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2-Lithio-2-trimethylsilyl-1-silacyclopentane as a Synthetic Equivalent of 1-Lithio-1,4-butanediol

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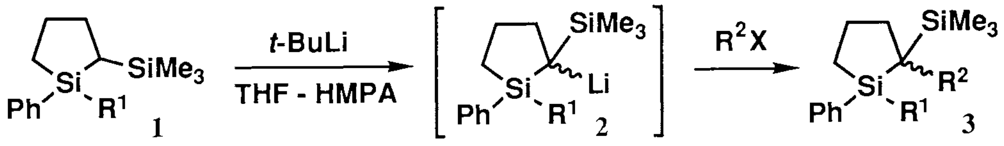
Addition of alkyl iodide to 2-lithio-2-trimethylsilyl-1-silacyclopentane provided 2-alkyl-2-trimethylsilyl-1-silacyclopentane which was converted into 1-alkyl-1,4-butanediol by treatment with H_2O_2-KF and *n*-Bu_4NF.

α-Metallated organosilanes play a fundamental role in preparative organosilicon chemistry.1) A wide range of variously functionalized organosilanes has been deprotonated α to silicon. Among them, bis(trimethylsilyl)methyllithium2) has been widely used for carbon-carbon bond formation. Here we wish to report a preparation of 2-lithio-trimethylsilyl-1-siliacyclopentane and its use for organic synthesis.

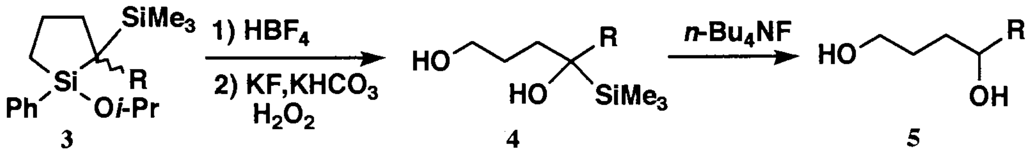
tert-Butyllithium (1.66 mol dm^{-3} pentane solution, 0.72 ml, 1.2 mmol) was added to a solution of 1,1-diphenyl-2-trimethylsilyl-1-silacyclopentane **1a** (0.31 g, 1.0 mmol) in THF (3.0 ml) and HMPA (0.4 ml) at -78 °C. The solution immediately turned dark red. After stirring for 30 min at -78 °C, iodomethane (0.19 ml, 3.0 mmol) was added and the resulting mixture was warmed to room temperature over 2 h. The mixture was poured into ice-cooled water and extracted with ethyl acetate (10 ml x 3). The combined organic layers were dried over Na_2SO_4 and concentrated. The residual oil was submitted to silica-gel column chromatography to give 1,1-diphenyl-2-methyl-2-trimethylsilyl-1-silacyclopentane **3a**3) (0.29 g) in 89% yield. The representative results are shown in Scheme 1. 1-Isopropoxy-1-phenyl-2-trimethylsilyl-1-silacyclopentane **1b** also afforded 2-lithio-2-trimethylsilyl-1-silacyclopentane **2b** (orange solution) which provided the corresponding alkylated silacyclopentane **3d**, **3e**, and **3f** as 1:1 stereoisomeric mixtures upon treatment with alkyl halides.

Oxidation of the silacyclopentane **3a** with HBF_4 followed by H_2O_2-KF-$KHCO_3$4) gave the expected diol **4a** only in 20% yield along with unidentified complex mixture. The oxidative cleavage of two carbon-silicon



1a	R^1 = Ph	R^2X = MeI	**3a**	89%
1a	R^1 = Ph	R^2X = *n*-$C_5H_{11}I$	**3b**	62%
1a	R^1 = Ph	R^2X = $PhCH_2Br$	**3c**	63%
1b	R^1 = O-*i*-Pr	R^2X = MeI	**3d**	65%
1b	R^1 = O-*i*-Pr	R^2X = *n*-$C_5H_{11}I$	**3e**	43%
1b	R^1 = O-*i*-Pr	R^2X = $PhCH_2Br$	**3f**	49%

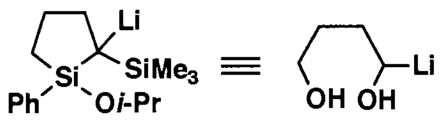
Scheme 1.



	4	5
3e R = n-C_5H_{11}	55%	75%
3f R = CH_2Ph	79%	85%

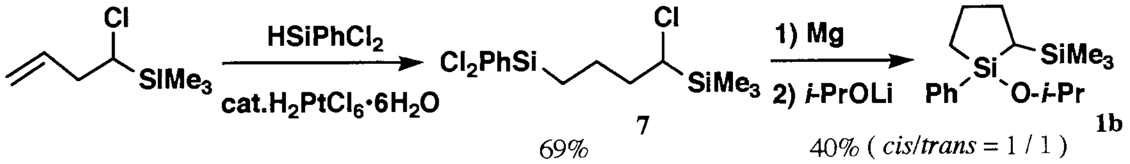
Scheme 2.

bonds of **3e** or **3f**, however, was easily performed by treatment with HBF_4 followed by H_2O_2-KF-$KHCO_3$ to provide the corresponding silyl alcohol **4e** or **4f.** Protodesilylation of **4** with n-Bu_4NF in DMF[5] gave 1,4-butanediol **5** (Scheme 2). Therefore, 1-isopropoxy-2-lithio-1-phenyl-2-trimethylsilyl-1-silacyclopentane **2b** can be regarded as a synthon of 1-lithio-1,4-butanediol **6**.



2b **6**

1,1-Diphenyl-2-trimethylsilyl-1-silacyclopentane **1a** was generated (45%) starting from 1,1-diphenyl-1-silacyclobutane according to the reported procedure (ICH_2SiMe_3, LDA).[6] Meantime, 1-isopropoxy-1-phenyl-2-trimethylsilyl-1-silacyclopentane **1b** was prepared as follows (Scheme 3). Hydrosilylation of 4-chloro-4-trimethylsilyl-1-butene with $HSiPhCl_2$ in the presence of H_2PtCl_6 gave **7** which was treated with Mg followed by i-PrOLi to afford **1b** as an isomeric mixture (*cis*/*trans* = 1:1).[7]



69% 40% (*cis*/*trans* = 1 / 1)

Scheme 3.

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References

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3) **3a**: Bp 112-114 °C (0.5 Torr, 1 Torr = 133.322 Pa, bath temp); IR (neat) 3066, 2944, 2856, 1428, 1247, 1109, 857, 833, 735, 699, 658 cm^{-1}; ^1H NMR ($CDCl_3$) δ -0.21 (s, 9H), 0.97 (s, 3H), 1.15-1.16 (m, 3H), 1.62-2.25 (m, 3H), 7.25-7.49 (m, 6H), 7.50-7.60 (m, 2H), 7.61-7.75 (m, 2H); ^{13}C NMR ($CDCl_3$) δ -2.35, 9.71, 14.19, 19.26, 22.29, 38.94, 127.52, 127.72, 128.90, 129.07, 135.03, 135.43, 135.56, 135.75. Found: C, 74.30; H, 8.69%. Calcd for $C_{20}H_{28}Si_2$: C, 74.00; H, 8.69%.

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7) Isomerically pure **1b** (*cis* or *trans*) as well as a 1:1 mixture of **1b** provided the same 1:1 isomeric mixtures **3d**, **3e**, and **3f**. Thus, a *cis*/*trans* mixture was used without separation.

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