SUPPORTING INFORMATION

The Acid Catalyzed Cyclization of Epoxyallylsilanes. An Unusual Rearrangement Cyclization Process

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Silylcupration of allene. Preparation of intermediate 1.

A solution of phenyldimethylsilyllithium (3 mmol) in THF (3 ml) was added by syringe to a stirred suspension of copper (I) cyanide (3 mmol) in THF (5ml) at 0ºC. The resulting black mixture was stirred at this temperature for an additional period of 30 min, and then cooled to –40ºC. A slight excess of allene was added from a balloon and the mixture was stirred for 1h at this temperature and then used immediately.

Reaction of 1 with α,β-unsaturated carbonyl compounds.

$BF_3.OEt_2$ (3 mmol) or TMSCl (3 mmol) was added at –40ºC to a solution of **2** (3 mmol) in THF and the mixture stirred for 5 min at this temperature. Then the α,β-unsaturated carbonyl compound (3.6 mmol) was added dropwise at –40ºC and the resulting mixture was kept at this temperature for 1h. After gentle warming to 0ºC the mixture was quenched with saturated ammonium chloride solution (10 ml) and extracted with ether (3x15 ml). The organic layer was dried over $MgSO_4$ and the solvent rotoevaporated. Purification by flash chromatography gave the oxoallylsilanes **11-17**.

4-Phenyl-5-phenyldimethylsilylmethyl-5-hexen-2-one (11)[13b].

4,4-Dimethyl-5-phenyldimethylsilylmethyl-5-hexen-2-one (13). Liquid (90%). IR (film) 1700, 1640, 1100, 836 cm^{-1}. ^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.58-7.37 (m, 5H , Ph-Si). 4.81 (br s, 1H, =C*H*H), 4.67 (br s, 1H, =CH*H*), 2.45 (s, 2H, CH_2-CO), 2.07 (s, 3H, CH_3-CO), 1.79 (s, 2H, CH_2-Si), 1.10 (s, 6H, 2xCH_3), 0.38 (s, 6H, $(CH_3)_2$-Si). ^{13}C-NMR (75 MHz, $CDCl_3$): δ 208.4 (C=O). 152.0 (=C), 139.5, 133.6, 128.9, 127.8 (Ph-Si), 108.7 (=CH_2), 53.7 (*C*H_2-CO), 39.5 (C), 32.0 (*C*H_3-CO), 26.9 (2xCH_3), 20.1 (CH_2-Si), -2.2 (($CH_3)_2$-Si). Anal. Calcd for $C_{17}H_{26}OSi$: C, 74.39; H, 9.55. Found: C, 74.55; H, 9.69.

3-Methyl-4-phenyldimethylsilylmethyl-4-pentenal (16). Liquid (72%). IR (film) 2820, 2720, 1725, 1633 cm-1. ^{1}H-NMR (300 MHz, $CDCl_3$): δ 9.54 (t, *J* = 2.3 Hz, 1H, CHO), 7.58-7.37 (m, 5H, Ph-Si), 4.68 (s, 1H, =C*H*H), 4.65 (s, 1H, =CH*H*), 2.49 (ddd, *J* = 15.2, 5.2 and 2.3 Hz, 1H, C*H*H-CO_3, 2.45-2.34 (m, 1H, C*H*-CH_3), 2.28 (ddd, *J* = 15.2, 7.4 and 2.3 Hz, 1H, CH*H*-CO), 1.82 (s, 2H, CH_2-Si), 1.04 (d, *J* = 6.6, 3H, CH_3), 0.38 (s, 3H, CH_3-Si), 0.37 (s, 3H, CH_3-Si). ^{13}C-NMR (75 MHz, $CDCl_3$): δ 202.2 (CHO), 150.0 (=C), 138.6, 133.6, 129.1, 127.8 (Ph), 107.3 (=CH_2), 49.3 (CH_2), 35.2 (CH), 25.0 (CH_2-Si), 19.7 (CH_3), -2.9 (CH_3Si), -3.0 (CH_3Si). Anal. Calcd for $C_{15}H_{22}OSi$: C, 73.11; H, 9.00. Found: C, 73.45; H, 9.19.

Synthesis of epoxyallylsilanes

To a solution of trimethylsulphonium iodide (1mmol) in dry THF (5ml) was added dropwise BuLi (1 mmol, 1.6 M ^{n}BuLi in hexanes) and the mixture stirred for 5 min at 0ºC. Then a solution of the oxoallylsilane (0.8 mmol) in THF (1ml) is added. After stirring for an additional 30 min at 0ºC and 1 h at r.t. brine (10 ml) is added and the mixture extracted with ether, dried and evaporated to dryness. The residue was purified by chromatography to give epoxyallylsilanes **18-24**.

[*2R*, 4R]-2-Methyl-4-phenyl-5-phenyldimethylsilylmethyl-1,2-epoxy-5-hexene (18a).** Solid (48%). m.p. 74.2-75.1ºC. IR (film) : 1630, 1240, 1100, 770 cm^{-1}. ^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.59-7.01 (m, 10H, 2xPh), 4.86 (s, 1H, =C*H*H), 4.77 (s, 1H, =CH*H*), 2.91 (dd, *J* = 11.7 and 3.6 Hz, 1H, CH-Ph), 2.25 (ddd, *J* = 11.7, 3.6 and 1.5 Hz, 1H, C*H*H), 2.12 (dd, *J* = 4.7 and 1.5 Hz, 1H, C*H*H-O), 1.81 (d, *J* = 4.7 Hz, 1H, CH*H*-O), 1.73 (d, *J* = 13.9 Hz, 1H, C*H*H-Si), 1.55 (d, *J* = 13.9 Hz, 1H, CH*H*-Si), 1.58-1.50 (m, 1H, CH*H*), 1.05 (s, 3H, CH_3), 0.38 (s, 3H, CH_3-Si), 0.32 (s, 3H, CH_3-Si). ^{13}C-NMR (75 MHz, $CDCl_3$): δ 149.0 (=C), 142.8, 138.9, 133.7, 129.2, 128.2, 128.1, 127.9, 126.5 (Ph), 107.3 (=CH_2), 55.8 (C-O), 54.5 (CH_2-O), 48.7 (CH), 42.2 (CH_2), 26.1 (CH_2-Si), 20.8 (CH_3), -2.6 (CH_3 –Si), -3.4 (CH_3-Si). MS(EI) *m/z*: 336 (M$^+$, 5%), 135 ($PhMe_2Si$, 100%).

[*2R*, 4S]-2-Methyl-4-phenyl-5-phenyldimethylsilylmethyl-1,2-epoxy-5-hexene (18b).** Solid (24%). m.p. 75.9-76.2ºC. IR (film) 1630, 1250, 1110, 780 cm^{-1}. ^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.55-7.08 (m, 10H, 2xPh), 4.83 (s, 1H, =C*H*H), 4.71 (s, 1H, =CH*H*), 3.02 (dd, *J* = 9.4 and 5.4 Hz, 1H, CH-Ph, 2.39 (s, 2H, CH_2-O), 2.06 (dd, *J* = 14.1 and 9.4 Hz, 1H, C*H*H), 1.94 (dd, *J* = 14.1 and 5.4 Hz, 1H, CH*H*), 1.71 (d, *J* = 13.9 Hz, 1H, C*H*H-Si), 1.57 (d, *J* = 13.9 Hz, 1H, CH*H*-Si), 0.96 (s, 3H, CH_3), 0.30 (s, 3H, CH_3-Si), 0.28 (s, 3H, CH_3-Si). ^{13}C-NMR (75 MHz, $CDCl_3$): δ 149.1 (=C), 143.0, 138.9, 133.7, 129.1, 128.3, 128.2, 127.8, 126.4 (Ph), 107.8 (=CH_2), 56.2 (C-O), 53.2 (CH_2-O), 49.3 (CH), 41.0 (CH_2), 25.1 (CH_2-Si), 21.7 (CH_3), -2.7 (CH_3-Si), -3.3 (CH_3-Si). HREI calc. for $C_{22}H_{28}OSi$ (M$^+$) 336.1909 found 336.1926.

2,4,4-Trimethyl-5-phenyldimethylsilylmethyl-1,2,-epoxy-5-hexene (20). Liquid (78%). IR (film) : 1620, 1240, 880 cm^{-1}. ^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.58-7.27 (m, 5H, Ph-Si), 4.88 (s, 1H, =C*H*H), 4.69 (s, 1H, =CH*H*), 2.63 (d, *J* = 4.9 Hz, 1H, C*H*H-O), 2.54 (d, *J* = 4.9 Hz, 1H, CH*H*-O), 1.98 (d, *J* = 14.3 Hz, 1H, C*H*H), 1.77 (s, 2H, CH_2-Si), 1.39 (d, *J* = 14.3 Hz, 1H, CH*H*), 1.31 (s, 3H, CH_3), 1.08 (s, 3H, CH_3), 1.06 (s, 3H, CH_3), 0.37 (s, 6H, $(CH_3)_2$-Si). ^{13}C-NMR (75 MHz, $CDCl_3$): δ 152.8 (=C), 139.6, 133.6, 128.9, 127.7 (Ph-Si), 109.1 (CH_2=), 55.9 (C-O), 54.8 (CH_2), 47.6 (CH_2), 39.4 (C), 28.5 (CH_3), 27.6 (CH_3), 22.1 (CH_3), 20.1 (CH_2-Si), -2.1 ((CH_3)$_2$-Si). Anal. Calcd for $C_{18}H_{28}OSi$: C, 74.94; H, 9.78. Found: C, 75.25; H, 9.99.

4-Methyl-5-phenyldimethylsilylmethyl-1,2-epoxy-5-hexene (23). Liquid (67%). IR (film) : 1631, 1248, 876 cm^{-1}. ^{1}H-NMR (300 MHz, $CDCl_3$): δ Isomer A: 7.65-7.27 (m, 5H, Ph-Si), 4.75 (s, 1H, =C*H*H), 4.67 (s, 1H, CH*H*), 2.90-2.83 (m, 1H, C*H*H-O), 2.73 (t, *J* = 4.7 Hz, 1H, CH-O), 2.44 (dd, *J* = 5.1 and 2.7 Hz, 1H, CH*H*-O), 2.17-2.08 (m, 1H, CH-CH_3), 1.86 (s, 2H, CH_2-Si), 1.85-1.66 (m, 1H, C*H*H), 1.49-1.35 (m, 1H, CH*H*), 1.10 (d, *J* = 6.8 Hz, 3H, CH_3), 0.40 (s, 6H, $(CH_3)_2$-Si). Isomer B: 2.71 (dd, *J* = 5.0 and 4.2 Hz, 1H, CH-O), 2.40 (dd, *J* = 5.0 and 2.7 Hz, 1H, CH*H*-O), 0.39 (s, 6H, $(CH_3)_2$Si). ^{13}C-NMR (75 MHz, $CDCl_3$): δ Isomer A: 151.0 (=C), 138.9, 133.6, 129.0, 127.7 (Ph-Si), 106.9 (=CH_2), 51.2 (CH-O), 47.4 (CH_2-O), 38.4 (CH_2), 38.2 (CH), 25.0 (CH_2-Si), 19.3 (CH_3), -2.8 ((CH_3)$_2$-Si). Isomer B: 150.9 (=C), 106.7 (=CH_2), 50.8 (CH-O) 46.9 (CH_2-O), 38.9 (CH), 38.7 (CH_2), 24.9 (CH_2), 20.1 (CH_3).

Cyclization of epoxyallylsilanes.

$BF_3.OEt_2$ (1.2 mmol) or $TiCl_4$ (0.7 mmol) was slowly added to a solution of **18-23** (1 mmol) in DCM (10 ml) under nitrogen. After stirring for 30 min at the corresponding temperature (0 or –78ºC) 2 ml of MeOH were added and the mixture allowed to warm to room temperature. The organic layer was washed with brine and dried over $MgSO_4$. The solvent was evaporated and the residue purified by chromatography.

[*1R*, 2R*, 4R]-2-Methyl-4-phenyl-5-methylenecyclohexanol (25).** Liquid (60%). IR (film): 3340, 1640, 1040 cm^{-1}. ^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.36-7.20 (m, 5H, Ph), 4.96 (br s, 1H, =C*H*H), 4.76 (br s, 1H, =CH*H*), 3.60 (t, *J* = 5.0 Hz, 1H, C*H*-Ph), 3.41 (td, *J* = 9.0 and 4.2 Hz, 1H, C*H*-OH), 2.57 (dd, *J* = 13.1 and 4.2 Hz, 1H, C*H*H-C=), 2.38 (ddd, *J* = 13.7, 5.3 and 3.8 Hz, 1H, C*H*H), 2.15 (dd, *J* = 13.1 and 9.0 Hz, 1H, CH*H*-C=), 1.74 (m, 1H, CH-Me), 1.58 (br s, 1H, OH), 1.57 (ddd, *J* = 13.7, 9.6 and 4.8 Hz, 1H, C*H*H), 1.09 (d, *J* = 6.6 Hz, 3H, CH_3). ^{13}C-NMR (75 MHz, $CDCl_3$): δ 147.8 (=C), 141.9, 128.3, 127.5, 126.0 (Ph), 112.5 (=CH_2), 75.9 (CH-OH), 45.4 (CH-Ph), 40.5 (CH_2), 35.7 (CH_2), 34.8 (CH), 17.7 (CH_3). MS(EI) *m/z*: 203 (M$^+$+1, 3 %), 202 (M$^+$, 7%), 184 (M$^+$-H_2O, 47%), 169 (M$^+$-H_2O-CH_3, 54%). NOESY enhancements were found between the following signals: (1) 3.41 (C_1-H_{ax}) to 1.09. (2) 7.36-7.20 (Ph) to 2.15 (C_6- H_{ax}).

[*1R*, 2R*, 4S]-2-Methyl-4-phenyl-5-methylenecyclohexanol (26).** Liquid (15%). IR (film): 3370, 1647, 1043, 903 cm^{-1}. ^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.49-7.16 (m, 5H, Ph), 4.77 (d, *J* = 1.7 Hz, 1H, =C*H*H), 4.08 (d, *J* = 1.7 Hz, 1H, =CH*H*), 3.35-3.24 (m, 2H, C*H*-OH, C*H*-Ph), 2.75 (dd, *J* = 12.6 and 4.7 Hz, 1H, C*H*H=), 2.24 (dd, *J* = 12.6 and 12.2 Hz, 1H, CH*H*-C=), 1.93 (dt, *J* = 12.6 and 3.8 Hz, 1H, C*H*H), 1.79-1.61 (m, 2H, C*H*-Me, OH), 1.52 (q, *J* = 12.6 Hz, 1H, CH*H*), 1.10 (d, *J* = 6.4 Hz, 3H, CH_3). ^{13}C-NMR (75 MHz, $CDCl_3$): δ 149.7 (=C), 142.3, 128.6, 128.1, 126.4 (Ph), 110.2 (=CH_2), 76.6 (CH-OH), 49.3 (CH-Ph), 45.2 (CH_2), 40.2 (CH), 39.7 (CH_2), 18.0 (CH_3). MS(EI) *m/z*: 202 (M$^+$, 7%), 184 (M$^+$-H_2O, 40 %), 91 (35%), 77 (10%). %). NOESY enhancements were found between the following signals: (1) 7.49-7.16 (Ph) to 1.52 (C_3-H_{ax}). (2) 1.52 (C_3-H_{ax}) to 1.10 (CH_3). (3) 3.35-3.24 (C_1-H_{ax}) to 1.52 (C_3-H_{ax}).

***cis*-2,4,4-Trimethyl-5-methylenecyclohexanol (29).** Liquid (7%). IR (film): 3426, 1643, 1055, 899 cm^{-1}. ^{1}H-NMR (300 MHz, $CDCl_3$): δ 4.86 (br s, 1H, =C*H*H), 4.77 (br s, 1H, =CH*H*), 3.76 (m, 1H, C*H*-OH), 2.62 (ddt, *J* = 14.0, 3.1 and 1.6 Hz, 1H, C*H*H-C=), 2.28 (dd, *J* = 14.0 and 3.3 Hz, 1H, CH*H*-C=), 1.95-1.825 (m, 1H, C*H*-Me), 1.38 (br s, 1H, OH), 1.25-1.20

(m, 2H, CH_2), 1.11 (s, 3H, CH_3), 1.07 (s, 3H, CH_3), 0.95 (d, *J* = 6.8 Hz, 3H, CH_3). ^{13}C-NMR (75 MHz, $CDCl_3$): δ 151.1 (=C), 109.8 (=CH_2), 71.5 (CH-OH), 43.5 (CH_2), 40.7 (CH_2), 36.3 (C), 32.4 (CH), 28.8 (CH_3), 26.1 (CH_3), 17.9 (CH_3). Anal. Calcd for $C_{10}H_{18}O$: C, 77.87; H, 11.76. Found: C, 78.15; H, 11.59.

***trans*-2,4,4-Trimethyl-5-methylenecyclohexanol (30).** Liquid (73%). IR (film): 3630, 3392, 1640, 1041, 897 cm^{-1}. ^{1}H-NMR (300 MHz, $CDCl_3$): δ 4.71 (s, 1H, =C*H*H), 4.70 (s, 1H, =CH*H*), 3.11 (ddd, *J* = 11.1, 9.9 and 5.0 Hz, 1H, C*H*-OH), 2.45 (dd, *J* = 12.8 and 5.0 Hz, 1H, C*H*H-C=), 2.33 (ddt, *J* = 12.8, 11.1 and 1.6 Hz, 1H, CH*H*-C=), 1.75-1.65 (m, 1H, C*H*-Me), 1.62-1.50 (m, 2H, OH, H), 1.46 (dd, *J* = 13.4 and 3.9 Hz, 1H), 1.09 (s, 6H, $(CH_3)_2C$), 0.99 (d, *J* = 6.4 Hz, 3H, CH_3).). ^{13}C-NMR (75 MHz, $CDCl_3$): δ 153.5 (=C), 107.2 (=CH_2), 77.4 (CH-OH), 47.6 (CH_2), 41.9 (CH_2), 36.3 (C), 35.8 (CH), 28.3 (CH_3), 26.7 (CH_3), 18.1 (CH_3). MS(EI) *m/z*: 137 (M^++1-H_2O, 19 %), 121 (M^+-H_2O-Me, 5%), 95 (27%), 28 (100%).

***cis*-4-Methyl-3-methylenecyclohexanol (34).** Liquid (42%). IR (film): 3400, 1648, 1094 cm^{-1}. ^{1}H-NMR (300 MHz, $CDCl_3$): δ 4.69 (s, 1H, =C*H*H), 4.62 (s, 1H, =CH*H*), 4.12 (tt, J = 4.5 and 3.8 Hz, 1H, C*H*-OH), 2.58-2.48 (m, 1H), 2.43-2.33 (m, 1H), 2.20 (dt, *J* = 13.3 and 5.1, 1H), 1.83-1.44 (m, 5H), 1.07 (d, *J* = 6.8 Hz, 3H, CH_3). ^{13}C-NMR (75 MHz, $CDCl_3$): δ 152.8 (=C), 105.2 (=CH_2), 66.6 (CH-OH), 43.0 (CH_2), 35.4 (CH_2), 32.6 (*C*H-CH_3), 29.9 (CH_2), 18.6 (CH_3). Anal. Calcd for $C_8H_{14}O$: C, 76.14; H, 11.18. Found: C, 76.49; H, 11.39.

***trans*-4-Methyl-3-methylenecyclohexanol (35).** Liquid (28%). IR (film): 3402, 1646, 1250, 1112 cm^{-1}. ^{1}H-NMR (300 MHz, $CDCl_3$): δ 4.74 (s, 1H, =C*H*H), 4.64 (s, 1H, =CH*H*), 3.81 (tt, *J* = 11.1 and 4.2 Hz, 1H, C*H*-OH), 2.37 (ddd, *J* = 13.0, 4.2 and 2.1 Hz, 1H, C*H*H-C=), 2.12-2.01 (m, 4H), 1.62 (br s, 1H, OH), 1.48-1.20 (m, 2H), 1.09 (d, *J* = 6.4 Hz, 3H, CH_3). ^{13}C-NMR (75 MHz, $CDCl_3$): δ 151.5 (=C), 105.5 (=CH_2), 70.3 (CH-OH), 45.1 (CH_2), 36.8 (CH_2), 34.6 (*C*H-CH_3), 33.7 (CH_2), 18.1 (CH_3).