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Potassium *t*–Butoxide or Silver Acetate Induced Ring Enlargement of Silacyclobutane into Silacyclopentane. Application to the Synthesis of 1,4–Diol

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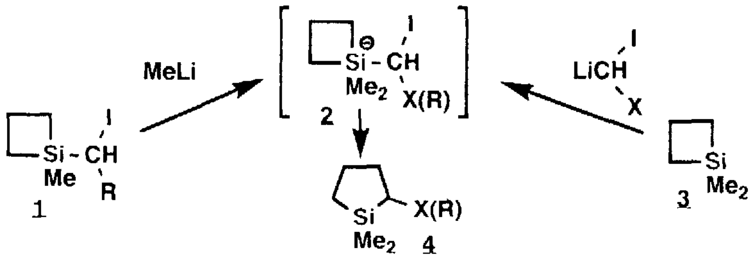
Key Words: silacyclobutane; silacyclopentane; ring enlargement; 1,4–diol

Abstract: *Treatment of 1–(1–iodoalkyl)–1–silacyclobutanes with t–BuOK or AgOAc provided 2–alkyl–1–silacyclopentanes which were easily converted into 1,4–diols by oxidative cleavage of carbon–silicon bonds.*

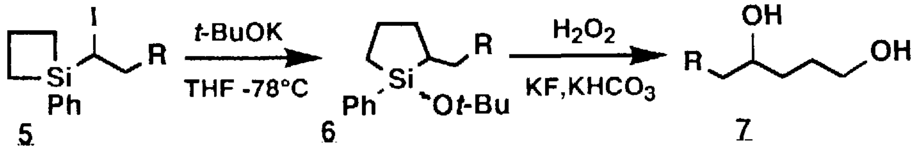
Recently we have reported[1] that an addition of lithium carbenoids to 1,1–dimethyl–1–silacyclobutane **3** provided silacyclopentanes **4**. The reaction might proceed via pentacoordinate silicate **2**. It then occurred to us that, if treatment of 1–(1–iodoalkyl)–1–methyl–1–silacyclobutane **1** with nucleophile such as methyllithium should afford the same pentacoordinate intermediate **2**, the procedure would give another route to silacyclopentanes **4** (Scheme 1).

Scheme 1



However, treatment of 1–(1–iodoalkyl)–1–phenyl–1–silacyclobutane **5a** with methyllithium or phenyllithium provided an expected silacyclopentane in only 7% or 5% yield along with unidentified complex products. Fortunately, the use of potassium *t*–butoxide in place of alkyllithium resulted in clean formation of silacyclopentane **6a**. A typical experiment is as follows. A solution of silacyclobutane **5a** (0.93 g, 1.5 mmol) in THF (2 ml) was added to a suspension of potassium *t*–butoxide (0.20 g, 1.8 mmol) in THF (6 ml) at −78 °C under argon atmosphere. After stirring for 20 min at −78 °C, dry ice–methanol bath was removed and the reaction mixture was warmed up to room temperature. The resulting mixture was poured into ice-cooled water and extracted with ethyl acetate (20 ml x 3). The combined organic layer was dried over anhydrous Na_2SO_4 and concentrated *in vacuo*. Distillation of the residual oil using Kugelrohr afforded silacyclopentane **6a**[2] (0.66 g, 65:35 diastereomeric mixture) in 77% yield. Oxidative cleavage of two carbon-silicon bonds of **6a** has been easily achieved by treatment with H_2O_2[3] to give 1,4-diol **7a**[4] (0.42 g) in 85% yield. The representative results are shown in Scheme 2.

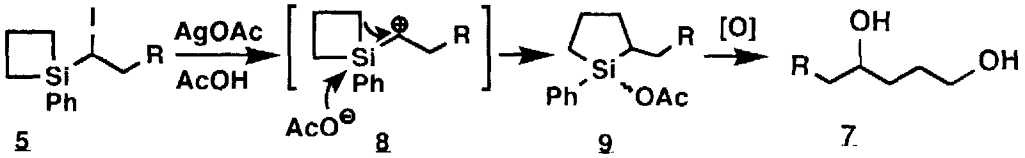
Scheme 2.



		6	7
a:	R= n-C_6F_{13}	77% (65:35)	85%
b:	R= t-C_4H_9	65% (52:48)	55%
c:	R= i-C_3H_7	81% (69:31)	86%
d:	R= CH_2I	64% (68:32)	67%

The rearrangement also took place upon treatment with silver acetate. Exposure of silacyclobutanes **5** to silver acetate in acetic acid at 25 °C provided acetoxysilacyclopentanes **9** as shown in Scheme 3. The reaction proceeds as follows: (1) Silver ion attacks iodine of **5** to afford silacyclobutylalkyl cation **8** and (2) the attack of acetate anion[5] on silicon of **8** causes one of carbon-silicon bonds of silacyclobutane to migrate to the α-carbon atom to give silacyclopentane **9**.[6,7] Treatment of **9** with H_2O_2-KF provided 1,4-diol **7** in the same way as **6**.

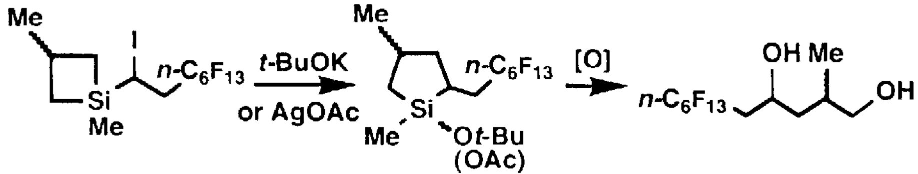
Scheme 3



		9	7
a:	R= n-C_6F_{13}	72%	53%
c:	R= i-C_3H_7	60%	60%

The ring enlargement of 3-methyl-1-silacyclobutane **10** was examined. Treatment of **10a** (mixture of diastereomers, 60:40) with t-BuOK gave the corresponding silacyclopentane **11** as a mixture of four diastereomers in 77% yield. Oxidation of **11** with H_2O_2-KF provided a mixture of two diastereomeric 1,4-diols **12** whose ratio was 74:26. Meantime, successive treatment of a substrate **10b** consisting of two diastereomers (95:5) with t-BuOK and H_2O_2-KF afforded another mixture of two diastereomeric 1,4-diols **12** which had a similar isomeric ratio (73:27). Thus, the stereochemistry of the starting material did not affect the stereochemical outcome. The reaction with silver acetate also proceeded non-stereospecifically. Exposure of **10a** or **10c** to silver acetate resulted in formation of same isomeric mixture of two diastereomers (46:54 or 45:55) (Scheme 4).

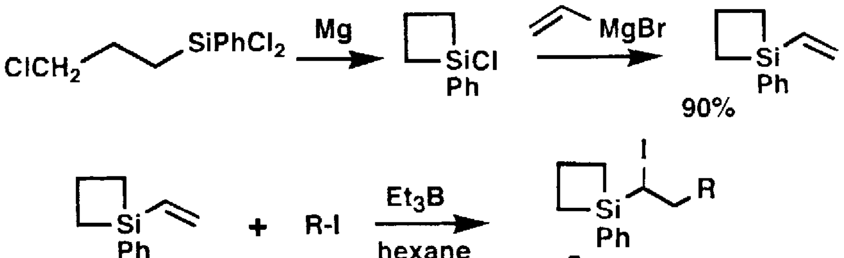
Scheme 4



	10	**11**	**12**
t-BuOK	**10a** (60:40)	77%	61% (74:26)
	10b (95: 5)		(73:27)
AgOAc	**10a** (60:40)	38%	75% (46:54)
	10c (85:15)		(45:55)

1-(1-Iodoalkyl)-1-phenyl-1-silacyclobutanes **5** were prepared as follows. Treatment of 3-chloropropyldichlorophenylsilane with magnesium gave 1-chloro-1-phenyl-1-silacyclobutane according to the reported procedure.[8] A successive addition of vinylmagnesium bromide to the solution of 1-chloro-1-phenyl-1-silacyclobutane provided 1-phenyl-1-vinyl-1-silacyclobutane in 90% overall yield. Triethylborane induced radical addition of iodoalkane[9] to 1-phenyl-1-vinyl-1-silacyclobutane afforded 1-(1-iodoalkyl)-1-phenyl-1-silacyclobutanes **5** in 39-90% yields (Scheme 5).[10,11]

Scheme 5



5

R= *n*-C_6F_{13}	90%	R= *t*-C_4H_9	52%	R= CF_3CH_2	48%
R= *i*-C_3H_7	39%	R= CH_2I	43%		

References and Notes

1. Matsumoto, K.; Oshima, K.; Utimoto, K. *Tetrahedron Lett.* **1990**, *31*, 6055-6058.
2. The diastereomeric mixture of **6a** (65/35) was separated by silica-gel column chromatography using hexane as an eluant. Faster moving band (minor product): Bp 104 °C (1.0 Torr, bath temp); IR (neat) 3070, 2974, 2930, 2860, 1459, 1430, 1392, 1367, 1241, 1194, 1145, 1116, 1048, 1023, 822, 734, 699 cm^{-1}; ^1H NMR ($CDCl_3$) δ0.74-0.96 (m, 1H), 1.05-1.61 (m, 4H), 1.24 (s, 9H), 1.88-2.26 (m, 3H), 2.33-2.69 (m, 1H), 7.35-7.54 (m, 3H), 7.59-7.71 (m, 2H); ^{13}C NMR ($CDCl_3$) δ13.15, 18.55, 24.75, 31.07 (t, J = 22 Hz) 31.91, 33.99, 73.23, 127.87, 129.63, 133.66, 138.06. Found: C, 44.30; H, 4.01%. Calcd for $C_{21}H_{23}F_{13}OSi$: C, 44.53; H, 4.09%. Slower moving band (major product): Bp 104 °C (1.0 Torr, bath

temp); IR (neat) 3070, 2974, 2932, 2862, 1456, 1430, 1391, 1367, 1241, 1194, 1145, 1115, 1058, 1023, 811, 736, 700 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ0.84–1.09 (m, 2H), 1.09–1.99 (m, 5H), 1.35 (s, 9H), 1.99–2.31 (m, 2H), 7.38–7.54 (m, 3H), 7.55–7.73 (m, 2H); ^{13}C NMR (CDCl$_3$) δ12.08, 20.39, 24.30, 31.29 (t, J = 23 Hz), 31.95, 33.43, 73.46, 127.79, 129.63, 134.04. Found: C; 44.63; H, 4.07%. Calcd for $C_{21}H_{23}F_{13}OSi$; C, 44.53; H, 4.09%.

3. Tamao, K.; Ishida, N.; Tanaka, T.; Kumada, M. *Organometallics* **1983**, *2*, 1694–1696.
4. **7a**: Mp 59.5–60.5 °C; IR (nujol) 3252, 1241, 1219, 1188, 1141, 1056, 696 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ1.48–1.66 (m, 4H), 1.97–2.38 (m, 4H), 3.44–3.79 (m, 2H), 4.06–4.26 (m, 1H); ^{13}C NMR (CDCl$_3$) δ28.41, 34.97, 38.00 (t, J = 21 Hz), 62.63, 65.15. Found; C, 31.35; H, 2.57%. Calcd for $C_{11}H_{11}F_{13}O_2$: C, 31.29; H, 2.63%.
5. Treatment of **5a** with $AgBF_4$ in dichloromethane gave 1-iodo-1-phenyl-2-alkyl-1-silacyclopentane which was transformed into 1-methyl-1-phenyl-2-alkyl-1-silacyclopentane in 30% overall yield upon treatment with methyllithium.
6. **9a** (57/43 diastereomeric mixture): Bp 123 °C (2.0 Torr, bath temp); IR (neat) 3072, 2936, 2862, 1729, 1431, 1373, 1241, 1145, 1119, 1076, 1048, 1019, 936, 733, 717, 699 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ0.89–2.73 (m, 12H), (2.15 (s) + 2.20 (s) total 3H), 7.40–7.73 (m, 5H); ^{13}C NMR (CDCl$_3$) sets of 57:43 peaks δ(10.68, 11.70), (18.38, 18.77), (23.38, 24.32), (30.81 (t, J = 23 Hz), 30.86 (t, J = 23 Hz)), (33.64, 33.83), (128.12, 128.21), (130.17, 130.47), (130.57, 130.65), (133.81, 133.98), (171.80, 172.02). Purification by silica-gel column chromatography caused decomposition. Distillation was not effective either for the preparation of analytically pure sample. Thus, the compound **9a** was converted into **6a** upon treatment with *t*-BuOK in THF at 0 °C and identified by comparison with a sample generated by the reaction of **5a** with *t*-BuOK.
7. The Wagner-Meerwein type rearrangement involving migration of an organic group from silicon to the α-carbon atom has been reported. Tamao, K.; Nakajima, T.; Kumada, M. *Organometallics* **1984**, *3*, 1655–1660.
8. Laane, J. *J. Am. Chem. Soc.* **1967**, *89*, 1144–1147.
9. We have reported an addition of iodoalkanes to silylacetylene (Ichinose, Y.; Matsunaga, S.; Fugami, K.; Oshima, K.; Utimoto, K. *Tetrahedron Lett.* **1989**, *30*, 3155–3158). Vinylsilanes were less reactive toward alkyl radicals than silylacetylene and the yields of adducts were lower than those of the reaction between silylacetylene and alkyl iodides.
10. **5b** (R = *t*-Bu): Bp 127 °C (1.0 Torr, bath temp); IR (neat) 2952, 2864, 1466, 1428, 1394, 1365, 1119, 848, 733, 697 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ0.93 (s, 9H), 1.20–1.50 (m, 4H), 1.85–2.20 (m, 4H), 3.45 (dd, J = 5.5, 6.5 Hz, 1H), 7.30–7.52 (m, 3H), 7.65–7.85 (m, 2H); ^{13}C NMR (CDCl$_3$) δ11.20, 15.63, 16.19, 16.30, 29.46, 32.71, 47.34, 127.78, 129.85, 134.64, 134.89. Found: C, 50.40; H, 6.49%. Calcd for $C_{15}H_{23}ISi$: C, 50.28; H, 6.47%.
11. Financial support by the Ministry of Education, Science and Culture of Japan (Grant-in-Aid for Scientific Research #026540624) is acknowledged.

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