

32. Syntheses of α,β -Epoxy Silyl Ketones

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The synthesis of the α,β -epoxy-acylsilanes **1** and **2** starting from the allylic silyl alcohols (*E*)- and (*Z*)-**3**, respectively, by epoxidation with *t*-BuOOH/VO(acac)₂ followed by oxidation with *Collins* reagent (CrO₃/pyridine) in up to 70% overall yields, is described. The acid-catalyzed rearrangement of the epoxy-silyl alcohols **4A** + **B** und **5A** + **B** led to the novel unstable diastereoisomeric α -silyl- β -hydroxy-aldehydes **9** and **10**, respectively. The structure of **10** was established by X-ray crystal-structure analysis of the corresponding alcohol **11**.

1. Introduction. – As a part of our studies of the intramolecular trapping of silyloxy-carbenes by reaction with various neighboring groups [2] [3], we investigated the photochemistry and thermolysis of α,β -epoxy-acylsilanes. Here, we describe the syntheses of **1** and **2** (*Scheme 1*) as two examples of this hitherto unknown class of compounds. The photochemical and thermal behavior of **1** and **2** will be discussed in a forthcoming paper.

2. Results and Discussion. – In the course of the syntheses of the cyclopropyl silyl ketones analogous to **1** and **2**, an efficient method for the preparation of the allylic silyl alcohols (*E*)- and (*Z*)-**3** (*Scheme 1*) was established [4]. Consequently, as a key step of the synthesis of **1** and **2**, (*E*)- and (*Z*)-**3** were epoxidized with *t*-BuOOH/VO(acac)₂ in benzene [5]. From first experiments, however, the desired epoxy-silyl alcohols **4A** + **B**⁶⁾ and **5A** + **B**⁶⁾ could not be isolated. Instead, a mixture of extremely labile aldehydes was formed. Therefore, the epoxidation was carried out at 4° and the mixture worked up carefully, avoiding any kind of acid. Thus, extraction of the hexane/Et₂O solution of the epoxides with aq. FeSO₄ to decompose excess *t*-BuOOH was omitted, the mixture was filtered through SiO₂, impregnated with Et₃N, and the filtrate washed with sat. aq. NaCl (see *Exper. Part*). By this procedure, the diastereoisomeric epoxy-silyl alcohols **4A** + **B** (3:2 mixture) and **5A** + **B** (4:1 mixture) were isolated. Due to their instability, the crude **4A** + **B** and **5A** + **B** were immediately further oxidized. Hence, reaction of

¹⁾ Taken in part from the Ph.D. thesis of M.E.S. [1].

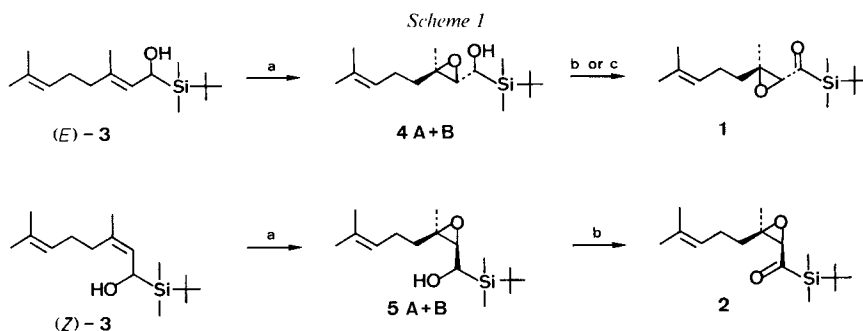
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³⁾ X-Ray analysis.

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⁵⁾ Presented in part by B.F. at the 'Herbstversammlung der Schweizerischen Chemischen Gesellschaft', October 18, 1985, Bern.

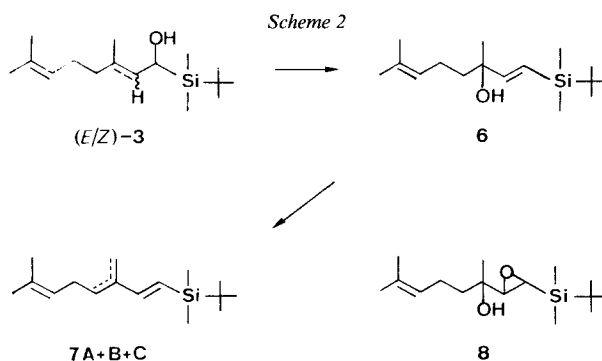
⁶⁾ The terms **A**, **B**, and **C** are used for the description of diastereoisomers, whose configurations were not assigned conclusively.



a) *t*-BuOOH/VO(acac)₂, b) DCC/DMSO, c) CrO₃/pyridine.

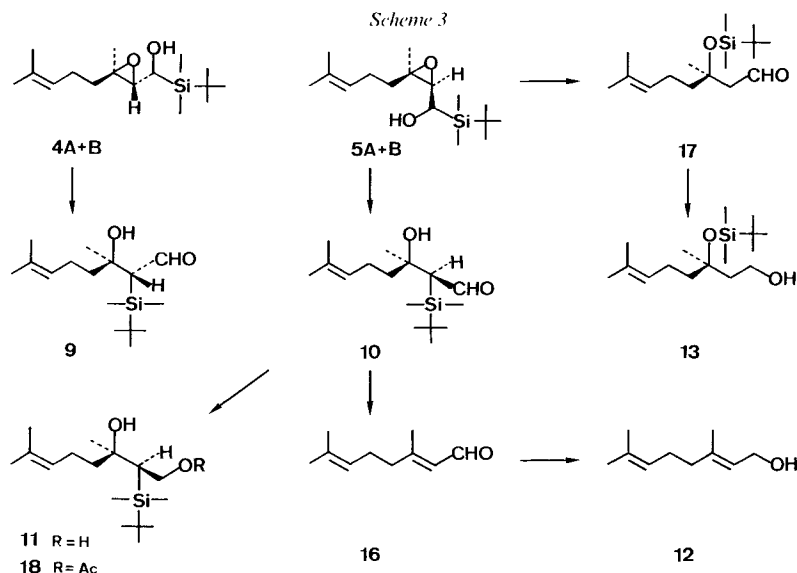
4A + B and **5A + B** with DCC/DMSO [6] gave the diastereoisomeric α,β -epoxyacylsilanes **1** (19%) and **2** (20%), respectively. Oxidation of **4A + B** with CrO₃/pyridine [7] gave **1** even in 69% yield⁷⁾.

For a better understanding of the epoxidation followed by secondary reactions, we investigated the side reactions leading to the aforementioned unstable aldehydes. It was found that already the allylic alcohols (*E/Z*)-**3** are quite unstable even at room temperature, undergoing allylic rearrangement to the isomer **6** (Scheme 2). On reaction of (*E/Z*)-**3** with TsOH, in addition to **6** (64%), dehydration products **7A + B + C**⁶⁾ (26%) were obtained. However, in the reaction mixture of (*E/Z*)-**3** with *t*-BuOOH/VO(acac)₂, neither **6** nor **7A + B + C** as well as the hypothetical epoxide **8** could be detected (Scheme 2).



This finding indicates that the alcohols (*E/Z*)-**3** are rapidly epoxidized to **4A + B** and **5A + B**, which subsequently undergo rearrangement to labile aldehydes. The compounds, for which the structures **9** and **10** of novel α -silyl- β -hydroxy-aldehydes were derived (Scheme 3), could be obtained by treatment of the epoxides **4A + B** and **5A + B** with oxalic acid as a catalyst. For structure elucidation, the crude mixture obtained on epoxidation of (*Z*)-**3** (containing the aldehyde **10**) was reduced with LiAlH₄ affording the alcohols **11** (14%), **12** (29%), **13** (2%, see Scheme 3), and, in addition, a complex mixture of alcohols of unknown structure (29%).

⁷⁾ Due to the low amounts of pure **5A + B** in our hands, the oxidation was not repeated with CrO₃/pyridine, the reagent which would have led to a higher yield of **2**.



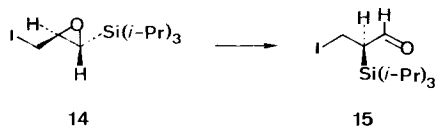
The structure of **11** indicates unequivocally that, on epoxidation of (*E/Z*)-**3**, the desired epoxy alcohols **5A + B** were formed, which, however, rapidly rearranged to the aldehyde **10**. Its formation may be explained by an initial C–O bond cleavage, leading to a stabilized intermediate with a positive charge in β -position to the silyl substituent followed by a 1,2-C,C migration of the *t*-Bu(Me)₂Si group⁸⁾.

The aldol **10** may undergo a '*syn*'-elimination of *t*-Bu(Me)₂SiOH leading to **16**, which, after reduction (LiAlH₄), was detected as geraniol (**12**). The alcohol **13**, the reduction product of the aldehyde **17**, was a minor product. Alternatively to **10**, the formation of the isomeric aldehyde **17** arose from a 1,3-C,O migration of the *t*-Bu(Me)₂Si group [9].

3. Spectroscopic Features of the Silyl Ketones 1 and 2, and the Alcohol 11. – In particular, compounds **1** and **2** show IR bands shifted to extremely long wavelengths (1635–1640 cm⁻¹). In the UV spectra, the expected structured n,π^* bands in the region of 370–410 nm are observed. In the ¹H-NMR spectra, **1** and **2** show s at 3.72 and 3.63 ppm, respectively, corresponding to H–C(2). In the ¹³C-NMR spectra, the signals of the C=O groups are shifted downfield to 242 ppm. In comparison, the methyl ketones corresponding to **1** and **2** show IR bands at *ca.* 1705 cm⁻¹, UV maxima at *ca.* 290 nm, and in the ¹³C-NMR spectra, signals for the C=O group at *ca.* 205 ppm [1]. For complete spectral data of **1** and **2** as well as for the other new compounds, see *Exper. Part*.

On the basis of the spectral data, the structure of **11** could not be assigned unequivocally. Evidence for a primary and a tertiary OH group was given by the reaction of **11** with Ac₂O/pyridine, leading to the mono-acetate **18** (Scheme 3). The position of the *t*-Bu(Me)₂Si group (C-linkage) and the relative configuration of **11** was finally established by X-ray analysis (see below).

⁸⁾ A similar rearrangement was reported by Muchowski *et al.* [8] on treatment of the epoxide **14** with SiO₂ leading to **15**.



4. X-Ray Analysis of 11. – Triclinic space group $P\bar{1}$, $Z = 2$, with cell dimensions $a = 8.796(2)$, $b = 9.370(2)$, $c = 12.905(6)$ Å, $\alpha = 66.10(3)$, $\beta = 80.41(3)$, $\gamma = 74.77(2)^\circ$. Intensities were measured at r.t. with an *Enraf Nonius CAD4* diffractometer equipped with a graphite monochromator ($\text{MoK}\alpha$, $\lambda = 0.7107$ Å). Of the 3279 independent reflections ($\theta \leq 25^\circ$), 2330 with $I > 3 \sigma(I)$ were used in the refinement. The structure was solved by direct methods with a pre-release version of SHELX 86 [10] and refined by full-matrix least-squares analysis (SHELX 72 [11], XRAY 72 [12]). A modified weighting scheme [13] with $r = 6$ Å² was used in the final refinement cycles. The refinement converged at $R = 0.039$, $R_w = 0.047$. Positions of the OH H-atoms were displaced along the O–H vectors to give O–H distances of about 0.9 Å. Atomic positional and anisotropic displacement parameters (H-atoms isotropic) are deposited with the *Cambridge Crystallographic Data Centre*, Cambridge, England.

The molecule does not show any exceptional structural features. Some discrepancies between observed bond lengths and corresponding standard values are associated with large atomic displacement parameters (C-atoms of the Me groups attached to the Si-atom and double bond). The two OH groups are involved in three H-bonds; one intramolecular $\text{O}(1) \cdots \text{O}(2)$ (Fig. 1) $d = 2.61$ Å and two intermolecular $\text{O}(1) \cdots \text{O}(1, -x, 1-y, 1-z)$

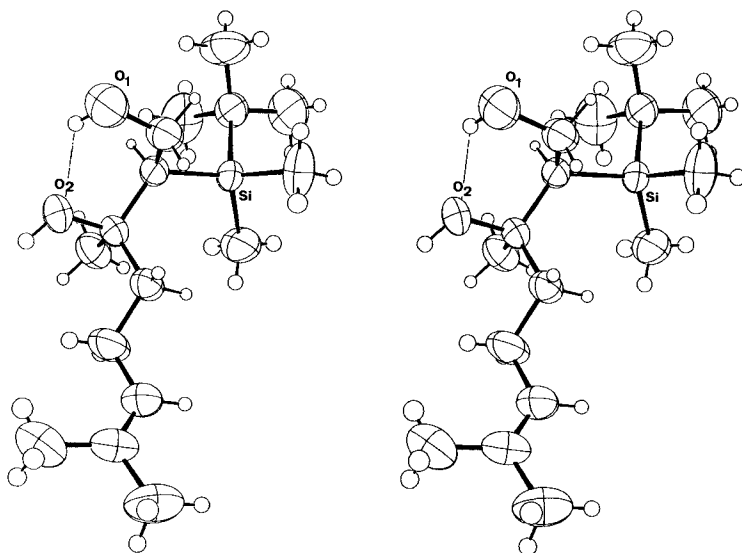


Fig. 1. Stereoscopic view of **11**. Vibrational ellipsoids at the 50% level, ORTEP [14].

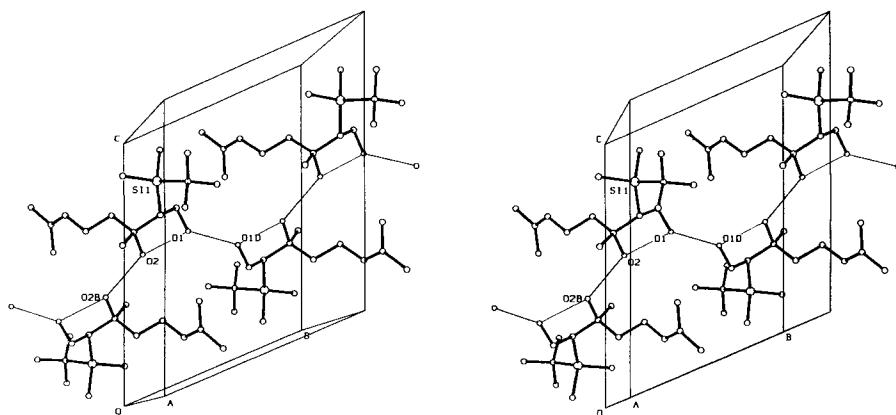


Fig. 2. Stereoscopic view of the unit cell of **11**. PLUTO [15].

$d = 2.73 \text{ \AA}$, and $\text{O}(2) \cdots \text{O}(2, -x, -y, 1-z) d = 2.82 \text{ \AA}$, both across inversion centers of symmetry. The three H-bonds form a chain through the crystal along the b axis (Fig. 2). In an ordered structure of the assumed space group $P\bar{1}$, there would be two H-atoms between the $\text{O}(2)$ -atoms of the intermolecular H-bonds and none between the $\text{O}(1)$ -atoms. With the available data, it is not possible to distinguish between an ordered structure in $P1$ and the disordered one in $P\bar{1}$ with two types of chains. In the first type, the H-atom on $\text{O}(1)$ forms the intermolecular H-bond, and the H-atom on $\text{O}(2)$ the intramolecular contact. In the second type, the inter- and intramolecular H-bonds are interchanged.

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Experimental Part

General. See [2]. $^1\text{H-NMR}$ spectra were measured in CDCl_3 solns. on a *Bruker WP-80 CW* instrument (80 MHz), or exceptionally (as indicated below) on a *Bruker WM 300* instrument (300 MHz), as well as the ^{13}C - and the $^{29}\text{Si-NMR}$.

1. Preparation of 1 and 2. – 1.1. *Epoxidation of (E/Z)-3*. 1.1.1. *Epoxidation of (E)-3*. Under Ar, a soln. of *(E)-3* [4] (3.21 g, 11.95 mmol) in abs. benzene (160 ml, filtered through Al_2O_3 super B) was cooled to 4° , until 2/3 of the soln. was frozen. After the addition of $\text{VO}(\text{acac})_2$ (66 mg, 0.25 mmol), a soln. of *t*-BuOOH (1.53 ml, 80%, 12.16 mmol) in abs. benzene (33 ml) was added during 20 min. After stirring for 20 min at 4° , a soln. of *t*-BuOOH (0.31 ml, 80%, 2.46 mmol) in benzene (6 ml) and $\text{VO}(\text{acac})_2$ (66 mg, 0.25 mmol) was added. The resulting deep red soln. was stirred for 2 h at 5° until *(E)-3* was fully converted (TLC). The soln. was worked up by the addition of hexane/ Et_2O (1:1) and then filtered through a sintered funnel (5 cm, packed with a 1-cm layer of *Celite* and a 2-cm layer of SiO_2 slurry in hexane/ Et_2O (1:1) and 1% of Et_3N). Further workup with sat. aq. NaCl and MgSO_4 afforded crude **4A + B** (3.40 g) which was immediately further processed. An anal. sample of *(E)-4A + B* was distilled ($120^\circ/0.06 \text{ Torr}$).

(2RS,3RS)-1-[*(tert-Butyl)dimethylsilyl*]-2,3-epoxy-3,7-dimethyl-6-octen-1-ol (**4A + B**; mixture of 2 diastereoisomers, ca. 3:2). B.p. $120^\circ/0.06 \text{ Torr}$. IR: 3580w, 3470w (br.), 2950s, 2930s, 2880s, 2850s, 1675w, 1455s, 1380s, 1360m, 1330w, 1245s, 1180w, 1150w, 1105w, 1070m, 1005m (sh), 980m, 935m, 905m, 890m. $^1\text{H-NMR}$ (80 MHz): 0.03, 0.08, 0.13 (3s, 2 $\text{CH}_3\text{-Si}$); 1.00 (s, *t*-Bu); 1.31, 1.41 (2s, $\text{CH}_3\text{-C}(3)$); 1.64, 1.70 (2s, $\text{CH}_3\text{-C}(7)$, 3 $\text{H-C}(8)$); 1.10–1.83 (m, 2 $\text{H-C}(4)$); 1.83–2.33 (m, 2 $\text{H-C}(5)$); 3.20 (*AB*, isomer A, $J = 10$, $\delta_A = 3.00$, $\delta_B = 3.40$, $\text{H-C}(1)$, $\text{H-C}(2)$); 3.23 (*AB*, isomer B, $J = 8$, $\delta_A = 2.85$, $\delta_B = 3.59$, $\text{H-C}(1)$, $\text{H-C}(2)$); 4.95–5.20 (m, $\text{H-C}(6)$). MS: 152 (1, $M^+ - \text{C}_6\text{H}_{16}\text{OSi}$), 101 (25), 75 (100), 69 (32), 59 (13), 43 (15), 41 (27).

1.1.2. *Epoxidation of (Z)-3*. The analogous reaction of *(Z)-3* (266 mg, 0.99 mmol) in abs. benzene (13 ml) with $\text{VO}(\text{acac})_2$ and *t*-BuOOH (0.2 ml, 80%, 1.58 mmol) in abs. benzene (3.7 ml) afforded **5A + B** (282 mg). An anal. sample was distilled ($120^\circ/0.06 \text{ Torr}$).

(2RS,3SR)-1-[*(tert-Butyl)dimethylsilyl*]-2,3-epoxy-3,7-dimethyl-6-octen-1-ol (**5A + B**; mixture of diastereoisomers, 4:1). B.p. $120^\circ/0.06 \text{ Torr}$. IR: 3580w, 3490w (br.), 2950s, 2930s, 2890s, 2860s, 1675m, 1465s, 1460s, 1445s, 1405m, 1390m, 1375s, 1360m, 1340m, 1245s, 1190w, 1155w, 1110m, 1100m, 1060w, 1005m, 985m, 940m, 890m. $^1\text{H-NMR}$ (80 MHz): 0.01, 0.06, 0.11 (3s, 2 $\text{CH}_3\text{-Si}$); 0.99 (s, *t*-Bu); 1.26, 1.34 (2s, $\text{CH}_3\text{-C}(3)$); 1.64, 1.70 (2s, $\text{CH}_3\text{-C}(7)$, 3 $\text{H-C}(8)$); 1.10–1.83 (m, 2 $\text{H-C}(4)$); 1.83–2.33 (m, 2 $\text{H-C}(5)$); 3.04 (*AB*, isomer A, $J = 8$, $\delta_A = 2.63$, $\delta_B = 3.45$, $\text{H-C}(1)$, $\text{H-C}(2)$); 3.18 (*AB*, isomer B, $J = 10$, $\delta_A = 2.95$, $\delta_B = 3.41$, $\text{H-C}(1)$, $\text{H-C}(2)$); 4.95–5.25 (m, $\text{H-C}(6)$). MS: 152 (5, $M^+ - \text{C}_6\text{H}_{16}\text{OSi}$), 108 (13), 101 (84), 94 (10), 84 (18), 77 (11), 76 (19), 75 (100), 72 (39), 69 (81), 59 (42), 55 (16), 45 (14), 43 (32), 41 (60).

1.2. *Oxidations*. 1.2.1. *Oxidation of 4A + B with CrO_3* . To a soln. of pyridine (15 ml) in abs. CH_2Cl_2 at 0° , CrO_3 (8.04 g, 80.4 mmol) was added carefully and the mixture stirred for 15 min. A soln. of **4A + B** (3.40 g, 11.95 mmol) in CH_2Cl_2 was added in one portion, and after stirring for ca. 1 h at r.t. (TLC control), the mixture was worked up by adding Et_2O (400 ml). CC (Et_2O /hexane 1:5) gave **1** (2.33 g, 69%).

(2RS,3SR)-1-[*(tert-Butyl)dimethylsilyl*]-2,3-epoxy-3,7-dimethyl-6-octen-1-one (**1**). B.p. $110^\circ/0.06 \text{ Torr}$. UV (2.934 mg in 2 ml): 360 (50), 374 (90), 390 (120), 407 (110). IR: 2950s, 2930s, 2880s, 2850s, 1720w, 1635s, 1465s, 1460s, 1445s (sh), 1435m (sh), 1405m (sh), 1390s, 1380s, 1360m, 1250s, 1105w, 1070w, 1005w, 980w, 940w, 905w. $^1\text{H-NMR}$ (300 MHz): 0.22, 0.23 (2s, 2 $\text{CH}_3\text{-Si}$); 0.96 (s, *t*-Bu); 1.14 (s, $\text{CH}_3\text{-C}(3)$); 1.61, 1.68 (2m, $w_{1/2} \approx 4$, $\text{CH}_3\text{-C}(7)$, 3 $\text{H-C}(8)$); 1.65–1.80 (m, 2 $\text{H-C}(4)$); 2.07–2.15 (m, 2 $\text{H-C}(5)$); 3.72 (s, $\text{H-C}(2)$); 5.10 (*ddm*, $J = 7, 7$, $w_{1/2} = 4$, $\text{H-C}(6)$). $^{13}\text{C-NMR}$ (75 MHz): -6.9, -6.8 (2q, 2 $\text{CH}_3\text{-Si}$); 16.3, 17.7, 25.7 (3q, $\text{CH}_3\text{-C}(3)$, $\text{CH}_3\text{-C}(7)$, $\text{C}(8)$); 26.5 (q, 3 $\text{CH}_3\text{-C-Si}$); 23.7, 38.3 (2t, $\text{C}(4)$, $\text{C}(5)$); 68.9 (d, $\text{C}(2)$); 123.3 (d, $\text{C}(6)$); 16.9 (s, C-Si); 64.4 (s, $\text{C}(3)$);

132.4 (s, C(7)); 242.5 (s, C(1)). $^{29}\text{Si-NMR}$ (59.6 MHz): -1.96 (Si–C(1)). MS: 282 (< 1 , M^+ , $\text{C}_{16}\text{H}_{30}\text{O}_2\text{Si}$), 254 (2), 225 (2), 186 (11), 185 (69), 115 (17), 75 (22), 73 (100). Anal. calc. for $\text{C}_{16}\text{H}_{30}\text{O}_2\text{Si}$ (282.50): C 68.03, H 10.70; found: C 68.20, H 10.87.

1.2.2. *Oxidation of 4A + B with DCC/DMSO*. To a soln. of **4A + B** (247 mg, 0.87 mmol) in abs. Et_2O (1.6 ml) under Ar at 0° , DCC (Fluka, 343 mg, 1.66 mmol) and abs. DMSO (5 ml, 73.9 mmol) were added. At 0° , a soln. of dry pyridine trifluoroacetate (159 mg, 0.825 mmol) in abs. DMSO (2.5 ml, 37.0 mmol) was added dropwise (1 drop/5 min). The mixture was warmed to r.t., stirred for 12 h, and worked up with hexane (300 ml). After washing with aq. sat. NaCl (4 $\times$ 50 ml), CC (hexane/ Et_2O 10:1) afforded **1** (46 mg, 19%).

1.2.3. *Oxidation of 5A + B with DCC/DMSO*. The analogous reaction of **5A + B** (230 mg, 0.81 mmol) in abs. Et_2O (1.6 ml) with DCC (343 mg, 1.66 mmol) and pyridine trifluoroacetate (159 mg, 0.823 mmol) in DMSO (2.5 ml, 37.0 mmol) afforded **2** (45 mg, 20%).

(2RS,3RS)-1-[(tert-Butyl)dimethylsilyl]-2,3-epoxy-3,7-dimethyl-6-octen-1-one (**2**). B.p. $110^\circ/0.06$ Torr. UV (2.282 mg in 2 ml): 350 (50), 374 (95), 390 (135), 408 (120). IR: 2950s, 2920s, 2880s, 2860s, 1640s, 1625m, 1465s, 1460s, 1400m, 1390s, 1365s, 1360m, 1340w, 1285w, 1250s, 1215w, 1155w, 1105w, 1060w, 1005w, 980w, 935w, 920w. $^1\text{H-NMR}$ (300 MHz): 0.23, 0.24 (2s, 2 CH_3 –Si); 0.97 (s, *t*-Bu); 1.35–1.50 (m, 2 H–C(4)); 1.44 (s, CH_3 –C(3)); 1.59, 1.66 (2m, $w_{1/2} = 4$, CH_3 –C(7), 3 H–C(8)); 1.95–2.20 (m, 2 H–C(5)); 3.63 (s, H–C(2)); 5.03 (ddm, $J = 7$, 7, $w_{1/2} = 4$, H–C(6)). $^{13}\text{C-NMR}$ (75 MHz): -6.9 , -6.7 (2q, 2 CH_3 –Si); 17.7, 22.1, 25.7 (3q, CH_3 –C(3), CH_3 –C(7), C(8)); 26.5 (q, 3 CH_3 –C–Si); 24.3, 32.2 (2t, C(4), C(5)); 70.5 (d, C(2)); 123.2 (d, C(6)); 16.9 (s, C–Si); 64.9 (s, C(3)); 132.3 (s, C(7)); 242.7 (s, C(1)). MS: 282 (< 1 , M^+ , $\text{C}_{16}\text{H}_{30}\text{O}_2\text{Si}$), 254 (4), 225 (4), 186 (13), 185 (83), 115 (27), 75 (22), 73 (100). Anal. calc. for $\text{C}_{16}\text{H}_{30}\text{O}_2\text{Si}$ (282.50): C 68.03, H 10.70; found: C 68.09, H 10.87.

2. Additional Experiments. 2.1. *Acid-Catalyzed Rearrangement of (E/Z)-3 to 6 and 7A + B + C*. To a soln. of (E/Z)-**3** (9:1, 425 mg, 1.58 mmol) in THF (5 ml) at r.t., a soln. of aq. HCl (1 ml, 2M) was added. After stirring the mixture for 18 h at r.t., workup and CC (hexane/ Et_2O 7:1) afforded **6** (207 mg, 64%) and **7A + B + C** (161 mg, 26%, 1:1:1; conversion of (E/Z)-**3**: 98%).

(E)-1-[(tert-Butyl)dimethylsilyl]-3,7-dimethyl-1,6-octadien-3-ol (**6**). B.p. $125^\circ/0.07$ Torr. IR: 3600w, 3530w (br.), 2950s, 2920s, 2875s, 2845s, 1670w, 1605w, 1460m (sh), 1455s, 1435m (sh), 1405w, 1370m, 1355m, 1340w, 1305m, 1245s, 1210w, 1095m (br.), 1060w, 990m, 935w, 915w. $^1\text{H-NMR}$ (300 MHz): 0.03 (s, 2 CH_3 –Si); 0.88 (s, *t*-Bu); 1.26 (s, CH_3 –C(3)); 1.46–1.63 (m, 2 H–C(4)); 1.59, 1.63 (2m, $w_{1/2} = 4$, CH_3 –C(7), 3 H–C(8)); 1.89–2.11 (m, 2 H–C(5)); 5.12 (tm, $J = 7.5$, $w_{1/2} = 4$, H–C(6)); 5.95 (AB, $\delta_A = 5.82$, $\delta_B = 6.08$, $J = 18.8$, H–C(1), H–C(2)). $^{13}\text{C-NMR}$ (75 MHz): -6.0 (q, J(C,Si) = -52 , 2 CH_3 –Si); 17.7, 25.7, 28.1 (3q, CH_3 –C(3), CH_3 –C(7), C(8)); 26.5 (q, 3 CH_3 –C–Si); 22.9, 42.1 (2t, C(4), C(5)); 122.7 (d, J(C,Si) = -64 , C(1)); 124.5 (d, C(6)); 154.0 (d, C(2)); 16.6 (s, J(C,Si) = -57 , C–Si); 74.5 (s, C(3)); 131.7 (s, C(7)). MS: 250 (3, $M^+ - \text{H}_2\text{O}$), 194 (15), 193 (79), 165 (10), 149 (10), 133 (14), 113 (19), 109 (13), 99 (11), 85 (11), 83 (11), 75 (43), 73 (100), 69 (50), 59 (61), 43 (14), 41 (26). Anal. calc. for $\text{C}_{16}\text{H}_{32}\text{OSi}$ (268.52): C 71.57, H 12.01; found: C 71.61, H 12.19.

1-[(tert-Butyl)dimethylsilyl]-3,7-dimethyl-1,3,6-octatriene (**7A + B**) and 1-[(tert-Butyl)dimethylsilyl]-7-methyl-3-methylidene-1,6-octadiene (**7C**). UV (0.279 mg in 20 ml): 244 (25000). IR: 3080w, 2950s, 2920s, 2895s, 2880s, 2850s, 2740w, 2710w, 1630w, 1570w, 1465m, 1460m, 1445m (sh), 1405w, 1390m, 1375m, 1360m, 1255s, 1245s, 1205w, 1100w, 1005w, 985s, 935w, 895m. $^1\text{H-NMR}$ (80 MHz): 0.11 (s, 2 CH_3 –Si); 0.95 (s, *t*-Bu); 1.60–1.95 (m, CH_3 –C(3), CH_3 –C(7), 3 H–C(8)); 2.10–2.40 (m, 2 H–C(4), 2 H–C(5) of isomer C); 2.88, 2.95 (2 tm, $J = 6$, $w_{1/2} = 4$, 2 H–C(5) of isomers A + B); 5.00–5.30, 5.30–5.66 (2m, H–C(4) of isomers A + B, H–C(6)); 5.08 (m, $w_{1/2} = 4$, CH_2 =C(3)); 6.15, 6.25, 6.45 (presumably 3 AB for H–C(1), H–C(2) [6.15 (AB, $J = 18$, $\delta_A = 5.70$, overlapped with m), $\delta_B = 6.59$ (overlapped with B part of the AB at 6.25)], 6.25 (AB, $J = 18$, $\delta_A = 5.91$, $\delta_B = 6.59$), 6.45 (AB, $J = 19$, $\delta_A = 5.86$, $\delta_B = 7.03$)). MS: 250 (3, M^+ , $\text{C}_{16}\text{H}_{30}\text{Si}$), 235 (< 1), 193 (48), 113 (19), 109 (8), 101 (6), 99 (9), 93 (8), 73 (100), 69 (39), 59 (58), 41 (23).

2.2. *Acid-Catalyzed Rearrangement of 4A + B*. To a soln. of **4A + B** (31 mg, 1.09 mmol) in dioxane (1 ml) at r.t., oxalic acid (5 mg, 0.06 mmol) was added. After stirring the mixture for 2 h at r.t., workup with Et_2O (20 ml) gave crude **9** (28.8 mg, 94%).

(2RS,3RS)-2-[(tert-Butyl)dimethylsilyl]-3-hydroxy-3,7-dimethyl-6-octenal (**9**; ca. 70% pure). IR: 3600w, 3520w (br.), 2950s, 2920s, 2880s, 2850s, 2720w, 1690s (sh), 1680s, 1460m, 1455m, 1430m, 1400m, 1390m, 1370m, 1360m, 1330w (br.), 1280w, 1250s, 1180w, 1155w, 1090w (br.), 1010m, 935w. $^1\text{H-NMR}$ (80 MHz): 0.09, 0.29 (2s, 2 CH_3 –Si); 0.95 (s, *t*-Bu); 1.30 (s, CH_3 –C(3)); 1.10–1.80 (m, 2 H–C(4)); 1.60, 1.66 (2m, $w_{1/2} = 4$, CH_3 –C(7), 3 H–C(8)); 1.83–2.50 (m, 2 H–C(5)); 2.76 (d, $J = 4$, H–C(2)); 2.70–3.10 (m, OH); 5.05 (tm, $J = 7$, $w_{1/2} = 4$, H–C(6)); 9.78 (d, $J = 4$, H–C(1)).

2.3. *Acid-Catalyzed Rearrangement of 5A + B*. The alcohol (Z)-**3** (358 mg, 1.258 mmol) was epoxidized as described in Sect. 1.1 with *t*-BuOOH (0.20 ml, 80%, 1.59 mmol) and $\text{VO}(\text{acac})_2$. During workup, the Et_2O soln.

was washed several times with sat. aq. FeSO_4 . Instead of the alcohol **5A** + **B**, a crude mixture containing the aldehyde **10** was detected (TLC, characteristic $^1\text{H-NMR}$ signals (80 MHz): 1.38 (s, $\text{CH}_3\text{-C(3)}$); 9.73 (d, $J = 4$, H-C(1))). Reduction with LiAlH_4 (100 mg, 2.63 mmol) followed by CC (hexane/ Et_2O 2:1) afforded **11** (55 mg, 14%), (*E*)-**12** (59 mg, 29%), **13** (9 mg, 2%), and a mixture of alcohols (111 mg, 29%) of unknown structure.

(2*RS*,3*RS*)-2-[(tert-Butyl)dimethylsilyl]-3,7-dimethyl-6-octene-1,3-diol (**11**). M.p.: 91–93° (from hexane/ Et_2O). IR: 3610w, 3510w (br.), 3330w (br.), 2950s, 2920s, 2880s, 2850s, 1460m, 1455m (sh), 1435m, 1410m, 1390m, 1375m, 1360m, 1255m (sh), 1250m, 1175w, 1140w, 1035m, 1020m, 1005m, 980w, 935w, 905w, 865w. $^1\text{H-NMR}$ (80 MHz): -0.01, 0.13 (2s, 2 $\text{CH}_3\text{-Si}$); 0.96 (s, *t*-Bu); 1.25–1.80, 1.85–2.30 (2m, H-C(2) , 2 H-C(4) , 2 H-C(5)); 1.33 (s, $\text{CH}_3\text{-C(3)}$); 1.66, 1.73 (2m, $w_{1/2} = 4$, $\text{CH}_3\text{-C(7)}$, 3 H-C(8)); 2.60–3.00 (m, OH); 3.50–4.20 (m, 2 H-C(1) , OH); 5.16 (tm, $J = 7$, $w_{1/2} = 4$, H-C(6)). $^{13}\text{C-NMR}$ (25 MHz): -6.0, -2.8 (2q, 2 $\text{CH}_3\text{-Si}$); 17.7, 25.6, 25.7 (3q, $\text{CH}_3\text{-C(3)}$, $\text{CH}_3\text{-C(7)}$, C(8)); 27.2 (q, 3 $\text{CH}_3\text{-C-Si}$); 22.1, 43.5 (2t, C(4) , C(5)); 62.8 (t, C(1)); 36.4 (d, C(2)); 124.5 (d, C(6)); 17.7 (s, C-Si); 77.6 (s, C(3)); 131.7 (s, C(7)). MS: 268 (1, $M^+ - \text{H}_2\text{O}$), 250 (14), 193 (36), 181 (10), 113 (12), 93 (9), 75 (48), 73 (100), 69 (27), 59 (25), 41 (13).

3-[(tert-Butyl)dimethylsilyloxy]-3,7-dimethyl-6-octen-1-ol (**13**). IR: 3630w, 3530w (br.), 2960s, 2930s, 2880s, 2855s, 2730w, 1650w (br.), 1470m, 1460m, 1435m (sh), 1410w, 1385m, 1375m, 1360m, 1340w, 1305w, 1250s, 1185w, 1155m, 1110m, 1090m, 1065m (sh), 1030s, 1000s, 960m, 950w, 940m, 905w, 855m (sh). $^1\text{H-NMR}$ (300 MHz): 0.12 (s, 2 $\text{CH}_3\text{-Si}$); 0.87 (s, *t*-Bu); 1.10–1.87 (m, 2 H-C(2) , 2 H-C(4)); 1.28 (s, $\text{CH}_3\text{-C(3)}$); 1.60, 1.68 (2m, $w_{1/2} = 4$, $\text{CH}_3\text{-C(7)}$, 3 H-C(8)); 1.95–2.05 (m, 2 H-C(5)); 2.40–2.55 (m, OH); 3.78 (t, $J = 6.3$, 2 H-C(1)); 5.08 (tm, $J = 7$, $w_{1/2} = 4$, H-C(6)). $^{13}\text{C-NMR}$ (75 MHz): -1.7 (q, 2 $\text{CH}_3\text{-Si}$); 17.7, 25.8, 27.8 (3q, $\text{CH}_3\text{-C(3)}$, $\text{CH}_3\text{-C(7)}$, C(8)); 26.0 (q, 3 $\text{CH}_3\text{-C-Si}$); 23.4, 42.9, 43.1 (3t, C(2) , C(4) , C(5)); 59.7 (t, C(1)); 124.3 (d, C(6)); 18.2 (s, C-Si); 77.0 (s, C(3)); 131.5 (s, C(7)). MS: 286 (< 1, M^+ , $\text{C}_{16}\text{H}_{34}\text{O}_2\text{Si}$), 241 (2), 154 (3), 137 (7), 121 (5), 109 (7), 81 (17), 75 (100), 69 (50), 41 (20).

2.4. Acetylation of **11**. To **11** (37.7 mg, 0.132 mmol) at r.t., a soln. of Ac_2O (0.3 ml, 324 mg, 3.17 mmol) in pyridine (2 ml) was added. After stirring for 24 h at r.t., workup and CC (hexane/ Et_2O 5:1) afforded **18** (22 mg, 51%).

(2*RS*,3*RS*)-2-[(tert-Butyl)dimethylsilyl]-3-hydroxy-3,7-dimethyl-6-octenyl] Acetate (**18**). IR: 3600w, 3600–3450w, 2960s, 2920s, 2880s, 2850s, 2730w, 2710w, 1735s, 1465m, 1460m, 1410w, 1385m (sh), 1380s, 1370s, 1360s, 1340w, 1250s (sh), 1230s (br.), 1190m, 1185m, 1095w, 1040m, 1015m, 950m, 935w, 905w. $^1\text{H-NMR}$ (300 MHz): 0.03, 0.20 (2s, 2 $\text{CH}_3\text{-Si}$); 0.92 (s, *t*-Bu); 1.24 (s, $\text{CH}_3\text{-C(3)}$); 1.45–1.75 (m, H-C(2) , 2 H-C(4) , OH); 1.63, 1.68 (2m, $w_{1/2} = 4$, $\text{CH}_3\text{-C(7)}$, 3 H-C(8)); 2.00–2.20 (m, 2 H-C(5)); 2.03 (s, $\text{CH}_3\text{-CO}$); 4.24 (AB, $J = 12.1$; $\delta_A = 4.18$, split in d, $J = 7.9$; $\delta_B = 4.30$, split in d, $J = 3.6$; 2 H-C(1)); 5.11 (tm, $J = 7$, $w_{1/2} = 4$, H-C(6)). $^{13}\text{C-NMR}$ (75 MHz): -4.7, -2.1 (2q, 2 $\text{CH}_3\text{-Si}$); 17.9, 21.3, 25.9, 27.4 (4q, $\text{CH}_3\text{-CO}$, $\text{CH}_3\text{-C(3)}$, $\text{CH}_3\text{-C(7)}$, C(8)); 27.2 (q, 3 $\text{CH}_3\text{-C-Si}$); 22.5, 42.6 (2t, C(4) , C(5)); 65.3 (t, C(1)); 35.0 (d, C(2)); 124.5 (d, C(6)); 17.7 (s, C-Si); 75.2 (s, C(3)); 131.9 (s, C(7)); 171.0 (s, C=O). MS: 250 (7, $M^+ - \text{H}_2\text{O}$, CH_3COOH), 193 (30), 151 (9), 115 (7), 93 (8), 75 (16), 73 (100), 69 (21), 59 (28), 43 (10), 41 (14).

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