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 (CrO_3/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/Et_2O solution of the epoxides with aq. $FeSO_4$ to decompose excess *t*-BuOOH was omitted, the mixture was filtered through SiO_2, impregnated with Et_3N, 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].

[2]) New address: *Ciba-Geigy Ltd.*, Additives Division, CH–4133 Schweizerhalle.

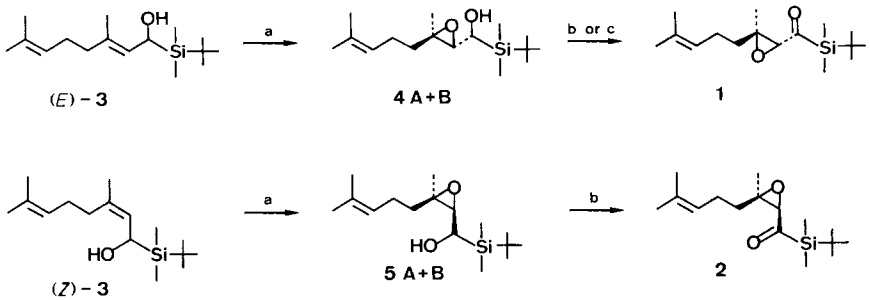
[3]) X-Ray analysis.

[4]) New address: *Ciba-Geigy Ltd.*, Agricultural Division, CH–4002 Basle.

[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.

Scheme 1

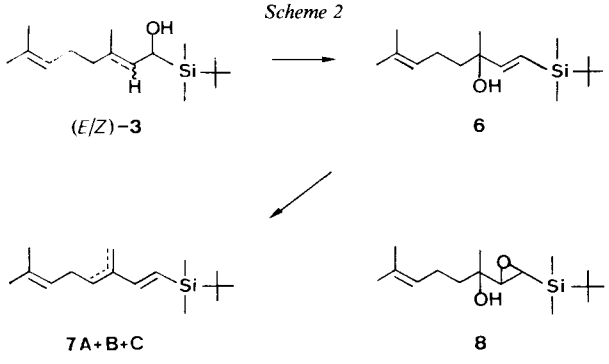


a) *t*-BuOOH/VO(acac)$_2$, b) DCC/DMSO, c) CrO_3/pyridine.

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 CrO_3/pyridine [7] gave **1** even in 69% yield[7]).

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 hypothetic epoxide **8** could be detected *(Scheme 2)*.

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 $LiAlH_4$ affording the alcohols **11** (14%), **12** (29%), **13** (2%, see *Scheme 3*), and, in addition, a complex mixture of alcohols of unknown structure (29%).

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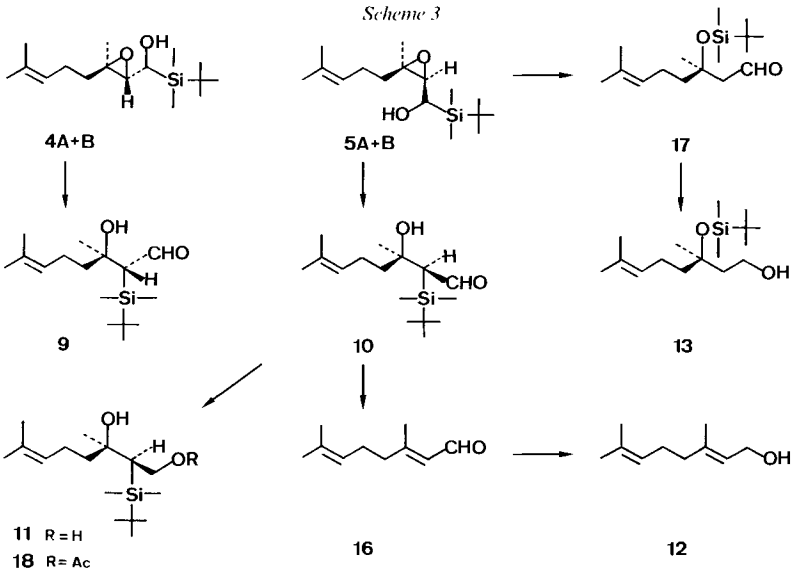
[7]) Due to the low amounts of pure **5A + B** in our hands, the oxidation was not repeated with CrO_3/pyridine, the reagent which would have led to a higher yield of **2**.

Scheme 3



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)$_2$Si group[8]).

The aldol **10** may undergo a *'syn'*-elimination of *t*-Bu(Me)$_2$SiOH leading to **16**, which, after reduction ($LiAlH_4$), 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)$_2$Si 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 ^{1}H-NMR spectra, **1** and **2** show *s* at 3.72 and 3.63 ppm, respectively, corresponding to H–C(2). In the ^{13}C-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 ^{13}C-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 Ac_2O/pyridine, leading to the mono-acetate **18** *(Scheme 3)*. The position of the *t*-Bu(Me)$_2$Si group (C-linkage) and the relative configuration of **11** was finally established by X-ray analysis (see below).

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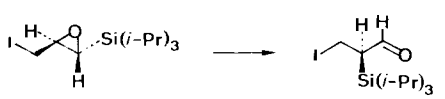
[8]) A similar rearrangement was reported by *Muchowski et al.* [8] on treatment of the epoxide **14** with SiO_2 leading to **15**.



14 **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, $\alpha = 66.10(3)$, $\beta = 80.41(3)$, $\gamma = 74.77(2)°$. Intensities were measured at r.t. with an *Enraf Nonius CAD4* diffractometer equipped with a graphite monochromator (Mo$K\alpha$, $\lambda = 0.7107$ Å). Of the 3279 independent reflections ($\theta \leq 25°$), 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 $r = 6$ Å^2 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 O(1)···O(2) *(Fig. 1)* $d = 2.61$ Å and two intermolecular O(1)···O(1, $-x$, 1-y, 1-z)

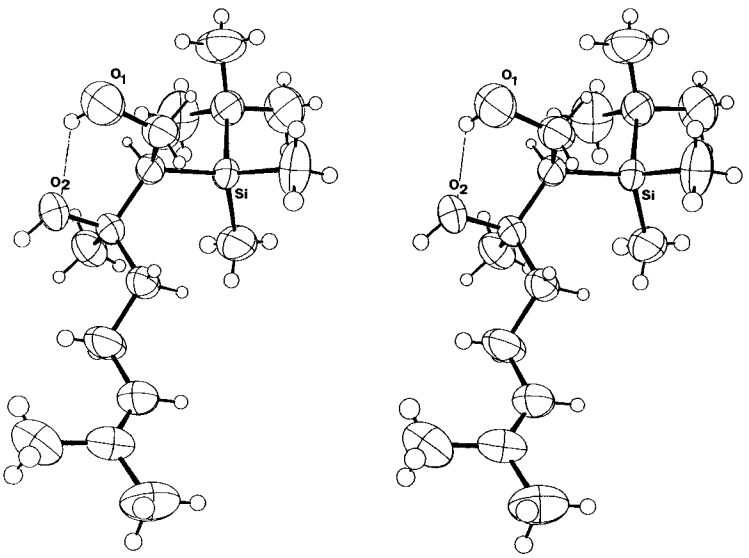


Fig. 1. *Stereoscopic view of* **11**. Vibrational ellipsoids at the 50% level, ORTEP [14].

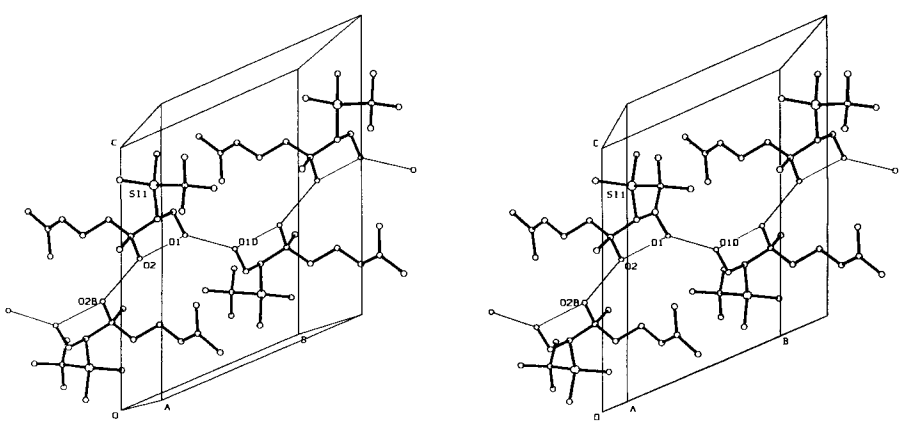


Fig. 2. *Stereoscopic view of the unit cell of* **11**. PLUTO [15].

$d = 2.73$ Å, and O(2)···O(2, -x, -y, 1-z) $d = 2.82$ Å, 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 O(2)-atoms of the intermolecular H-bonds and none between the 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 O(1) forms the intermolecular H-bond, and the H-atom on 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}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}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 $VO(acac)_2$ (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 $VO(acac)_2$ (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 sinterred 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°/0.06 Torr).

*(2*RS*,3*RS*)-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°/0.06 Torr. IR: 3580*w*, 3470*w* (br.), 2950*s*, 2930*s*, 2880*s*, 2850*s*, 1675*w*, 1455*s*, 1380*s*, 1360*m*, 1330*w*, 1245*s*, 1180*w*, 1150*w*, 1105*w*, 1070*m*, 1005*m* (sh), 980*m*, 935*m*, 905*m*, 890*m*. ^{1}H-NMR (80 MHz): 0.03, 0.08, 0.13 (3*s*, 2 CH_3–Si); 1.00 (*s*, *t*-Bu); 1.31, 1.41 (2*s*, CH_3–C(3)); 1.64, 1.70 (2*s*, CH_3–C(7), 3 H–C(8)); 1.10–1.83 (*m*, 2 H–C(4)); 1.83–2.33 (*m*, 2 H–C(5)); 3.20 (*AB*, isomer A, $J = 10$, $\delta_A = 3.00$, $\delta_B = 3.40$, H–C(1), H–C(2)); 3.23 (*AB*, isomer B, $J = 8$, $\delta_A = 2.85$, $\delta_B = 3.59$, H–C(1), H–C(2)); 4.95–5.20 (*m*, H–C(6)). MS: 152 (1, $M^{+\cdot} - C_6H_{16}OSi$), 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 $VO(acac)_2$ 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°/0.06 Torr).

*(2*RS*,3*SR*)-1-[(*tert*-Butyl)dimethylsilyl]-2,3-epoxy-3,7-dimethyl-6-octen-1-ol* (**5A** + **B**; mixture of diastereoisomers, 4:1). B.p. 120°/0.06 Torr. IR: 3580*w*, 3490*w* (br.), 2950*s*, 2930*s*, 2890*s*, 2860*s*, 1675*m*, 1465*s*, 1460*s*, 1445*s*, 1405*m*, 1390*m*, 1375*s*, 1360*m*, 1340*m*, 1245*s*, 1190*w*, 1155*w*, 1110*m*, 1100*m*, 1060*w*, 1005*m*, 985*m*, 940*m*, 890*m*. ^{1}H-NMR (80 MHz): 0.01, 0.06, 0.11 (3*s*, 2 CH_3–Si); 0.99 (*s*, *t*-Bu); 1.26, 1.34 (2*s*, CH_3–C(3)); 1.64, 1.70 (2*s*, CH_3–C(7), 3 H–C(8)); 1.10–1.83 (*m*, 2 H–C(4)); 1.83–2.33 (*m*, 2 H–C(5)); 3.04 (*AB*, isomer A, $J = 8$, $\delta_A = 2.63$, $\delta_B = 3.45$, H–C(1), H–C(2)); 3.18 (*AB*, isomer B, $J = 10$, $\delta_A = 2.95$, $\delta_B = 3.41$, H–C(1), H–C(2)); 4.95–5.25 (*m*, H–C(6)). MS: 152 (5, $M^{+\cdot} - C_6H_{16}OSi$), 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%).

*(2*RS*,3*SR*)-1-[(*tert*-Butyl)dimethylsilyl]-2,3-epoxy-3,7-dimethyl-6-octen-1-one* (**1**). B.p. 110°/0.06 Torr. UV (2.934 mg in 2 ml): 360 (50), 374 (90), 390 (120), 407 (110). IR: 2950*s*, 2930*s*, 2880*s*, 2850*s*, 1720*w*, 1635*s*, 1465*s*, 1460*s*, 1445*s* (sh), 1435*m* (sh), 1405*m* (sh), 1390*s*, 1380*s*, 1360*m*, 1250*s*, 1105*w*, 1070*w*, 1005*w*, 980*w*, 940*w*, 905*w*. ^{1}H-NMR (300 MHz): 0.22, 0.23 (2*s*, 2 CH_3–Si); 0.96 (*s*, *t*-Bu); 1.14 (*s*, CH_3–C(3)); 1.61, 1.68 (2*m*, $w_{1/2} \approx 4$, CH_3–C(7), 3 H–C(8)); 1.65–1.80 (*m*, 2 H–C(4)); 2.07–2.15 (*m*, 2 H–C(5)); 3.72 (*s*, H–C(2)); 5.10 (*ddm*, $J = 7, 7$, $w_{1/2} = 4$, H–C(6)). ^{13}C-NMR (75 MHz): –6.9, –6.8 (2*q*, 2 CH_3–Si); 16.3, 17.7, 25.7 (3*q*, CH_3–C(3), CH_3–C(7), C(8)); 26.5 (*q*, 3 CH_3–C–Si); 23.7, 38.3 (2*t*, C(4), C(5)); 68.9 (*d*, C(2)); 123.3 (*d*, C(6)); 16.9 (*s*, C–Si); 64.4 (*s*, C(3));

132.4 (*s*, C(7)); 242.5 (*s*, C(1)). ^{29}Si-NMR (59.6 MHz): –1.96 (Si–C(1)). MS: 282 (< 1, M^+, $C_{16}H_{30}O_2Si$), 254 (2), 225 (2), 186 (11), 185 (69), 115 (17), 75 (22), *73* (100). Anal. calc. for $C_{16}H_{30}O_2Si$ (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 × 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 trifluoracetate (159 mg, 0.823 mmol) in DMSO (2.5 ml, 37.0 mmol) afforded **2** (45 mg, 20%).

*(2*RS*,3*RS*)-1-[(*tert*-Butyl)dimethylsilyl]-2,3-epoxy-3,7-dimethyl-6-octen-1-one* (**2**). B.p. 110°/0.06 Torr. UV (2.282 mg in 2 ml): 350 (50), 374 (95), 390 (135), 408 (120). IR: 2950*s*, 2920*s*, 2880*s*, 2860*s*, 1640*s*, 1625*m*, 1465*s*, 1460*s*, 1400*m*, 1390*s*, 1365*s*, 1360*m*, 1340*w*, 1285*w*, 1250*s*, 1215*w*, 1155*w*, 1105*w*, 1060*w*, 1005*w*, 980*w*, 935*w*, 920*w*. ^{1}H-NMR (300 MHz): 0.23, 0.24 (2*s*, 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 (2*m*, $w_{½}$ = 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, $w_{½}$ = 4, H–C(6)). ^{13}C-NMR (75 MHz): –6.9, –6.7 (2*q*, 2 CH_3–Si); 17.7, 22.1, 25.7 (3*q*, CH_3–C(3), CH_3–C(7), C(8)); 26.5 (*q*, 3 CH_3–C–Si); 24.3, 32.2 (2*t*, 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^+, $C_{16}H_{30}O_2Si$), 254 (4), 225 (4), 186 (13), 185 (83), 115 (27), 75 (22), *73* (100). Anal. calc. for $C_{16}H_{30}O_2Si$ (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°/0.07 Torr. IR: 3600*w*, 3530*w* (br.), 2950*s*, 2920*s*, 2875*s*, 2845*s*, 1670*w*, 1605*w*, 1460*m* (sh), 1455*s*, 1435*m* (sh), 1405*w*, 1370*m*, 1355*m*, 1340*w*, 1305*m*, 1245*s*, 1210*w*, 1095*m* (br.), 1060*w*, 990*m*, 935*w*, 915*w*. ^{1}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 (2*m*, $w_{½}$ = 4, CH_3–C(7), 3 H–C(8)); 1.89–2.11 (*m*, 2 H–C(5)); 5.12 (*tm*, *J* = 7.5, $w_{½}$ = 4, H–C(6)); 5.95 (*AB*, δ_A = 5.82, δ_B = 6.08, *J* = 18.8, H–C(1), H–C(2)). ^{13}C-NMR (75 MHz): –6.0 (*q*, *J*(C,Si) = –52, 2 CH_3–Si); 17.7, 25.7, 28.1 (3*q*, CH_3–C(3), CH_3–C(7), C(8)); 26.5 (*q*, 3 CH_3–C–Si); 22.9, 42.1 (2*t*, 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^+ – H_2O), 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 $C_{16}H_{32}OSi$ (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: 3080*w*, 2950*s*, 2920*s*, 2895*s*, 2880*s*, 2850*s*, 2740*w*, 2710*w*, 1630*w*, 1570*w*, 1465*m*, 1460*m*, 1445*m* (sh), 1405*w*, 1390*m*, 1375*m*, 1360*m*, 1255*s*, 1245*s*, 1205*w*, 1100*w*, 1005*w*, 985*s*, 935*w*, 895*m*. ^{1}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, $w_{½}$ = 4, 2 H–C(5) of isomers **A + B**); 5.00–5.30, 5.30–5.66 (2*m*, H–C(4) of isomers **A + B**, H–C(6)); 5.08 (*m*, $w_{½}$ = 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, δ_A = 5.70, (overlapped with *m*), δ_B = 6.59 (overlapped with *B* part of the *AB* at 6.25)), 6.25 (*AB*, *J* = 18, δ_A = 5.91, δ_B = 6.59), 6.45 (*AB*, *J* = 19, δ_A = 5.86, δ_B = 7.03)]. MS: 250 (3, M^+, $C_{16}H_{30}Si$), 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%).

*(2*RS*,3*RS*)-2-[(*tert*-Butyl)dimethylsilyl]-3-hydroxy-3,7-dimethyl-6-octenal* (**9**; *ca.* 70% pure). IR: 3600*w*, 3520*w* (br.), 2950*s*, 2920*s*, 2880*s*, 2850*s*, 2720*w*, 1690*s* (sh), 1680*s*, 1460*m*, 1455*m*, 1430*m*, 1400*m*, 1390*m*, 1370*m*, 1360*m*, 1330*w* (br.), 1280*w*, 1250*s*, 1180*w*, 1155*w*, 1090*w* (br.), 1010*m*, 935*w*. ^{1}H-NMR (80 MHz): 0.09, 0.29 (2*s*, 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 (2*m*, $w_{½}$ = 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, $w_{½}$ = 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 $VO(acac)_2$. 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}H-NMR signals (80 MHz): 1.38 (*s*, CH_3–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: 3610*w*, 3510*w* (br.), 3330*w* (br.), 2950*s*, 2920*s*, 2880*s*, 2850*s*, 1460*m*, 1455*m* (sh), 1435*m*, 1410*m*, 1390*m*, 1375*m*, 1360*m*, 1255*m* (sh), 1250*m*, 1175*w*, 1140*w*, 1035*m*, 1020*m*, 1005*m*, 980*w*, 935*w*, 905*w*, 865*w*. ^{1}H-NMR (80 MHz): –0.01, 0.13 (2*s*, 2 CH_3–Si); 0.96 (*s*, *t*-Bu); 1.25–1.80, 1.85–2.30 (2*m*, H–C(2), 2 H–C(4), 2 H–C(5)); 1.33 (*s*, CH_3–C(3)); 1.66, 1.73 (2*m*, $w_{1/2}$ = 4, CH_3–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}C-NMR (25 MHz): –6.0, –2.8 (2*q*, 2 CH_3–Si); 17.7, 25.6, 25.7 (3*q*, *C*H_3–C(3), *C*H_3–C(7), C(8)); 27.2 (*q*, 3 *C*H_3–C–Si); 22.1, 43.5 (2*t*, 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, $M^+ - H_2O$), 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: 3630*w*, 3530*w* (br.), 2960*s*, 2930*s*, 2880*s*, 2855*s*, 2730*w*, 1650*w* (br.), 1470*m*, 1460*m*, 1435*m* (sh), 1410*w*, 1385*m*, 1375*m*, 1360*m*, 1340*w*, 1305*w*, 1250*s*, 1185*w*, 1155*m*, 1110*m*, 1090*m*, 1065*m* (sh), 1030*s*, 1000*s*, 960*m*, 950*w*, 940*m*, 905*w*, 855*m* (sh). ^{1}H-NMR (300 MHz): 0.12 (*s*, 2 CH_3–Si); 0.87 (*s*, *t*-Bu); 1.10–1.87 (*m*, 2 H–C(2), 2 H–C(4)); 1.28 (*s*, CH_3–C(3)); 1.60, 1.68 (2*m*, $w_{1/2}$ = 4, CH_3–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}C-NMR (75 MHz): –1.7 (*q*, 2 CH_3–Si); 17.7, 25.8, 27.8 (3*q*, *C*H_3–C(3), *C*H_3–C(7), C(8)); 26.0 (*q*, 3 *C*H_3–C–Si); 23.4, 42.9, 43.1 (3*t*, 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^+, $C_{16}H_{34}O_2Si$), 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: 3600*w*, 3600–3450*w*, 2960*s*, 2920*s*, 2880*s*, 2850*s*, 2730*w*, 2710*w*, 1735*s*, 1465*m*, 1460*m*, 1410*w*, 1385*m* (sh), 1380*s*, 1370*s*, 1360*s*, 1340*w*, 1250*s* (sh), 1230*s* (br.), 1190*m*, 1185*m*, 1095*w*, 1040*m*, 1015*m*, 950*m*, 935*w*, 905*w*. ^{1}H-NMR (300 MHz): 0.03, 0.20 (2*s*, 2 CH_3–Si); 0.92 (*s*, *t*-Bu); 1.24 (*s*, CH_3–C(3)); 1.45–1.75 (*m*, H–C(2), 2 H–C(4), OH); 1.63, 1.68 (2*m*, $w_{1/2}$ = 4, CH_3–C(7), 3 H–C(8)); 2.00–2.20 (*m*, 2 H–C(5)); 2.03 (*s*, CH_3–CO); 4.24 (*AB*, *J* = 12.1; δ_A = 4.18, split in *d*, *J* = 7.9; δ_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}C-NMR (75 MHz): –4.7, –2.1 (2*q*, 2 CH_3–Si); 17.9, 21.3, 25.9, 27.4 (4*q*, *C*H_3–CO, *C*H_3–C(3), *C*H_3–C(7), C(8)); 27.2 (*q*, 3 *C*H_3–C–Si); 22.5, 42.6 (2*t*, 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, $M^+ - H_2O$, 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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