Hydroxy- and Carboxy-Substituted Allylsilanes: A Simple and Stereoselective Method of Preparation

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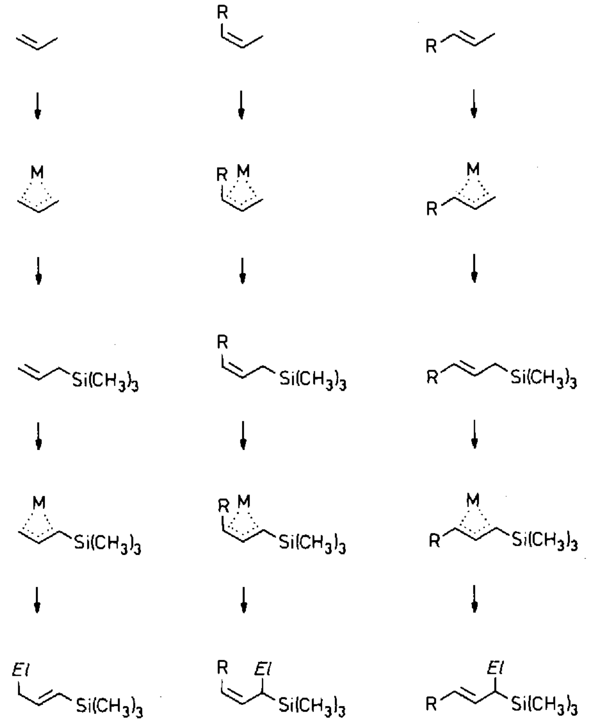
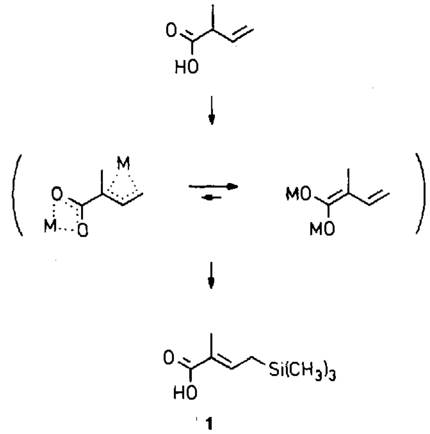
When treated with two equivalents of a butyllithium/potassium *tert*-butoxide mixture, terminal olefins carrying unprotected hydroxy or carboxy groups generate allylmetal intermediates which can be trapped with chlorotrimethylsilane to afford functionalized (Z)-2-alkenyltrimethylsilanes. One equivalent of the superbasic reagent suffices if the unsaturated alcohols are first protected as acetals before being subjected to the metalation/silylation/hydrolysis sequence.

Allylsilanes are versatile intermediates for organic synthesis[1]. They are most readily accessible by metalation of suitable olefins with the superbasic mixture of butyllithium and potassium *tert*-butoxide ("LICKOR" reagent[2]) followed by reaction with chlorotrimethylsilane[3,4].

Allylsilanes themselves undergo the superbase-promoted hydrogen/metal exchange very readily. 1-(Trimethylsilyl)allylpotassium[5] combines with electrophiles mainly to form enylsilanes. In contrast, 1-(trimethylsilyl)alk-2-enylpotassium species carrying an alkyl substituent R at one of the allyl termini react with methyl iodide exclusively and with butyl iodide preferentially at the 1-position leading to substituted allylsilanes[6]. The configuration of the initial precursor is retained throughout the entire metalation/trapping sequence. Thus, a *cis*-olefin generates an *endo*-alkenylmetal intermediate which is converted into a *cis*-allylsilane. Deprotonation of the latter affords a silylated *endo*-alkenylmetal species which forms a *cis*-allylsilane derivative. Analogously, the reaction of a *trans*-olefin leads via an *exo*-alkenylmetal conformer to a *trans*-allylsilane derivative[6].



We wondered whether this metal-mediated silylation method would tolerate the presence of acidic functional groups such as hydroxy or carboxy. The first model compound studied was 2-methyl-3-butenoic acid. When exposed to the action of two equivalents of the LIC-KOR reagent, an intermediate was formed which, since colorless, had presumably a dienediolate (two metal atoms located at the heteroatoms) rather than a (metaloxycarbonyl)allylmetal structure. Reaction with chlorotrimethylsilane produced virtually pure (*E*)-2-methyl-4-trimethylsilyl-2-butenoic acid (**1**; 51%).



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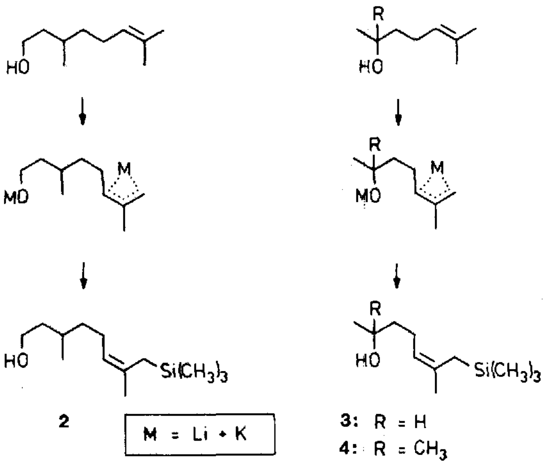
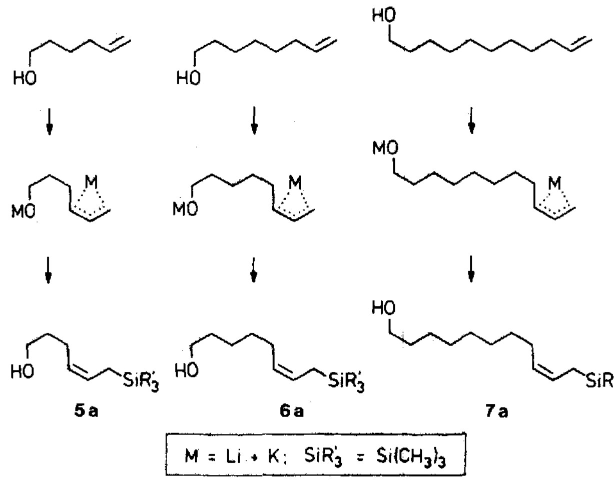
Next we turned to unsaturated alcohols choosing substrates with primary, secondary and tertiary hydroxy groups. 3,7-Dimethyl-6-octen-1-ol (citronellol), 6-methyl-5-hepten-2-ol and 2,6-dimethyl-5-hepten-2-ol were dissolved in hexane and treated with two equivalents of butyllithium in the presence of suspended potassium *tert*-butoxide. Upon subsequent addition of chlorotrimethylsilane, (*Z*)-(8-

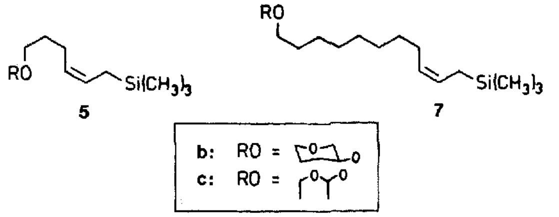
hydroxy-2,6-dimethyloct-2-enyl)trimethylsilane (**2**; 38%), (*Z*)-(6-hydroxy-2-methylhept-2-enyl)trimethylsilane (**3**; 56%) and (*Z*)-(6-hydroxy-2,6-dimethylhept-2-enyl)trimethylsilane (**4**; 37%) were obtained as the only new products. Their (*Z*) configuration was to be expected since the crucial organometallic intermediates are known to have a strong preference for *endo* geometries[5,7].



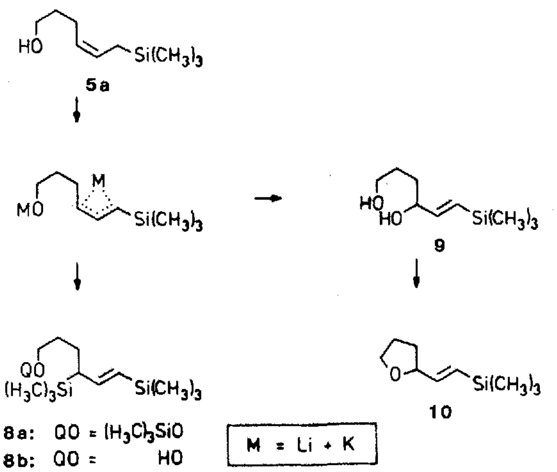
The yields are only moderate because of the poor solubility of alcoholates in a paraffinic medium. We selected hex-5-en-1-ol, oct-7-en-1-ol and undec-10-en-1-ol as model compounds for optimization of the reaction conditions. The yields of the corresponding silanes **5a**, **6a** and **7a** improved significantly (55–75%) when the metalation was carried out in tetrahydropyran. In order to achieve acceptable stereoselectivities (*Z*/*E* ratios ≥95:5), small amounts of transmetalation promotors such as 1-pentene or 1-nonene had to be introduced into the reaction mixture. Without such additives, the torsional equilibration[7] proceeded with extreme sluggishness. The ordinary stereomutation catalysts, in particular magnesium[8] or mercury[8] compounds, failed to show any effect with metaloxa-bearing allyl derivatives.



Satisfactory yields can also be obtained if the hydroxy group is protected as an acetal function. Thus, metalation with trimethylsilylmethylpotassium[9] in tetrahydrofuran or tetrahydropyran and electrophilic trapping of 6-(2-tetrahydropyranyloxy)hex-1-ene, 11-(2-tetrahydropyranoyloxy)undec-1-ene and 11-[(1-ethoxy)ethoxy]undec-1-ene afforded [(*Z*)-6-(2-tetrahydropyranyl)hex-2-enyl]trimethylsilane (**5b**; 72%; *Z*/*E* = 98:2) [(*Z*)-11-(2-tetrahydropyranyloxy)undec-2-enyl]trimethylsilane (**7b**; 63%; *Z*/*E* = 99:1) and [(*Z*)-11-(1-ethoxy)ethoxy)undec-2-enyl]trimethylsilane (**7c**; 78%; *Z*/*E* = 96:4), respectively.

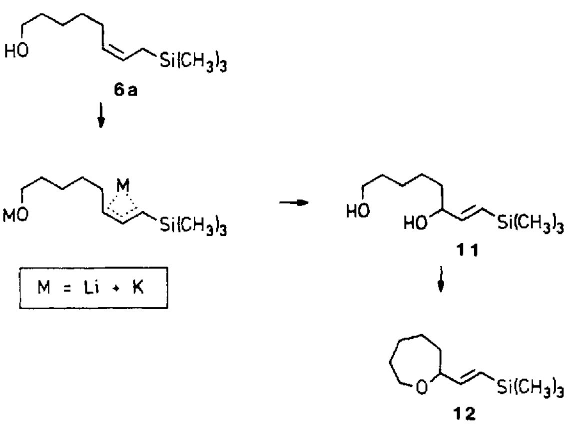


As outlined above, allylsilanes themselves easily undergo metalation. The lithium alcoxide derived from silane **5a** (RO = LiO) can be selectively deprotonated with the LIC-KOR reagent at the methylene group adjacent to the silicon atom. Condensation with chlorotrimethylsilane gave first the silyloxy compound **8a** and, after *O*-silyl ether cleavage with acid, the bis(trimethylsilyl)-substituted alcohol **8b** while the borylation/oxidation sequence[10] yielded the diol **9**. Acid treatment of the latter compound gave the tetrahydrofuran derivative **10**.



In the same way, (*Z*)-(8-hydroxyoct-2-enyl)trimethylsilane (**6a**) was converted into the dihydroxylated enylsilane **11**. Cyclization of the latter afforded 2-[2-(trimethylsilyl)-ethenyl]oxepane (**12**).

Even simple (i.e., unbranched) ω-hydroxy-substituted allylsilanes may serve as key building blocks. After conversion into ω-(trimethylsilyl)alk-(ω − 2)-enals, the latter may undergo Lewis acid catalyzed, regio- and stereoselective cyclization affording 2-vinylcycloalkanols[11]. Intramolecular addition of a (*Z*)-alk-2-enylsilane moiety to acylimmonium ions[12] or oxime-derived imino cations[13] leads to alcaloid-related N-heterocycles. Analogous intramolecular 1,4-addition reactions with α,β-unsaturated carbonyl compounds yield a variety of bicyclo[4.3.0]nonanones and bicyclo-[4.4.0]decanones of spiro[4.5]decanones[13]. Oxidation of



(*Z*)- or (*E*)-6- or-7-(hydroxyalk-2-enyl)trimethylsilanes with cerium ammonium nitrate furnished 2,5,6,7-tetrahydrooxepenes and 2-vinyltetrahydrofurans or -tetrahydropyrans[14]. So far, all the required silane precursors had to be prepared by multi-step procedures giving poor over-all yields.

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Experimental Section

1. *Generalities:* For standard laboratory practice, technical details and abbreviations, see previous related articles[3]. – Gas chromatography SE-30 = silicone rubber, Ap-L = Apiezon L, C-20M = Carbowax having an average molecular weight of 20000.

2. *An Unsaturated Carboxylic Acid as the Starting Material. – (E)-2-Methyl-4-(trimethylsilyl)but-2-enoic Acid* (**1**): At −75 °C, a solution of potassium *tert*-butoxide (6.7 g, 60 mmol) in tetrahydrofuran (50 ml) and 2-methylbut-3-enoic acid (3.1 ml, 3.0 g, 30 mmol) were added to a solution of butyllithium (60 mmol) in hexane (40 ml). The mixture was allowed to stand for 9 h at −75 °C, then chlorotrimethylsilane (10.0 ml, 8.6 g, 79 mmol) was added with vigorous stirring. The decolorized suspension was treated with concentrated hydrochloric acid (6 ml) and washed with brine (3 × 25 ml). The gas-chromatographic analysis (1.5 m, 10% Ap-L, 160 °C; undecane as an "internal standard") of the organic layer revealed the presence of 52% of **1**. This product was isolated by distillation (b.p. 79–81 °C/0.2 Torr). It solidified upon standing to yield 2.6 g (51%); m.p. 67.0–68.5 °C. The (*E*) configuration was assigned on the basis of the chemical shift of the signal of the olefinic hydrogen atom[15]. – ^1H NMR (80 MHz): δ = 10.9 (1 H, s, br.), 7.12 (1 H, t, *J* = 9), 1.85 (3 H, s), 1.78 (2 H, d, *J* = 9), 0.09 (9 H, s). – MS (180 °C); *m/z* (%): 172 (0.8) [M$^+$], 73 (100). – $C_8H_{16}O_2Si$ (172.30): calcd. C 55.77, H 9.36; found C 55.82, H 9.26.

3. *Unsaturated Alcohols as Starting Materials.* – a) *(Z)-(6-Hydroxy-2-methylhept-2-en-1-yl)trimethylsilane* (**2**): 3,7-Dimethyloct-6-en-1-ol (citronellol; 9.1 ml, 7.8 g, 50 mmol) and potassium *tert*-butoxide (7.4 ml, 66 mmol) were added to a solution of butyllithium (60 mmol) in hexane (40 ml). After 24 h of vigorous stirring at 25 °C, the mixture was cooled to −75 °C and treated with a cooled solution of chlorotrimethylsilane (8.2 ml, 7.1 g, 65 mmol) in tetrahydrofuran (40 ml). The solvents were evaporated. Pyridine (5.1 ml, 5.0 g, 63 mmol) and 2 M sulfuric acid (16 ml, 32 mmol) were added to the residue. The mixture was stirred 1 h at 25 °C, then extracted with hexane (3 × 15 ml). Analytical gas chromatography (2 m, 10% Ap-L, 160 °C; 1-octanol as internal standard) showed the presence of 38% of **2**. The product was isolated by bulb-to-bulb ("Kugelrohr") distillation (170–180 °C/10 Torr) and purified by preparative gas chromatography (3 m, 20% C-20M, 180 °C). – ^1H NMR (80 MHz): δ = 5.02 (1 H, t, *J* = 6), 3.73 (2 H, t, *J* = 6), 1.6 (13 H, m), 0.96 (3 H, d, *J* = 6), 0.10 (9 H, s). – MS (180 °C); *m/z* (%): 228 (0.5) [M$^+$], 73 (100). – $C_{13}H_{28}OSi$ (228.45): calcd. C 68.35, H 12.35; found C 68.56, H 12.34.

b) *(Z)-(6-Hydroxy-2-methylhept-2-en-1-yl)trimethylsilane* (**3**): Analogously as described in the preceding paragraph, 6-methylhept-5-en-2-ol (4.6 ml, 3.8 g, 30 mmol) was treated with butyllithium in the presence of potassium *tert*-butoxide and subsequently with chlorotrimethylsilane to afford 3.4 g (56%) of **3**; b.p. 140–150 °C/10 Torr ("Kugelrohr"). – ^1H NMR (80 MHz): δ = 5.02 (1 H, t, *J* = 6), 3.84 (1 H, sext, *J* = 6), 1.9 (10 H, m), 1.24 (3 H, d, *J* = 6), 0.10 (9 H, s). – MS (180 °C); *m/z* (%): 200 (1) [M$^+$], 73 (100). – $C_{11}H_{24}OSi$ (200.40): calcd. C 65.93, H 12.07; found C 66.96, H 12.16.

c) *(Z)-(6-Hydroxy-2,6-dimethylhept-2-en-1-yl)trimethylsilane* (**4**): A similar reaction, as described above (Section 3.a), was performed with 2,6-dimethylhept-5-en-2-ol[16] (7.1 g, 50 mmol) and gave 4.0 g (37%) of **4**; b.p. 140–150 °C/10 Torr ("Kugelrohr"). – ^1H NMR (80 MHz): δ = 5.02 (1 H, t, *J* = 7), 2.0 (2 H, m), 1.28 (6 H, s), 0.10 (9 H, s). – MS (180 °C); *m/z* (%): 124 (0.3) [M$^+$], 73 (100). – $C_{12}H_{26}OSi$ (214.42): calcd. C 67.22, H 12.22; found C 67.33, H 12.30.

d) *(Z)-Trimethyl[6-(trimethylsilyloxy)hex-2-enyl]silane:* At −25 °C, precooled tetrahydropyran (60 ml), hex-5-en-1-ol (2.4 ml, 2.0 g, 20 mmol) and potassium *tert*-butoxide (6.7 g, 60 mmol) were consecutively added to butyllithium (40 mmol) from wich the commercial solvent (hexane) had been stripped off. The solution, once homogeneous, was kept for 2 h at 0 °C, before pent-1-ene (2.0 ml, 1.3 g, 18 mmol) was introduced. After standing for 1 h at 0 °C and for 20 h at −25 °C, the mixture was cooled to −75 °C and treated with chlorotrimethylsilane (10.1 ml, 8.7 g, 80 mmol), whereupon the deep orange-red color disappeared and a thick white precipitate formed. Distillation afforded a colorless liquid; b.p. 70–73 °C/1 Torr; n_D^{20} = 1.4360; (*Z*/*E*) ratio 95:5 by gas chromatography (30 m DB-1, 130 °C, 30 m DB-Wax, 130 °C); 3.6 g (74%). – ^1H NMR (250 MHz): δ = 5.40 (1 H, dtt, *J* = 10.8, 8.3, 1.4), 5.24 (1 H, dtt, *J* = 10.6, 6.9, 1.2), 3.58 (2 H, t, *J* = 6.8), 2.02 (2 H, q, *J* = 7.4), 1.58 (2 H, dq, *J* = 8.0, 6.8), 1.47 (2 H, d, *J* = 8.5), 0.12 (9 H, s), 0.01 (9 H, s). – $C_{12}H_{28}OSi_2$ (244.53): calcd. C 58.94, H 11.54; found C 59.15, H 11.67. – Brief shaking of an ethereal solution of the silyl ether (1.5 g) with 6 M hydrochloric acid, gave *(Z)-(6-hydroxyhex-2-enyl)trimethylsilane*[12] (**5a**), (*Z*/*E*) ratio 95:5 (determined by gas chromatography: 30 m DB-1, 120 °C; 30 m DB-Wax, 190 °C); b.p. 54–55 °C/0.2 Torr; n_D^{20} = 1.4590; 1.0 g (98%).

e) *(Z)-(8-Hydroxyoct-2-enyl)trimethylsilane* (**6a**): At −25 °C, precooled tetrahydropyran (50 ml), oct-7-en-1-ol (2.2 ml, 3.2 g, 25 mmol) and potassium *tert*-butoxide (8.4 g, 75 mmol) were added to neat butyllithium (50 mmol). After 2 h of stirring at 0 °C, pent-1-ene (1.1 ml, 0.7 g, 10 mmol) was added to the bright red solution which was then kept for 50 h at −25 °C before being treated with chlorotrimethylsilane (9.5 ml, 8.1 g, 75 mmol). When the temperature of the mixture had reached 25 °C, it was vigorously shaken with 6 M hydrochloric acid (25 ml), washed with water (2 × 25 ml) and brine (25 ml) and concentrated. Distillation of the residue afforded a colorless liquid; b.p. 85–89 °C/1 Torr; n_D^{20} = 1.4700; 2.8 g (55%). Gas chromatography (30 m, DB-1, 140 °C; 30 m, DB-Wax, 190 °C) revealed a (*Z*/*E*) ratio of 95:5. – ^1H NMR (400 MHz): δ = 5.38 (1 H, dtt, *J* = 10.8, 8.5, 1.3), 5.25 (1 H, dtt, *J* =

10.8, 6.9, 1.3), 3.63 (2H, t, J = 6.5), 2.0 (2H, m), 1.6 (1H, s, br.), 1.6 (2H, m), 1.45 (2H, d, J = 8.5), 1.34 (4H, symm. m), 0.00 (9H, s). – $C_{11}H_{24}OSi$ (200.39): calcd. C 65.93, H 12.07; found C 65.95, H 11.87.

f) *(Z)-[11-(Trimethylsilyloxy)undec-2-enyl]silane:* Application of the same procedure as described above (Section 3.d) to undec-10-en-1-ol (5.0 ml, 4.3 g, 25 mmol) gave the expected product as a colorless oil; b.p. 105–108°C/0.2 Torr; n_D^{20} = 1.4460; (*Z*/*E*) ratio 95:5 (determined by gas chromatography: 30 m DB-1, 190°C, 30 m DB-Wax, 160°C); 5.5 g (70%). – ^{1}H NMR (250 MHz): δ = 5.37 (1H, dtt, J = 10.8, 8.4, 1.3), 5.25 (1H, dtt, J = 10.8, 6.9, 1.2), 3.65 (2H, t, J = 6.7), 1.97 (2H, q-like, J = 6.5), 1.5 (2H, m), 1.47 (2H, d, J = 8.0), 1.30 (10H, s-like, m), 0.12 (9H, s), 0.03 (9H, s). – $C_{17}H_{38}OSi_2$ (314.66): calcd. C 64.89, H 12.17; found C 65.06, H 12.06. – Shaking of an ethereal solution of the silyl ether (2.0 g) with 6 M hydrochloric acid afforded *(Z)-(11-hydroxyundec-10-enyl)trimethylsilane* (**7a**); b.p. 112–114°C/0.8 torr; n_D^{20} = 1.4620; (*Z*/*E*) ratio 95:5 (determined by gas chromatography: 30 m DB-1, 170°C; 30 m DB-Wax, 170°C); 1.5 g (98%). – ^{1}H NMR (250 MHz): δ = 5.38 (1H, dtt, J = 10.9, 8.4, 1.3), 5.25 (1H, dtt, J = 10.9, 6.9, 1.1), 3.64 (2H, t, J = 6.6), 1.97 (2H, symm. m), 1.6 (2H, m), 1.46 (2H, d, J = 8.0), 1.3 (10H, m), 0.00 (9H, s). – MS (CI); m/z (%): 260 (5) [M^+ + NH_4], 243 (6) [M^+], 90 (75), 73 (100). – $C_{14}H_{30}OSi$ (242.48): calcd. C 69.35, H 12.45; found C 68.94, H 11.77. – When the same procedure was repeated with isolation of the trimethylsilyloxy intermediate, the hydroxysilane **7a** was obtained in a (*Z*/*E*) ratio of again 95:5 and 68% yield.

4. *Unsaturated Acetals as Starting Materials.* – a) *(Z)-Trimethyl[6-(tetrahydropyran-2-yloxy)hex-2-enyl]silane* (**5b**): For the preparation of trimethylsilylpotassium[9] (20 mmol), a solution of bis(trimethylsilylmethyl)mercury (2.5 ml, 3.7 g, 10 mmol) was stirred with 78:22 potassium/sodium alloy (3.5 ml, 3.0 g, 60 mmol) in pentane (50 ml), the paraffinic solvent was replaced by precooled (–75°C) tetrahydrofuran (50 ml), and the cold, supernatant solution was removed from the metal residues by means of a pipet and transferred into a Schlenk tube containing 6-(tetrahydropyran-2-yloxy)hex-2-ene[17] (0.4 g, 22 mmol) at –75°C. After 20 h at –50°C, chlorotrimethylsilane (2.6 ml, 2.2 g, 20 mmol) was added. Extraction and distillation afforded product **5b** as a colorless liquid; b.p. 96–98°C/1 Torr; n_D^{20} = 1.4263; (*Z*/*E*) ratio 98:2 (determined by gas chromatography: 30 m DB-1, 120 → 220°C; 30 m DB-Wax 100 → 220°C); 3.5 g (68%). – ^{1}H NMR (250 MHz): δ = 5.39 (1H, dtt, J = 10.8, 8.5, 1.4), 5.25 (1H, dtt, J = 10.8, 6.6, 1.3), 4.57 (1H, t, J = 3.5), 3.87 (1H, symm. m), 3.74 (1H, dt, J = 10.0, 6.8), 3.5 (1H, m), 3.40 (1H, dt, J = 10.0, 6.8), 2.06 (2H, q, J = 7.0), 1.8 (1H, m), 1.6 (7H, m), 1.48 (2H, d, J = 8.5), 0.01 (9H, s). – $C_{14}H_{28}O_2Si$ (256.46): calcd. C 65.57, H 11.00; found C 65.53, H 11.02. – The acetal **5b** (10 mmol) was dissolved in methanol (10 ml) that contained a small amount (approx. 1 mmol) of boron trifluoride–diethyl ether. After 20 h at 25°C, the volatile components were evaporated and the alcohol **5a** was isolated in quantitative yield; (*Z*/*E*) ratio 98:2.

b) *(Z)-Trimethyl[11-(tetrahydropyran-2-yl)undec-2-enyl]silane* (**7b**): In the same way as described in the preceding paragraph, 11-(tetrahydropyran-2-yloxy)undec-1-ene[18] was converted into the silane **7b**; b.p. 130–133°C/0.1 Torr; n_D^{20} = 1.4633; (*Z*/*E*) ratio 98:2 (by gas chromatography: 30 m DB-1, 220°C; 30 m DB-Wax, 220°C); 4.2 g (65%). – ^{1}H NMR (250 MHz): δ = 5.37 (1H, dtt, J = 10.8, 8.2, 1.2), 5.25 (1H, dtt, J = 10.8, 6.9, 1.2), 4.57 (1H, t, J = 3.5), 3.9 (1H, m), 3.72 (1H, dt, J = 9.4, 6.9), 3.49 (1H, dt, J = 11.5, 5.3), 3.37 (1H, dt, J = 9.4, 6.9), 1.96 (2H, q-like, $J \approx 7$), 1.8 (2H, m), 1.5 (6H, m), 1.45 (2H, d, J = 8.0), 1.30 (10H, s-like m), –0.01 (9H, s). – $C_{19}H_{38}O_2Si$ (326.59): calcd. C 69.88, H 11.73; found C 70.41, H 11.80. – The acid-catalyzed hydrolysis of acetal **7b** (2.0 g) in methanol (see preceding paragraph) gave alcohol **7a**; (*Z*/*E*) ratio 98:2; 1.3 g (97%).

c) *(Z)-[11-([1-Ethoxy]ethoxy)undec-2-enyl]trimethylsilane* (**7c**): 11-[(1-Ethoxy)ethoxy]undec-2-ene (4.8 g, 20 mmol; prepared from undec-10-en-1-ol and ethyl vinyl ether in dichloromethane in the presence of catalytic amounts of pyridinium *p*-toluenesulfonate) was consecutively treated with trimethylsilylmethylpotassium and chlorotrimethylsilane as described above (Section 4.a). Product **7c** was isolated by distillation; b.p. 120–125°C/1 Torr; n_D^{20} = 1.4533; (*Z*/*E*) ratio 96:4 (determined by gas chromatography: 3 m, 5% SE-30, 200°C; 3 m, 5% C-20-M, 200°C); 5.0 g (79%). – ^{1}H NMR (250 MHz): δ = 5.38 (1H, dt, J = 10.9, 8.1), 5.23 (1H, dtt, J = 10.8, 7.0, 0.8), 4.66 (1H, q, J = 5.4), 3.60 (1H, dq, J = 9.4, 7.0), 3.53 (1H, dd, J = 9.5, 7.0), 3.47 (1H, dd, J = 9.2, 7.0), 3.39 (1H, dt, J = 9.0, 6.7), 1.96 (2H, q-like, J = 6.8), 1.54 (2H, symm. m), 1.45 (2H, d, J = 8.0), 1.3 (10H, m), 1.19 (3H, t, J = 7.0), –0.01 (9H, s). – $C_{18}H_{38}O_2Si$ (314.58): calcd. C 68.72, H 12.18; found C 67.76, H 12.15. – The acid-catalyzed hydrolysis of the acetal **7c** in methanol (see above) gave the alcohol **7a**; (*Z*/*E*) ratio 96:4; 1.4 g (98%).

5. *Metalation and Subsequent Substitution of ω-Hydroxy-alk-2-enylsilanes.* – a) *(E)-[3-(4-Trimethylsilyloxy)propyl]prop-1-ene-1,3-diylbis(trimethylsilane)* (**8a**): Precooled (–75°C) tetrahydropyran (30 ml), (6-hydroxyhex-2-enyl)trimethylsilane (**5a**; 4.3 g, 25 mmol) having a (*Z*/*E*) ratio of 90:10 and potassium *tert*-butoxide (6.0 g, 54 mmol) were consecutively added to butyllithium (54 mmol) from which the commercial solvent (hexane) had been evaporated. After 2 h at 0°C, the mixture was cooled to –75°C and chlorotrimethylsilane (9.5 ml, 8.1 g, 75 mmol) was added. The white suspension was concentrated. Distillation of the residue yielded a colorless oil; b.p. 45–49°C/0.01 Torr; n_D^{20} = 1.4409; 5.3 g (67%). – ^{1}H NMR (250 MHz): δ = 5.81 (1H, dd, J = 18.8, 8.5), 5.40 (1H, dd, J = 18.7, 1.0), 3.56 (2H, t, J = 6.4), 1.5 (5H, m), 0.12 (9H, s), 0.03 (9H, s), –0.04 (9H, s). – $C_{15}H_{36}OSi_3$ (316.71): calcd. C 56.89, H 11.46; found C 56.75, H 11.30. – When the product (2.0 g) was dissolved in diethyl ether and the solution thoroughly shaken with 6 M hydrochloric acid, *(E)-[3-(4-hydroxybutyl)]-1,3-prop-1-enylenebis(trimethylsilane)* (**8b**) formed which was isolated by distillation; b.p. 48–50°C/0.05 Torr; n_D^{20} = 1.4598; 1.5 g (97%). – ^{1}H NMR (250 MHz): δ = 5.82 (1H, dd, J = 18.6, 8.3), 5.42 (1H, dd, J = 18.6, 1.0), 3.62 (2H, symm. m), 1.5 (5H, m), 1.29 (1H, s, br.), 0.04 (9H, s), –0.04 (9H, s). – MS (CI); m/z (%): 262 (<1) [M^+ + NH_4], 244 (18) [M^+], 157 (7), 90 (100). – $C_{12}H_{28}OSi$ (244.52): calcd. C 58.94, H 11.54; found C 58.86, H 11.13.

b) *(E)-(3,6-Dihydroxyhex-2-enyl)trimethylsilane* (**9**): (*Z*)-(6-Hydroxyhex-2-enyl)trimethylsilane (**5a**; 10.4 g, 60 mmol) with a (*Z*/*E*) ratio of 90:10 was treated with butyllithium (120 mmol) and potassium *tert*-butoxide (120 mmol) essentially as described in the preceding paragraph although neat tetrahydrofuran (120 ml) instead of tetrahydropyran was used as the solvent. After 1 h at –50°C, fluorodimethoxyborane–diethyl ether (45 ml, 40 g, 0.24 mol) was added to the orange-red reaction mixture which immediately decolorized. At 25°C, 30% aqueous hydrogen peroxide (41 ml, 45 g, 0.40 mol) was added. After 2 h of vigorous stirring, the aqueous phase was extracted with diethyl ether (3 × 30 ml). The combined organic layers were concentrated and the residue was absorbed on silica gel. Elution with a 1:1 mixture of diethyl ether and hexane gave the diol **9** as a colorless liquid which was distilled; b.p. 105–110°C/0.2 Torr; n_D^{20} = 1.4696; yield 63%. – ^{1}H NMR

(250 MHz): δ = 6.04 (1H, dd, J = 18.9, 5.0), 5.86 (1H, dd, J = 18.9, 1.0), 4.3 (1H, m), 3.66 (2H, td, J = 5.7, 1.8), 2.60 (2H, s, br.), 1.7 (4H, m), 0.06 (9H, s). – $C_9H_{20}O_2Si$ (188.34): calcd. C 57.39, H 10.70; found C 57.47, H 10.68.

c) *(E)-2-[(2-Trimethylsilyl)vinyl]tetrahydrofuran* (**10**): A mixture of diol **9** (4.7 g, 25 mmol), *p*-toluenesulfonyl chloride (4.8 g, 25 mmol) and pyridine (4.1 ml, 4.0 g, 51 mmol) in toluene (50 ml) was heated for 2 h to reflux. At 25°C, water (50 ml) was added and the aqueous phase was extracted with diethyl ether (3 × 20 ml). The combined organic layers were washed with brine (2 × 30 ml), dried and the solvent was evaporated. Distillation of the residue afforded a colorless liquid; b.p. 48–50°C/2 Torr; n_D^{20} = 1.4364; 2.3 g (54%). – ^1H NMR (250 MHz): δ = 6.01 (1H, dd, J = 18.8, 5.5), 5.86 (1H, d, J = 18.8), 4.26 (1H, q, J = 6.5), 3.91 (1H, dt, J = 8.3, 6.8), 3.78 (1H, td, J = 7.7, 6.9), 2.0 (1H, m), 1.9 (2H, m), 1.62 (1H, symm. m), 0.06 (9H, s). – $C_9H_{18}OSi$ (170.31): calcd. C 63.47, H 10.65; found C 63.27, H 10.51.

d) *(E)-3,8-Dihydroxyoct-2-enyl)trimethylsilylsilane* (**11**): As described above (Section 5.b), a solution of (*Z*)-(8-hydroxyoct-2-enyl) trimethylsilane (**6a**; 50 mmol) in tetrahydrofuran (0.10 l) was consecutively treated at −75°C with butyllithium (0.10 mol), potassium *tert*-butoxide (0.10 mol), fluorodimethoxyborane–diethyl ether (0.20 mol) and hydrogen peroxide (0.30 mol). Elution from silica gel using a 1:2 mixture of diethyl ether and hexane as the eluent afforded a colorless oil; b.p. 113–115°C/0.2 Torr; n_D^{20} = 1.4691; 4.8 g (44%). – ^1H NMR (250 MHz): δ = 6.04 (1H, dd, J = 18.5, 5.3), 5.84 (1H, dd, J = 18.5, 1.1), 4.09 (1H, q, J = 5.3), 3.64 (2H, t, J = 6.4), 1.7 (2H, s, br.), 1.5 (4H, m), 1.4 (4H, m), 0.09 (9H, s). – $C_{11}H_{24}O_2Si$ (216.39): calcd. C 61.06, H 11.18; found C 60.92, H 11.06.

e) *2-[2-(Trimethylsilyl)ethenyl]oxepane* (**12**): Applying the same procedure as described for diol **9** (Section 5.c), diol **10** (25 mmol) was treated with *p*-toluenesulfonyl chloride in the presence of an excess of pyridine. Product **12** was purified by chromatography on silica gel to give a colorless liquid; b.p. 55–66°C/2 Torr; n_D^{20} = 1.4369; 2.6 g (52%). – ^1H NMR (250 MHz): δ = 6.04 (1H, dd, J = 18.9, 5.4), 5.84 (1H, d, J = 18.9), 4.09 (1H, q, J = 5.6), 3.54 (2H, t, J = 6.4), 1.79 (2H, q, J = 6.5), 1.5 (6H, m), 0.07 (9H, s). – $C_{11}H_{22}OSi$ (198.38): calcd. C 66.60, H 11.18; found C 66.71, H 11.26.

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