Stereochemistry of the Reaction of Si-Phenyl Silenes with Butadienes: Elaboration of the Silacycloadducts to Provide A Novel Route to Substituted Lactones

Mahesh J. Sanganee[†], Patrick. G. Steel[¥] and Daniel K. Whelligan[¥]*

Department of Chemistry, University of Durham, Science Laboratories, South Road Durham, DH1 3LE, UK and Synthetic Chemistry, GlaxoSmithKline, Gunnels Wood Road, Stevenage, Herts. SG1 2NY, UK.

Standard Protocols

Reduction of Silacyclohexenes

A suspension of the catalyst in a solution of the silacycle in solvent was repeatedly evacuated and flushed with hydrogen from a balloon. The mixture was then stirred under the hydrogen atmosphere until tlc indicated complete consumption of starting material. The mixture was then filtered through a celite pad and washed through with ether. The filtrate was concentrated and dried *in vacuo*. Flash column chromatography gave the title compound.

Oxidations of silacyclohexane to diols

Stage 1

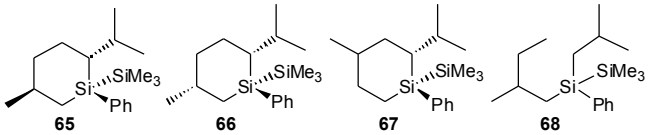
To a solution of silacycle (2.45 mmol) in dry chloroform (28 ml) was added trifluoroborane-acetic acid complex (49.0 mmol). The mixture was then heated to reflux and stirred for 18 h. The solution was then allowed to cool to RT and saturated sodium hydrogen carbonate solution (40 ml) was added. The aqueous layer was separated and extracted with DCM (3 x 40 ml). The combined organic layers were then dried over $MgSO_4$, filtered, concentrated and dried *in vacuo* to give a dark orange oil. This could be purified but was normally used directly in stage 2

Stage 2

To the dark orange oil was added potassium hydrogen carbonate (9.43 mmol) and potassium fluoride (9.75 mmol). The mixture was dissolved in THF/MeOH solution (1:1, 19 ml) and hydrogen peroxide (35 % w/w solution in water, 58.4 mmol) was added. The mixture was heated to reflux and stirred for 19 h. The mixture was then allowed to cool to RT and saturated sodium thiosulfate solution (19 ml) was added together with

ethyl acetate (30 ml). The aqueous layer was separated and extracted with ethyl acetate (3 x 30 ml). The combined organic extracts were dried over $MgSO_4$, filtered, concentrated and dried *in vacuo*. Flash column chromatography gave the title compound

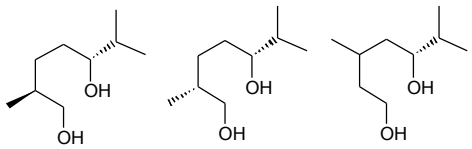
3-Methyl-1-phenyl-6-(prop-2'-yl)-1-(trimethylsilyl)silacyclohexane **65, 66**, *4-Methyl-1-phenyl-6-(prop-2'-yl)-1-(trimethylsilyl)silacyclohexane* **67 ,** *1-(2'-methylbut-1'-yl)-1-(2'-methylpropyl)-1-phenyl-2,2,2-trimethyldisilane* **68**



65 **66** **67** **68**

Reduction of silanes **39**, **40** and *1-(2'-methylpropyl)- 1-phenyl-1-(2'-methylene-but-3'-enyl)- 2,2,2-trimethyl disilane* in ethyl acetate using platinum dioxide hydrate gave the title compounds as a clear oil (0.29 g, 58 %); R_f (pet. ether) 0.79 as a mixture in a ratio of 62 : 16 : 8 : 4 : 10 % (ratio of product peak integrals by GC), which consisted of 4 silacycle isomers **65** - **67**; *m/z* (GCMS, EI) 304 (M^+, 32 %), 231 (M^+-$SiMe_3$, 98 %), 189 (48 %), 175 (60 %), 161 (100 %), 135 (79 %), 121 (94 %), 107 (64 %), 105 ($PhSi^+$, 73 %) and *1-(2'-methylbut-1'-yl)-1-(2'-methylpropyl)-1-phenyl-2,2,2-trimethyldisilane* **68** . *m/z* (GCMS, EI) 306 (M^+, 14 %), 233 (M^+-$SiMe_3$, 50 %), 179 (61 %), 177 (88 %), 163 (50 %), 135 (68 %), 121 (100 %), 107 (100 %), 105 ($PhSi^+$, 47 %), 99 (Si-$CH_2CH(CH_3)CH_2CH_3^+$, 38 %), 85 (Si-$CH_2CH(CH_3)_2^+$, 20 %).

(±)-(2S,5S*) 2,6-dimethylheptane-1,5-diol* **69**, *(±)-(2R*,5S*) 2,6-dimethylheptane-1,5-diol* **70**, *(±)-(3S*,5S*) 3,6-dimethylheptane-1,5-diol* **71**

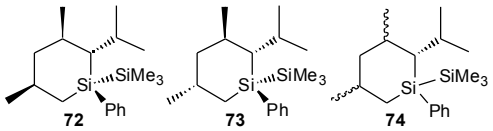


69 **70** **71**

Silane mixture **65-67** was oxidized following the standard protocol as described to afford the title compounds as an inseparable mixture as a viscous colourless oil (0.03 g, 19 %); R_f (pet. ether/ethyl acetate [1:1]) 0.20; ν_{max} (thin film) 3355 (broad, O-H), 2956, 2930, 2873, 1463, 1384, 1367, 1108, 1042, 993 cm^{-1}; NMR data for the major isomer **69**: δ_H (500 MHz; $CDCl_3$)(discernable peaks) 3.45 (2 H, m, 1-H_2), 3.32 (1 H, ddd, J 8.5, 5.0, 3.5, 5-*H*), 0.90 (3 H, d, J 6.5, 7-H_3 or 8-H_3), 0.90 (3 H, d, J 6.0 7-H_3 or 8-H_3), 0.89 (3 H, d, J 7.0, 7-H_3 or 8-H_3); δ_C (126 MHz; $CDCl_3$) 77.13 (5-*C*), 67.59 (1-*C*), 35.83, 33.49, 31.28,

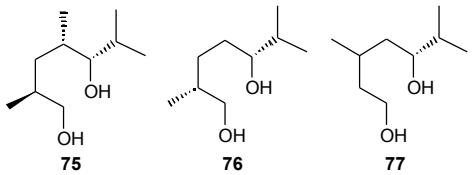
29.43, 18.82 (7-*C* or 8-*C*), 17.10 (7-*C* or 8-*C*), 16.89 (7-*C* or 8-*C*); *m/z* (ES^+) 183 ($M+Na^+$, 100 %); HRMS (ES^+) Found MNa^+, 183.1364; $C_9H_{20}O_2Na$ requires *MNa* 183.1361.

3,5-dimethyl-1-phenyl-6-(prop-2'-yl)-1-(trimethylsilyl)silacyclohexane **72-74**



Reduction of silanes **44** in ethyl acetate using platinum dioxide hydrate gave the products as a mixture of 5 isomers (0.56 g, 74 %); in a ratio of 44 : 39 : 9 : 6 : 1 : 1 % (ratio of product peak integrals by GC); R_f (pet. ether) 0.86; *m/z* (GCMS, EI) 318 (M^+, 13 %), 303 (M^+-Me, 1 %), 245 (M^+-$SiMe_3$, 80 %), 203 (34 %), 189 (34 %), 175 (48 %), 161 (100 %), 147 (27 %), 135 (52 %), 125 (45 %), 121 (71 %).

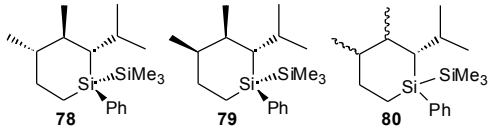
(±)-(2S,4R*,5S*),2,4,6-trimethylheptane-1,5-diol* **75**



Silane mixture **72-74** was oxidized following the standard protocol to afford the title compound as a colourless oil (0.02 g, 10 %); R_f (pet. ether/ethyl acetate [1:1]) 0.47; ν_{max} (thin film) 3362 (broad, O-H), 2957, 2927, 2872, 1464, 1460, 1385, 1090 cm^{-1}; δ_H (500 MHz; $CDCl_3$) 3.53 (1 H, dd, J 5.0, 11.0, 1-*H*H), 3.50 (1 H, dd, J 5.0, 11.0, 1-H*H*), 3.07 (1 H, dd, J 6.5, 5.0, 5-*H*), 1.81 (1 H, septet d, J 6.5, 1.5, 6-*H*), 1.72 (1 H, m, 2-*H*), 1.65 (1 H, m, 4-*H*), 1.24 (2 H, m, 3-H_2), 0.97 (3 H, d, J 7.0, 8-H_3), 0.93 (3 H, d, J 7.0, $CH(CH_3)_2$), 0.90 (3 H, d, J 7.0, 9-H_3), 0.88 (3 H, d, J 7.0, $CH(CH_3)_2$); δ_C (126 MHz; $CDCl_3$) 81.73 (5-*C*), 67.03 (1-*C*), 36.03 (3-*C*), 33.72 (4-*C*), 33.42 (2-*C*), 29.92 (6-*C*), 20.04 ($CH(CH_3)_2$), 18.75 (8-*C*), 17.42 (9-*C*), 15.82 ($CH(CH_3)_2$); *m/z* (ES^+) 197 ($M+Na^+$, 100 %); HRMS (ES^+) Found MNH_4^+, 192.1955; $C_{10}H_{26}O_2N$ requires *MNH4*, 192.1958. Accompanied by an inseparable mixture of diastereoisomers of 2,4,6-trimethylheptane-1,5-diol **76-77** as a clear oil (0.02 g, 10 %); R_f (pet. ether/ethyl acetate [1:1]) 0.32; ν_{max} (thin film) 3353 (broad, O-H), 2961, 2935, 2877, 1468, 1385, 1076, 1050 cm^{-1}; NMR data for the major isomer **77**: δ_H (500 MHz; $CDCl_3$) 3.45 (2 H, d, J 6.0, 1-H_2), 3.08 (1 H, d, J 6.0, 5-*H*), 1.80 (1 H, oct, 6-*H*), 1.75 (1 H, m, 2-*H*), 1.71 (1 H, m, 4-*H*), 1.34 (1 H, ddd, J 13.0, 10.0, 3.5, 3-*H*H), 1.25 (1 H, ddd, J 13.0, 10.0, 1.5, 3-H*H*), 0.92 (3 H, d, J 7.0, $CH(CH_3)_2$), 0.91 (3

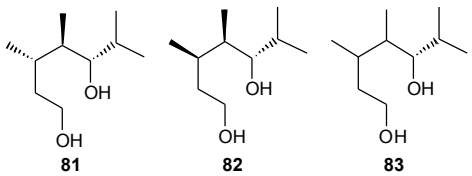
H, d, J 7.0, CH(C*H*$_3$)$_2$), 0.90 (3 H, d, J 4.5, 9-*H*$_3$), 0.88 (3 H, d, J 4.0, 8-*H*$_3$); δ_C (126 MHz; $CDCl_3$) 81.56 (5-*C*), 69.13 (1-*C*), 34.30 (3-*C*), 32.94 (2-*C*), 32.48 (4-*C*), 30.09 (6-*C*), 19.85 (CH(*C*H$_3$)$_2$), 16.68 (9-*C*), 16.59 (CH(*C*H$_3$)$_2$), 16.00 (8-*C*); *m/z* (ES^+) 197 ($M+Na^+$); HRMS (ES^+) Found MNH_4^+, 192.1961; $C_{10}H_{26}O_2N$ requires *MNH*$_4$, 192.1958.

4,5-dimethyl-1-phenyl-6-(prop-2'-yl)-1-trimethylsilyl-silacyclohexane **78-80**



2.2 ml of a solution of Ir(P(C_6H_{11})$_3$)(cod)pyr.PF_6 (207 mg, 0.257 mmol) in dry, degassed (freeze-pump-thaw method) DCM (10.3 ml) was added to a solution of silacycle mixture **47** (0.34 g, 1.08 mmol) in dry, degassed DCM (45 ml) under nitrogen. The vessel was repeatedly evacuated and flushed with hydrogen from a balloon and the mixture was stirred for 1 h. Another 2.2 ml of catalyst solution was added and stirred for 1 h. This was repeated twice more and stirred for 20 h. The remaining catalyst solution (1.5 ml) was added and the solution stirred for 160 h. The mixture was then concentrated in vacuo and pet. ether was added to form a suspension of the catalyst. This was filtered through celite and washed with pet. ether. The filtrate was concentrated and dried in vacuo. Flash column chromatography (pet. ether) gave the title compounds as a colourless oil (0.12 g, 35 %); R_f (pet. ether) 0.88 as a mixture of isomers in a ratio of 66 : 26 : 5 : 2 : 1 % (ratio of product peak integrals by GC); *m/z* (GCMS, EI) 318 (M^+, 24 %), 303 (M^+-Me, 2 %), 245 (M^+-$SiMe_3$, 100 %), 217 (8 %), 203 (14 %), 189 (38 %), 175 (87 %), 161 (89 %), 135 (79 %), 121 (90 %). Further elution gave starting silacycles **47** (0.07 g, 19 %).

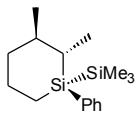
(±)-(3S,4R*,5S*) 3,4,6-trimethylheptane-1,5-diol* **81**



Silane mixture **78-80** was oxidised following the standard protocol to afford the title compound as a thick colourless oil (11 %); R_f (pet. ether/ethyl acetate [1:1]) 0.28; ν_{max} (thin film) 3358 (broad, O-H), 2959, 2931, 2875, 1463, 1383, 1367, 1058, 992 cm^{-1}; δ_H (500 MHz; $CDCl_3$) 3.76 (1 H, ddd, J 10.5, 6.5, 5.0, 1-*H*H), 3.63 (1 H, dd, J 10.5, 9.0, 5.5,

1-H*H*), 3.29 (1 H, dd, J 10.0, 2.5, 5-*H*), 2.11 (1 H, m, 3-*H*), 1.84 (1 H, sept d, J 7.0, 2.5, 6-*H*), 1.71 (1 H, m, 2-*H*H), 1.53 (1 H, m, 4-*H*), 1.21 (1 H, m, 2-H*H*), 1.00 (3 H, d, J 7.0, CH(CH_3)$_2$), 0.96 (3 H, d, J 7.0, 8-H_3), 0.83 (3 H, d, J 7.0, CH(CH_3)$_2$), 0.74 (3 H, d, J 7.0, 9-H_3); δ_C (126 MHz; $CDCl_3$) 77.59 (5-*C*), 61.88 (1-*C*), 41.01 (4-*C*), 33.26 (3-*C*), 29.36 (2-*C*), 28.61 (6-*C*), 20.82 (CH(*C*H_3)$_2$), 19.15 (8-*C*), 13.94 (CH(*C*H_3)$_2$), 10.50 (9-*C*); *m/z* (ES^+) 197 ($M+Na^+$, 100 %); HRMS (ES^+) Found, MNa^+, 197.1527; $C_{10}H_{22}O_2Na$ requires *MNa*, 197.1517; accompanied by a mixture of diastereoisomers of 3,4,6-trimethylheptane-1,5-diol **82-83** as a clear oil (5 mg, 7 %); R_f (pet. ether/ethyl acetate [1:1]) 0.13; ν_{max} (thin film) 3352 (broad, O-H), 2959, 2925, 2875, 1455, 1384, 1059, 988 cm^{-1}; NMR data for major isomer **83**: δ_H (500 MHz; $CDCl_3$) 3.72 (1 H, dt, J 10.5, 7.0, 1-*H*H), 3.69 (1 H, dt, J 10.5, 7.0, 1-H*H*), 3.26 (1 H, dd, J 2.5, 10.0, 5-*H*), 2.15 (1 H, hex d, J 7.0, 2.5, 3-*H*), 1.83 (1 H, sept d, J 7.0, 2.5, 6-*H*), 1.56-1.50 (3 H, m, 2-H_2 and 4-*H*), 1.00 (3 H, d, J 7.0, CH(CH_3)$_2$), 0.82 (3 H, d, J 7.0, CH(CH_3)$_2$), 0.81 (3 H, d, J 7.0, 8-H_3), 0.71 (3 H, d, J 7.0, 9-H_3); δ_C (126 MHz; $CDCl_3$) 77.51 (5-*C*), 61.29 (1-*C*), 39.43 (3-*C*), 38.72 (6-*C*), 29.27 (2-*C*), 27.98 (4-*C*), 20.67 (CH(*C*H_3)$_2$), 13.69 (CH(*C*H_3)$_2$), 13.40 (8-*C*), 9.71 (9-*C*); *m/z* (ES^+) 197 ($M+Na^+$); HRMS (ES^+) Found MNa^+, 197.1525; $C_{10}H_{22}O_2Na$ requires *MNa*, 197.1517.

1-phenyl-1-trimethylsilyl-2-methyl-3-methylsilacyclohexane 84

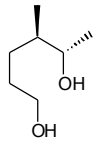


84

Reduction of silanes **50** in toluene using Pd/C in dry toluene gave the title compound as a mixture of four isomers in a ratio of 80 : 10 : 5 : 5 (90%) (ratio of product peak integrals by GC); ν_{max} (thin film) 3067, 3049, 2949, 2921, 2906, 2866, 2852, 1454, 1427, 1376, 1258, 1243, 1169, 1101, 1047, 851, 833, 791, 731, 698, 666 cm^{-1}; NMR data for major isomer **84**: δ_H (500 MHz; $CDCl_3$) 7.51-7.49 (2 H, m, *meta* Ar-*H*), 7.33-7.32 (3 H, m, *ortho* and *para* Ar-*H*), 2.05 (1 H, m, 5-*H*H), 1.73 (1 H, dq, J 14.0, 2.5, 2-*H*), 1.55-1.44 (2 H, m, 4-*H*H and 5-H*H*), 1.19 (3 H, d, J 7.5, 8-H_3), 1.16 (1 H, m, 6-*H*H), 1.03 (1 H, m, 4-H*H*), 1.00 (3 H, d, J 7.5, 7-H_3), 0.94-0.82 (2 H, m, 6-H*H* and 3-*H*), 0.18 (9 H, s, Si(CH_3)$_3$); δ_C (126 MHz; $CDCl_3$) 138.66 (*ipso-Ar*), 134.32 (*meta-Ar*), 128.34 (*para-Ar*), 127.70 (*ortho-Ar*), 39.03 (4-*C*), 38.76 (2-*C*), 26.23 (3-*C*), 24.37 (5-*C*), 21.77 (7-*C*), 15.90 (8-*C*), 12.06 (6-*C*), 0.18 (Si(*C*H_3)$_3$); *m/z* (EI) 276 (M^+, 78 %), 261 (M^+-Me, 9 %), 203 (M^+-$SiMe_3$, 100 %), 187 (28 %), 175 (81 %), 161 (76 %), 147 (80 %), 140 (48 %), 135

(92 %), 125 (74 %), 121 (89 %), 107 (91 %), 105 (80 %), 97 (48 %); HRMS (EI) Found M^+, 276.1723; $C_{16}H_{28}Si_2$ requires *M*, 276.1724.

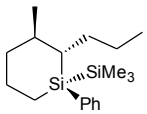
(±)-(4R,5S*) 4-Methyl-hexane-1,5-diol* **85**



85

Silacycle **84** was oxidised following the standard protocol to afford the title compound as a thick colourless oil (56 %); R_f (pet. ether/ethyl acetate [1:4]) 0.26; ν_{max} (thin film) 3354 (broad, O-H), 2964, 2927, 2876, 1456, 1379, 1269, 1098, 1056 cm^{-1}; δ_H (400 MHz; $CDCl_3$) 3.65 (3 H, m, 1-*H* and 5-*H*), 1.72-1.60 (3 H, m, 2-*H*H and OH's), 1.58-1.46 (3 H, m, 2-H*H*, 3-*H*H and 4-*H*), 1.18 (1 H, m, 3-H*H*), 1.15 (3 H, d, J 6.5, 6-H_3), 0.89 (3 H, d, J 7.0, 7-H_3); δ_C (101 MHz; $CDCl_3$) 71.71 (5-*C*), 63.12 (1-*C*), 39.85 (4-*C*), 30.15 (2-*C*), 28.53 (3-*C*), 19.74 (6-*C*), 14.79 (7-*C*); *m/z* (ES) 155 ($M+Na^+$, 100 %).

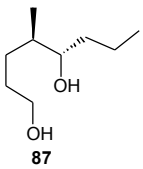
3-methyl-1-phenyl-2-propyl-1-(trimethylsilyl)silacyclohexane **86**



86

Reduction of silanes **52** in toluene using Pd/C in dry toluene gave the title compound as a mixture of three diastereoisomers in a ratio of 81 : 11 : 8 % (ratio of product peak integrals by GC); ν_{max} (thin film) 3067, 3054, 2953, 2921, 2868, 1457, 1427, 1243, 1100, 851, 833, 732, 698 cm^{-1}; NMR data for major isomer **86**: δ_H (500 MHz; $CDCl_3$) 7.52-7.50 (2 H, m, *meta* Ar-*H*), 7.32-7.30 (3 H, m, *ortho* and *para* Ar-*H*), 1.97 (1 H, dm, J 13.5, 5-*H*H), 1.71 (1 H, dm, J 13.5, 4-*H*H), 1.60 (2 H, m, 3-*H*H and 1'-*H*H), 1.50 (2 H, m, 5-H*H* and 1'-H*H*), 1.25 (2 H, m, 2'-H_2), 1.08 (2 H, m, 4-H*H* and 6-*H*H), 0.97 (3 H, d, J 6.5, 7-H_3), 0.86 (1 H, m, 2-*H*), 0.83 (1 H, m, 6-H*H*), 0.80 (3 H, t, J 7.0, 3'-H_3), 0.20 (9 H, s, Si(CH_3)$_3$); δ_C (126 MHz; $CDCl_3$) 139.64 (*ipso-Ar*), 134.37 (*meta-Ar*), 128.20 (*para-Ar*), 127.64 (*ortho-Ar*), 38.30 (4-*C*), 37.41 (3-*C*), 34.14 (1'-*H*), 32.13 (2-*H*), 23.98 (2'-*H*), 23.67 (5-*H*), 22.66 (7-*H*), 14.63 (3'-*H*), 12.50 (6-*C*), 0.17 (Si(CH_3)$_3$); *m/z* (EI) 304 (M^+, 40 %), 289 (M^+-Me, 6 %), 231 (M^+-$SiMe_3$, 99 %), 203 (24 %), 189 (23 %), 175 (71 %), 163 (51 %), 161 (80 %), 153 (42 %), 147 (73 %), 135 (92 %); HRMS (EI) Found M^+, 304.2045; $C_{18}H_{32}Si_2$ requires *M*, 304.2043.

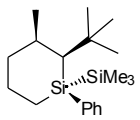
(±)-(4R,5S*) 4-Methyloctane-1,5-diol* **87**



87

Silacycle **86** was oxidised following the standard protocol to afford the title compound as a white solid (16 %) consisting of a mixture of two diastereoisomers in a ratio of 74 : 26 (NMR); R_f (pet. ether/ethyl acetate [1:1]) 0.15; ν_{max} (thin film) 3355 (broad, O-H), 2956, 2930, 2874, 1460, 1372, 1108, 1059, 976 cm^{-1}; NMR data for major isomer **87**: δ_H (500 MHz; $CDCl_3$) 3.65 (2 H, t, J 7.0, 1-H_2), 3.45 (1 H, m, 5-*H*), 1.68 (1 H, m, 2-*H*H), 1.56-1.48 (3 H, m, 2-H*H*, 3-*H*H and 4-*H*), 1.44-1.32 (4 H, m, 6-H_2 and 7-H_2), 1.19 (1 H, m, 3-H*H*), 0.94 (3 H, t, J 7.0, 8-H_3), 0.91 (3 H, d, J 7.0, 9-H_3); δ_C (126 MHz; $CDCl_3$) 75.66 (5-*C*), 63.22 (1-*C*), 38.60 (4-*C*), 35.74 (6-*C*), 30.31 (2-*C*), 27.95 (3-*C*), 19.18 (7-*C*), 15.41 (9-*C*), 14.15 (8-*C*); *m/z* (CI) 178 ($M+NH_4^+$, 12 %), 161 ($M+H^+$, 3 %), 52 (100 %).

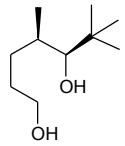
2-methyl-3-(2'-methylprop-2'-yl)-1-phenyl-1-(trimethylsilyl)methylsilacyclohexane **88**



88

Reduction of silanes **54** using PtO_2 in ethyl acetate gave the title compound as a mixture of 3 detectable diastereoisomers in a ratio of 90 : 6 : 4 (87%) (ratio of product peak integrals by GC); ν_{max} (thin film) 3066, 3049, 2954, 2911, 2862, 1469, 1427, 1391, 133, 1323, 1244, 1168, 1154, 1097, 835, 744, 733, 699 cm^{-1}; NMR data for major isomer **88**: δ_H (500 MHz; $CDCl_3$) 7.51-7.49 (2 H, m, *meta*-Ar-*H*), 7.33-7.27 (3 H, m, *ortho* and *para*-Ar-*H*), 2.21 (1 H, m, 3-*H*), 1.81 (1 H, m, 5-*H*H), 1.70-1.62 (2 H, m, 5-H*H* and 4-*H*H), 1.39 (1 H, m, 4-H*H*), 1.24 (1 H, dt, J 15.0, 6.0, 6-*H*H), 1.08-1.07 (10 H, m, $C(CH_3)_3$ and 2-*H*), 0.82 (1 H, m, 6-H*H*), 0.75 (3 H, d, J 7.5, 7-H_3), 0.05 (9 H, s, $Si(CH_3)_3$); δ_C (126 MHz; $CDCl_3$) 141.12 (*ipso-Ar*), 134.13 (*meta-Ar*), 127.52 (*ortho-Ar*), 127.49 (*para-Ar*), 44.68 (2-*C*), 34.28 ($C(CH_3)_3$), 33.78 (4-*C*), 31.77 (3-*C*), 31.51 ($C(CH_3)_3$), 24.30 (7-*C*), 17.94 (5-*C*), 8.73 (6-*C*), -1.06 ($Si(CH_3)_3$); *m/z* (EI) 318 (M^+, 32 %), 303 (M^+-Me, 6 %), 245 (M^+-$SiMe_3$, 96 %), 217 (12 %), 189 (26 %), 187 (70 %), 175 (72 %), 167 (47 %), 161 (74 %), 147 (58 %), 145 (49 %), 135 (91 %), 121 (100 %).

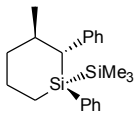
(±)-(4S,5S*) 4,6,6-Trimethylheptane-1,5-diol* **89**



89

Silacycle mixture **88** was oxidised following the standard protocol to afford the title compound as as a mixture of diastereoisomers (21 %); R_f (pet. ether/ethyl acetate [1:4]) 0.32; ν_{max} (thin film) 3388 (broad, O-H), 2956, 2874, 1482, 1468, 1104, 1064 cm^{-1}; NMR data for major diastereoisomer **89**: δ_H (500 MHz; $CDCl_3$) 3.62 (2 H, t, J 6.0, 1-H_2), 3.11 (1 H, d, J 3.0, 5-*H*), 1.73-1.65 (2 H, m, 4-*H* and 2-*H*H), 1.62 (1 H, m, 3-*H*H), 1.48 (1 H, m, 2-H*H*), 1.13 (1 H, m, 3-H*H*), 1.00 (3 H, d, J 7.0, 8-H_3), 0.92 (9 H, s, $C(CH_3)_3$); δ_C (126 MHz; $CDCl_3$) 84.05 (5-*C*), 63.20 (1-*C*), 35.89 (6-*C*), 33.91 (4-*C*), 30.82 (2-*C*), 27.12 (3-*C*), 26.65 ($C(CH_3)_3$), 20.45 (8-*C*); *m/z* (ES^+) 197 ($M+Na^+$, 100 %); HRMS (ES^+) Found MNa^+, 197.1503; $C_{10}H_{22}O_2Na$ requires *MNa*, 197.1517.

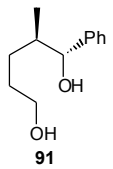
3-methyl-1,2-diphenyl-1-(trimethylsilyl)silacyclohexane **90**



90

Reduction of silanes **56** using Pd/C in dry toluene gave the title compound as a mixture of 2 detectable diastereoisomers in a ratio of 93 : 7 % (ratio of product peak integrals by GC); ν_{max} (thin film) 3067, 3028, 2948, 2922, 2908, 2868, 2856, 1600, 1487, 1451, 1427, 1243, 1101, 855, 832, 763, 733, 699 cm^{-1}; NMR data for major isomer **90**: δ_H (400 MHz; $CDCl_3$) 7.32-7.11 (8 H, m, Ar-*H*), 7.01 (2 H, d, J 7.5, Ar-*H*), 2.24 (1 H, m, 3-*H*), 2.21 (1 H, m, 5eq-*H*), 2.10 (1 H, d, J 12.5, 2-*H*), 1.94 (1 H, dm, J 14.0, 4eq-*H*), 1.70 (1 H, qt, J 14.0, 3.0, 5ax-*H*), 1.33 (1 H, dm, J 14.0, 6eq-*H*), 1.21 (1 H, qd, J 14.0, 2.5, 4ax-*H*), 1.08 (1 H, td, J 14.0, 5.0, 6ax-*H*), 0.86 (3 H, d, J 6.5, 7-H_3), 0.08 (9 H, s, $Si(CH_3)_3$); δ_C (101 MHz; $CDCl_3$) 144.01 (*Ar*), 137.30 (*Ar*), 134.79 (*Ar*), 128.43 (*Ar*), 128.46 (*Ar*), 128.07 (*Ar*), 127.37 (*Ar*), 124.43 (*Ar*), 44.30 (2-*C*), 38.88 (4-*C*), 36.69 (3-*C*), 24.47 (5-*C*), 22.71 (7-*C*), 11.76 (6-*C*), -0.32 ($Si(CH_3)_3$); *m/z* (EI) 338 (M^+, 68 %), 323 (M^+-Me, 33 %), 268 (70 %), 265 (M^+-$SiMe_3$, 81 %), 253 (70 %), 237 (67 %), 233 (66 %), 197 (84 %), 189 (70 %), 188 (77 %), 183 (93 %), 159 (72 %), 145 (80 %), 135 (100 %).

*(±)-(4R*5S*) 4-Methyl-5-phenylpentane-1,5-diol* **91**



91

Silacycle mixture **90** was oxidised in two discrete stages following the standard protocol to afford the title compound (29 %); R_f (pet. ether/ethyl acetate [1:1]) 0.22; ν_{max} (thin film) 3255 (broad, O-H), 1493, 1463, 1454, 1385, 1310, 1261, 1134, 1108, 1076, 1051, 1009, 928, 915, 761, 703, 555 cm^{-1}; δ_H (500 MHz; $CDCl_3$) 7.30 (5 H, m, Ar-*H*), 4.39 (1 H, d, J 7.5, 5-*H*), 3.63 (2 H, t, J 6.5, 1-*H*), 1.84 (1 H, m, 4-*H*), 1.79-1.66 (2 H, m, 2-*H*H and 3-*H*H), 1.51 (1 H, m, 2-H*H*), 1.24 (1 H, m, 3-H*H*), 0.74 (3 H, d, J 7.5, 6-*H*); δ_C (126 MHz; $CDCl_3$) 143.47 (*ipso-Ar*), 128.22 (Ar-*H*), 127.49 (*para-Ar*), 126.67 (Ar-*H*), 79.03 (5-*C*), 62.92 (1-*C*), 39.71 (4-*C*), 28.83 (2-*H*), 28.31 (3-*C*), 15.86 (6-*C*); *m/z* (CI) 212 ($M+NH_4^+$, 44 %), 194 (M^+, 100 %), 177 (M^+-OH, 58 %).