at −5 to −10 °C in a test tube until TLC indicated complete conversion of the vinylsilane. The mixture was transfered to a round-bottomed flask and cooled in an ice bath, 0.5 g of 4-Å molecular sieves was added, and the solution was stirred for 10 min. After addition of 25 mol % of Ti(O-*i*-Pr)$_4$, stirring at 0 °C was continued until the hydroperoxide was converted completely (TLC). The mixture was decanted from the molecular sieves into an Erlenmeyer flask, and methyl *tert*-butyl ether (an amount equal to the dichloromethane employed) was used to wash the molecular sieves and added to the dichloromethane solution. Water [1 mL per mmol Ti(O-*i*-Pr)$_4$] was added and the mixture was stirred vigorously for 1–2 h. The precipitate was removed by filtration over Celite under suction and washed three times with methyl *tert*-butyl ether, and the filtrate was dried ($MgSO_4$) and concentrated (20 °C/20 Torr). The residue was purified by distillation, crystallization, or column chromatography.

(*R,*R**)-α-Methyl-2-(trimethylsilyl)oxiranemethanol (3a).**[6] By following general procedure, 1.92 g (15.0 mmol) of vinylsilane **1a** was photooxygenated for 6 h and subsequently allowed to react with Ti(O-*i*-Pr)$_4$ for an additional 6 h. Kugelrohr distillation gave 1.56 g of **3a** as a colorless liquid: ot 140 °C/28 Torr; diastereomeric ratio (*R**,*R**/*R**,*S**) = 93:7. **(*R**,*R**)-3a**: ^{1}H NMR (250 MHz, $CDCl_3$) δ 0.08 (s, 9H), 1.18 (d, *J* = 6.4 Hz, 3H), 2.20 (s, 1H), 2.54 (d, *J* = 4.9 Hz, 1H), 2.90 (d, *J* = 4.9 Hz, 1H), 4.01 (q, *J* = 6.3 Hz, 1H); ^{13}C NMR (63 MHz, $CDCl_3$) δ −3.1 (q), 19.3 (q), 45.8 (t), 54.8 (s), 65.3 (d); IR (neat) ν 3650–3300 cm^{-1}. **(*R**,*S**)-3a**: ^{1}H NMR (250 MHz, $CDCl_3$) δ = 0.11 (s, 9H), 1.24 (d, *J* = 6.7 Hz, 3H), 2.20 (s, 1H), 2.63 (d, *J* = 4.9 Hz, 1H), 2.69 (d, *J* = 4.9 Hz, 1H), 3.49 (q, *J* = 6.6 Hz, 1H); ^{13}C NMR (63 MHz, $CDCl_3$) δ −2.3 (q), 20.1 (q), 48.7 (t), 56.1 (s), 73.4 (d).

(*R,*R**)-α-Methyl-2-(dimethylphenylsilyl)oxiranemethanol (3b).** By following general procedure A, 476 mg (2.50 mmol) of **1b** was photooxygenated for 7 h and subsequently allowed to react with Ti(O-*i*-Pr)$_4$ for 4 h. Column chromatography on silica gel [45 g, petroleum ether (bp 56–60 °C)/methyl *tert*-butyl ether (2:1) as eluant] gave 368 mg (66%) of **3b** as a colorless oil: diastereomeric ratio (*R**,*R**/*R**,*S**) = 97:3. **(*R**,*R**)-3b**: ^{1}H NMR (250 MHz, $CDCl_3$) δ 0.39 (s, 3H), 0.40 (s, 3H), 1.04 (d, *J* = 6.3 Hz, 3H), 2.11 (s, 1H), 2.58 (d, *J* = 4.9 Hz, 1H), 2.92 (d, *J* = 4.9 Hz, 1H), 3.97 (q, *J* = 6.3 Hz, 1H), 7.35–7.42 (m, 2H), 7.54–7.61 (m, 3H); ^{13}C NMR (63 MHz, $CDCl_3$) δ −5.0 (q), −4.6 (q), 19.3 (q), 45.9 (t), 54.7 (s), 65.4 (d), 127.9 (d), 129.7 (d), 134.1 (d), 135.4 (s); IR (neat) ν 3600–3140 cm^{-1}. **(*R**,*S**)-3b**: ^{1}H NMR (250 MHz, $CDCl_3$) δ 0.38 (s, 6H), 1.12 (d, *J* = 6.7 Hz, 3H), 1.26 (s, 1H), 2.59 (d, *J* = 4.9 Hz, 1H), 2.71 (d, *J* = 4.9 Hz, 1H), 3.53 (q, *J* = 6.7 Hz, 1H), 7.31–7.44 (m, 3H), 7.52–7.60 (m, 2H); ^{13}C NMR (63 MHz, $CDCl_3$) δ −4.0 (q), −3.9 (q), 20.2 (q), 48.7 (t), 55.9 (s), 73.1 (d), 127.8 (d), 129.4 (d), 134.1 (d), 136.3 (s). Anal. Calcd for $C_{12}H_{18}O_2Si$ (222.4): C, 64.82; H, 8.16. Found: C, 64.64; H, 8.19.

(*R,*R**)-α-Butyl-2-(trimethylsilyl)oxiranemethanol (3c).**[6] By following general procedure A, 466 mg (2.73 mmol) of **1c** was photooxygenated for 4 h and subsequently allowed to react with Ti(O-*i*-Pr)$_4$ for 7 h. Column chromatography on silica gel [45 g, petroleum ether (bp 50–60 °C)/methyl *tert*-butyl ether (3:1) as eluant] gave 326 mg (59%) of **3c** as a colorless oil: ^{1}H NMR (250 MHz, $CDCl_3$) δ 0.09 (s, 9H), 0.90 (t, *J* = 6.7 Hz, 3H), 1.20–1.70 (m, 6H), 2.11 (s, 1H), 2.56 (d, *J* = 4.9 Hz, 1H), 2.92 (d, *J* = 4.9 Hz, 1H), 3.87 (m, 1H); ^{13}C NMR (63 MHz, $CDCl_3$) δ −3.1 (q), 14.0 (q), 22.7 (t), 27.9 (t), 33.4 (t), 46.1 (t), 53.9 (s), 69.1 (d); IR (neat) 3650–3400 cm^{-1}.

(*R,*R**)-α-Cyclohexyl-2-(trimethylsilyl)oxiranemethanol (3d).** By following general procedure A, 980 mg (5.00 mmol) of **1d** was photooxygenated for 6 h and subsequently allowed to react with Ti(O-*i*-Pr)$_4$ for 8 h. Column chromatography on silica gel [80 g, petroleum ether (bp 50–60 °C)/methyl *tert*-butyl ether (10:1) as eluent] gave 644 mg (56%) of **3d** as colorless needles; mp 44–45 °C; ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.08 (s, 9H), 1.10–1.31 (m, 4H), 1.42–1.85 (m, 7H), 1.93 (br s, 1H), 2.57 (d, *J* = 5.0 Hz, 1H), 2.98 (d, *J* = 5.0 Hz, 1H), 3.72 (br s, 1H); ^{13}C NMR (50 MHz, $CDCl_3$) δ −3.1 (q), 26.0 (t), 26.2 (2t), 26.9 (t), 30.9 (t), 40.7 (d), 46.3 (t), 52.8 (s), 73.4 (d); IR (CCl_4) ν 3560 cm^{-1}. Anal. Calcd for $C_{12}H_{24}O_2Si$ (228.4): C, 63.10; H, 10.59. Found: C, 63.17; H, 10.84.

α,α-Dimethyl-2-(dimethylphenylsilyl)oxiranemethanol (3e). By following general procedure A, 409 mg (2.00 mmol) of **1e** was photooxygenated for 2.5 h and subsequently allowed to react with Ti(O-*i*-Pr)$_4$ for 6 h. Column chromatography on silica gel [30 g, petroleum ether (bp 50–60 °C)/methyl *tert*-butyl ether (3:1) as eluant] gave 331 mg (70%) of **3e** as a colorless oil: ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.42 (s, 3H), 0.44 (s, 3H), 1.07 (s, 3H), 1.20 (s, 3H), 2.10 (br s, 1H), 2.50 (d, *J* = 5.1 Hz, 1H), 2.89 (d, *J* = 5.1 Hz, 1H), 7.20–7.40 (m, 3H), 7.50–7.60 (m, 2H); ^{13}C NMR (50 MHz, $CDCl_3$) δ −3.2 (q), 26.0 (q), 29.3 (q), 47.9 (t), 57.3 (s), 70.8 (s), 127.8 (d), 129.5 (d), 134.2 (d), 137.0 (s); IR (neat) ν 3550–3200 cm^{-1}. Anal. Calcd for $C_{13}H_{20}O_2Si$ (236.4): C, 66.05; H, 8.53. Found: C, 65.84; H, 8.37.

(1α,2β,5β)-1-(Trimethylsilyl)-6-oxabicyclo[3.1.0]hexan-2-ol (3f). By following general procedure A, 1.40 g (10.0 mmol) of **1f** was photooxygenated for 4.5 h and subsequently allowed to react with Ti(O-*i*-Pr)$_4$ for 4 h. Kugelrohr distillation yielded 1.21 g (70%) of **3f** as a colorless liquid, ot 100 °C/0.1 Torr, that solidified as a colorless solid: mp 39–40 °C; ^{1}H NMR (250 MHz, $CDCl_3$) δ 0.11 (s, 9H), 1.10–1.34 (m, 1H), 1.49–1.63 (m, 1H), 1.82–1.94 (m, 2H), 2.09 (dd, *J* = 14.0, 8.2 Hz, 1H), 3.26 (br s, 1H), 4.17 (dt, *J* = 10.4, 7.9 Hz, 1H); ^{13}C NMR (63 MHz, $CDCl_3$) δ −3.2 (q), 26.3 (t), 27.6 (t), 60.7 (d), 61.4 (s), 76.1 (d); IR (CCl_4) ν 3560 cm^{-1}. Anal. Calcd for $C_8H_{16}O_2Si$ (172.3): C, 55.77; H, 9.36. Found: C, 56.10; H, 9.72.

General Procedure B for One-Step Operation. A solution of the vinylsilane (2–40 mmol) and 25 mol % of Ti(O-*i*-Pr)$_4$ in dichloromethane (5–15 mL for reactions in the test tube, 90 mL in the immersion lamp apparatus) and ca. 5 × 10^{-4} M in TPP was photooxygenated at −5 to −10 °C in the presence of 0.5–2 g of 4-Å molecular sieves. TLC monitoring indicated complete conversion of the vinylsilane and intermediary hydroperoxide and workup was performed as described above.

(1α,2β,6β)-1-(Trimethylsilyl)-7-oxabicyclo[4.1.0]heptan-2-ol (3g). By following general procedure B, 1.75 g (11.3 mmol) of **1g** was photooxygenated for 20 h in the immersion lamp apparatus in the presence of Ti(O-*i*-Pr)$_4$ to afford after column chromatography [100 g of silica gel, petroleum ether (bp 30–50 °C)/methyl *tert*-butyl ether (1:1) as eluant] 1.47 g (70%) of **3g** as a colorless oil, which solidified as colorless cubes, mp 38–39 °C. On a larger scale, 6.17 g (40.0 mmol) of **1g** yielded after distillation 4.73 g (63%) of **3g**: bp 54–56 °C/0.1 Torr; ^{1}H NMR (250 MHz, $CDCl_3$) δ 0.08 (s, 9H), 1.05–2.00 (m, 7H), 3.18 (dd, *J* = 3.4, 1.2 Hz, 1H), 3.98 (m, 1H); ^{13}C NMR (63 MHz, $CDCl_3$) δ

-3.6 (q), 17.0 (t), 24.0 (t), 29.8 (t), 57.3 (s), 58.7 (d), 67.7 (d); IR (CCl_4) ν 3610, 3580 cm^{-1}. Anal. Calcd for $C_9H_{18}O_2Si$ (186.3): C, 58.04; H, 9.74. Found: C, 58.34; H, 9.94.

(1α,2β,8β)-1-(Trimethylsilyl)-9-oxabicyclo[6.1.0]nonan-2-ol (3h). By following general procedure **B**, 902 mg (5.00 mmol) of **1h** was photooxygenated for 16 h in the immersion lamp apparatus in the presence of Ti(O-*i*-Pr)$_4$. Crystallization from pentane gave 776 mg (72%) of **3g** as colorless cubes: mp 57–58 °C; ^{1}H NMR (250 MHz, $CDCl_3$) δ 0.06 (s, 9H), 1.07–1.25 (m, 1H), 1.34–1.66 (m, 5H), 1.74–1.90 (m, 1H), 1.97–2.23 (m, 3H), 2.47 (br s, 1H), 2.80 (dd, J = 10.6, 4.6 Hz, 1H), 4.36 (m, 1H); ^{13}C NMR (63 MHz, $CDCl_3$) δ -3.1 (q), 19.2 (t), 24.3 (t), 24.5 (t), 25.7 (t), 33.4 (t), 57.6 (s), 60.1 (d), 67.4 (d); IR (CCl_4) ν 3540 cm^{-1}. Anal. Calcd for $C_{11}H_{22}O_2Si$ (214.4): C, 61.62; H, 10.34. Found: C, 61.94, H 10.66.

(1α,2β,6β)-2-(Chloromethyl)-1-(trimethylsilyl)-7-oxabicyclo[4.1.0]heptan-2-ol (3j). By following general procedure **B**, 304 mg (1.50 mmol) of **1j** was photooxygenated for 8 h in a test tube in the presence of Ti(O-*i*-Pr)$_4$. Crystallization of the solid residue from pentane/methyl *tert*-butyl ether (5:1) gave 205 mg (58%) of **3j** as colorless needles: mp 99.5–100.5 °C; ^{1}H NMR (250 MHz, $CDCl_3$) δ 0.12 (s, 9H), 1.27–1.43 (m, 1H), 1.46–1.61 (m, 1H), 1.62–1.72 (m, 2H), 1.72–1.86 (m, 1H), 1.93–2.10 (m, 1H), 2.27 (s, 1H), 3.14 (dd, J = 3.2, 1.2 Hz, 1H), 3.62 (dd, J = 11.3, 0.6 Hz, 1H), 3.82 (d, J = 11.3 Hz, 1H); ^{13}C NMR (63 MHz, $CDCl_3$) δ -1.6 (q), 17.0 (t), 22.1 (t), 30.4 (t), 49.4 (t), 58.5 (s), 58.9 (d), 75.1 (s); IR (CCl_4) ν 3580, 3560 cm^{-1}. Anal. Calcd for $C_{10}H_{19}ClO_2Si$ (234.8): C, 51.15; H, 8.15. Found: C, 51.22, H, 7.90.

(1α,2β,6β)-2-Methyl-1-(trimethylsilyl)-7-oxabicyclo[4.1.0]heptan-2-ol (3k). By following general procedure **B**, 336 mg (2.00 mmol) of **1k** was photooxygenated for 6 h in a test tube in the presence of Ti(O-*i*-Pr)$_4$. Crystallization of the residue from pentane gave 172 mg (43%) of **3k** as colorless needles: mp 56–57 °C; ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.12 (s, 9H), 1.16–1.84 (m, 5H), 1.36 (s, 3H), 1.91–2.07 (m, 1H), 2.16 (br s, 1H), 3.15 (dd, J = 3.4, 1.3 Hz, 1H); ^{13}C NMR (50 MHz, $CDCl_3$) δ -1.6 (q), 17.6 (t), 23.1 (t), 25.5 (q), 37.1 (t), 59.1 (d), 60.2 (s), 71.5 (s); IR (CCl_4) ν 3570, 3540, 3500–3300 cm^{-1}. Anal. Calcd for $C_{10}H_{20}O_2Si$ (200.3): C, 59.95; H, 10.06. Found: C, 60.16, H, 10.34.

Preparation of Authentic Samples. 3-(Trimethylsilyl)-3-buten-2-ol (2a).[30] A solution of 5.13 g (40.0 mmol) of **1a** and 40 mg of Rose Bengal in 90 mL of methanol was photooxygenated for 5 h in the immersion lamp apparatus at -5 °C. The reaction mixture was transfered into a round-bottomed flask and cooled by means of an ice bath, and 1.70 g (45 mmol) of $NaBH_4$ was added in portions within 30 min. Stirring was continued overnight at room temperature. Water (100 mL) was added and the mixture was extracted with methyl *tert*-butyl ether (5 × 30 mL). The combined organic layers were washed with a saturated, aqueous $NaHCO_3$ solution (30 mL) and brine (30 mL) and dried ($MgSO_4$). The solvent was removed by distillation on a 10-cm Vigreux column. Distillation of the residue yielded 3.04 g (53%) of **2a** as a colorless liquid: bp 86–88 °C/58 Torr (lit.[30] bp 72–74 °C/28 Torr); ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.14 (s, 9H), 1.29 (d, J = 6.4 Hz, 3H), 1.55 (br s, 1H), 4.47 (br q, J = 6.1 Hz, 1H), 5.37 (dd, J = 2.5, 1.1 Hz, 1H), 5.80 (dd, J = 2.5, 1.4 Hz, 1H); ^{13}C NMR (50 MHz, $CDCl_3$) δ -0.7 (q), 24.0 (q), 71.8 (d), 122.7 (t), 156.6 (s); IR (neat) ν 3620–3140 cm^{-1}.

(30) Chan, T. H.; Ong, B. S. *J. Org. Chem.* **1978**, *43*, 2994–3001.

3-(Dimethylphenylsilyl)-3-buten-2-ol (2b).[31] As above, 500 mg (2.63 mmol) of **1b** was photooxygenated for 6 h to afford after Kugelrohr distillation 285 mg (52%) of **2b** as a colorless liquid: ot 125 °C/0.1 Torr; ^{1}H NMR (250 MHz, $CDCl_3$) δ 0.44 (s, 3H), 0.46 (s, 3H), 1.21 (d, J = 6.5 Hz, 3H), 1.57 (br s, 1H), 4.45 (br q, J = 6.3 Hz, 1H), 5.47 (dd, J = 2.3, 1.1 Hz, 1H), 5.92 (dd, J = 2.3, 1.5 Hz, 1H), 7.34–7.41 (m, 3H), 7.52–7.59 (m, 2H); ^{13}C NMR (63 MHz, $CDCl_3$) δ -2.2 (q), -2.1 (q), 24.1 (q), 71.7 (d), 124.7 (t), 127.9 (d), 129.1 (d), 133.9 (d), 138.4 (s), 155.0 (s); IR (neat) ν 3670–3140 cm^{-1}. Anal. Calcd for $C_{12}H_{18}OSi$ (206.4): C, 69.84; H, 8.79. Found: C, 69.59, H, 8.86.

(*R,*R**/*R**,*S**)-3a.** A mixture of 288 mg (2.00 mmol) of **2a** and 300 mg of $NaHCO_3$ in 7 mL of dichloromethane was cooled by means of an ice bath and 542 mg of *m*-CPBA (70%, 2.20 mmol) was added in portions. Stirring at 0 °C was continued for 17 h, water (20 mL) was added, the layers were separated, the aqueous layer was extracted with dichloromethane (3 × 20 mL), and the combined organic layers were washed with an aqueous NaS_2O_3 solution (20 mL), a saturated, aqueous $NaHCO_3$ solution (5 × 20 mL), and brine (20 mL), dried ($MgSO_4$), and concentrated to afford 265 mg (83%) of **3a**; diasteromeric ratio *R**,*R**/*R**,*S** was 67:33.

(*R,*R**/*R**,*S**)-3b.** As above, 84.0 mg (0.400 mmol) of **2b** was allowed to react with 100 mg (70%, 0.400 mmol) of *m*-CPBA to give 68.0 mg (76%) of **3b**; diastereomeric ratio *R**,*R**/*R**,*S** was 65:35.

(1α,2β,6β/1α,2α,6β)-3g. As above, a mixture of 170 mg (1.00 mmol) of **2g**,[5b] 170 mg of $NaHCO_3$, and 251 mg (70%, 102 mmol) of *m*-CPBA was allowed to react at room temperature for 48 h to yield 174 mg (94%) of **3g**; diastereomeric ratio 1α,2β,6β/1α,2α,6β was 75:25.

(1α,2α,6β)-3g: ^{1}H NMR (250 MHz, $CDCl_3$) δ 0.08 (s, 9H), 1.00–2.00 (m, 7H), 3.03 (m, 1H), 4.03 (m, 1H); ^{13}C NMR (63 MHz, $CDCl_3$) δ -2.9 (q), 14.6 (t), 24.3 (t), 30.3 (t), 55.6 (d), 56.2 (s), 68.9 (d).

Desilylation of the Epoxy Alcohols 3g,h. (1α,2α,6α)-7-Oxabicyclo[4.1.0]heptan-2-ol (8g). A sample of 315 mg (1.00 mmol) of *n*-$Bu_4NF{\cdot}3H_2O$ was dissolved in 5 mL of dry THF, 200 mg of molecular sieves was added, and the mixture was stirred for 10 min at room temperature. To this was added 186 mg (1.00 mmol) of (1α,2β,6β)-**3g**, and stirring was continued for 4 d. The mixture was passed through a small column of silica gel (12 g) by using methyl *tert*-butyl ether as eluant to afford 70.0 mg (61%) of **8g** as a colorless oil. The spectral data were identical with those of an authentic sample prepared by the literature method.[18]

(1α,2α,8α)-9-Oxabicyclo[6.1.0]heptan-2-ol (8h). As above, 214 mg (1.00 mmol) of (1α,2β,8β)-**3h** was allowed to react for 24 h to yield 140 mg (98%) of **8h** as a colorless oil. The spectral data were identical with those of an authentic sample prepared by the literature method.[20]

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