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BASE INDUCED REACTION OF SILACYCLOBUTANE WITH ALDEHYDE OR EPOXIDE

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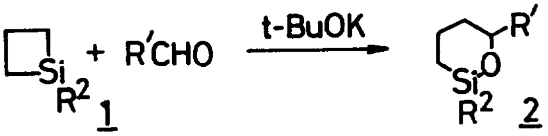
Summary: The reaction of silacyclobutane with benzaldehyde in the presence of a catalytic amount of potassium t-butoxide gave six-membered cyclic silyl ether. Meanwhile, treatment of a mixture of silacyclobutane and epoxide with lithium diisopropylamide provided silacyclopentane derivative.

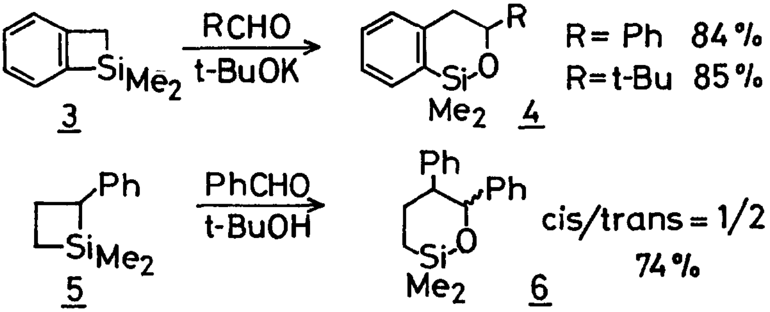
Silacyclobutane derivatives have attracted much attention as a source of polymer containing silicon[1] or as a precursor of silenes.[2] The synthetic use, however, has been limited.[3] The interest in the development of synthetically useful reaction has motivated the present studies on the reaction of silacyclobutane with carbonyl compounds or epoxides in the presence of base.

A catalytic amount of potassium t-butoxide (34 mg, 0.3 mmol) was added to a solution of 1,1-dimethyl-1-silacyclobutane (**1a**, R = Me, 0.30 g, 3.0 mmol) and benzaldehyde (0.32 g, 3.0 mmol) in THF (5.0 ml) at 0 °C under an argon atmosphere. The resulting mixture was stirred at 0 °C for 2 h and poured into ice water. Workup (ethyl acetate, brine) followed by purification by silica-gel column chromatography gave cyclic silyl ether **2a** (R = Me, R' = Ph)[4] (0.40 g) in 65% yield. Pivalaldehyde provided the corresponding cyclic silyl ether **2b** (R = Me, R' = t-Bu)[5] in 72% yield.[6]

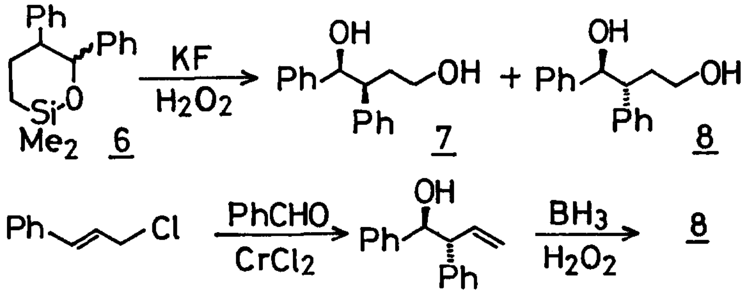


R = Me	R' = Ph	65%	R = Ph	R' = Ph	82%
R = Me	R' = t-Bu	72%	R = Ph	R' = t-Bu	56%

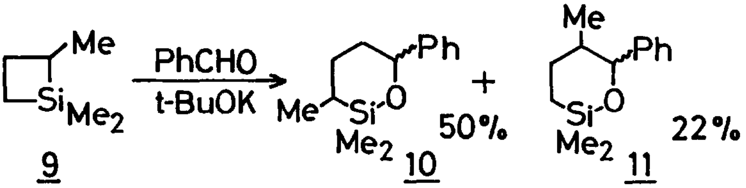
1,1-Dimethyl-2,3-benzo-1-sila-2-cyclobutene **3**[7] and 1,1-dimethyl-2-phenyl-1-silacyclobutane **5** also provided the corresponding oxasilacyclohexanes **4** and **6** in good yields. The compound **3** was more reactive than 1,1-dimethyl-1-silacyclobutane **1a** and the reaction with aldehydes was performed at -78 °C. In these examples, one of two C-Si bonds was cleaved selectively. The product **6** consists of two stereoisomers (cis/trans = 1/2).



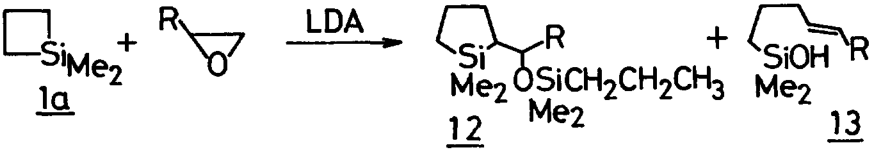
The stereochemistry of **6** was determined as follows. The mixture **6** (cis/trans = 1/2) was treated with KF-H_2O_2[8] to give a mixture of syn- and anti-diol (**7** and **8**, **7**/**8** = 1/2). The latter diol **8** was identical with a sample prepared from (E)-cinnamyl chloride following the procedure depicted below: (1) Grignard-type carbonyl addition of cinnamyl chloride by means of chromous salt[9] and (2) hydroboration followed by oxidation.



In contrast, 1,1,2-trimethyl-1-silacyclobutane (**9**) gave a mixture of two isomers (**10** and **11**) upon treatment with benzaldehyde in the presence of potassium t-butoxide. Each product (**10** or **11**) is a stereoisomeric mixture (cis/trans = 1/1). The products **2**, **4**, **10**, and **11** were easily converted into 1,4-diols as well as **6** by treatment with KF and H_2O_2. Thus, the new method provided us with a synthetic route to 1,4-diols.

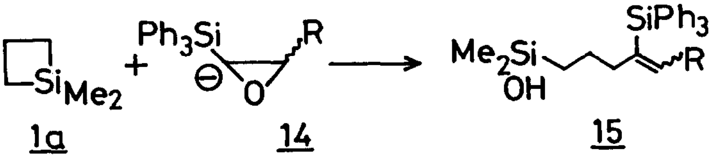


Next, the reaction of silacyclobutane with epoxides such as 1,2-epoxypropane or 1,2-epoxyhexane was examined. A THF solution of 1,1-dimethyl-1-silacyclobutane (**1a**, 0.50 g, 5.0 mmol) and 1,2-epoxypropane (0.29 g, 5.0 mmol) were added to a THF (20 ml) solution of lithium diisopropylamide (5.0 mmol) at -78 °C under an argon atmosphere. The resulting mixture was stirred at -78 °C for 1 h. Then dry ice bath was removed and the reaction mixture was warmed to room temperature. The reaction mixture was poured into water and extracted with ethyl acetate. Purification of the products by silica-gel column chromatography gave silacyclopentane **12a** (R = Me, 0.43 g) and olefinic silanol **13a**[10] (R = Me, 0.12 g) in 67% and 15% (based on **1a**) yields, respectively. 1,2-Epoxyhexane also afforded a mixture of **12b** (R = n-C_4H_9) and **13b** in 44% and 33% yields.



Treatment of **12a** with K_2CO_3/MeOH and KH gave **13a** in 82% overall yield. Conversion of **13a** into (E)-4-hexen-1-ol was performed in accordance with the literature procedure with KF-H_2O_2.[8]

The reaction of silacyclobutane **1a** with triphenylsilyl-substituted oxiranyl anion **14**, generated from epoxytriphenylsilane with n-butyllithium,[11] gave olefinic silanol **15** in 44% (R = H) or 64% (R = Me) yield.[12,13]

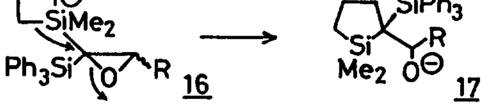


References and Notes

1. D. R. Weyenberg and L. E. Nelson, J. Org. Chem., **30**, 2618 (1965); N. V. Ushakov, V. M. Vdovin, M. V. Pozdnyakova, and N. A. Pritula, Izv. Akad. Nauk. SSSR. Ser. Khim., **1983**, 2125.
2. L. E. Gusel'nikov and N. S. Nametkin, Chem. Rev., **79**, 529 (1979).
3. H. Sakurai and T. Imai, Chem. Lett., **1975**, 891.
4. **2a**: Bp 125 °C (bath temp, 25 Torr); IR (neat) 2924, 2852, 1251, 1140, 1065, 1045, 947, 915, 863, 836, 789, 746, 697 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ0.23 (s, 3H), 0.25 (s, 3H), 0.63-0.75 (m, 2H), 1.38-1.63 (m, 1H),

1.66-1.95 (m, 2H), 2.04-2.20 (m, 1H), 4.83 (dd, J = 2.1, 10.8 Hz, 1H), 7.19-7.48 (m, 5H); ^{13}C NMR ($CDCl_3$) δ-2.43, 0.07, 12.8, 22.2, 39.0, 76.7, 125.3, 126.9, 128.2, 145.5. Found: C, 69.57; H, 8.99%. Calcd for $C_{12}H_{18}OSi$: C, 69.84; H, 8.79%. Oxidation of **2a** with KF-H_2O_2 gave diol $Ph(OH)CHCH_2CH_2CH_2OH$.

5. R. D. Walkup, R. R. Kane, and N. U. Obeyesekere, Tetrahedron Lett., 31, 1531 (1990).
6. Ketone such as acetophenone was recovered unchanged under the same reaction conditions. However, treatment of acetophenone (1.0 mmol) or cyclohexanone (1.0 mmol) with lithium diisopropylamide (1.0 mmol) in the presence of 1,1-dimethyl-1-silacyclobutane (1.0 mmol) provided the corresponding oxasilacyclohexane in 31% or 22% yield.
7. C. Eaborn, D. R. M. Walton, and M. Chan, J. Organomet. Chem., 9, 251 (1967).
8. K. Tamao, N. Ishida, T. Tanaka, and M. Kumada, Organometallics, 2, 1694 (1983).
9. T. Hiyama, Y. Okude, K. Kimura, and H. Nozaki, Bull. Chem. Soc. Jpn., 55, 561 (1982).
10. **13a**: Bp 100°C (bath temp, 20 Torr); IR (neat) 3240, 2976, 2860, 2826, 1254, 968, 865, 843, 778 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ0.10 (s, 6H), 0.51-0.66 (m, 2H), 1.30-1.49 (m, 2H), 1.59-1.69 (m, 3H), 1.79-2.10 (m, 3H including OH proton), 5.31-5.55 (m, 2H); ^{13}C NMR ($CDCl_3$) δ-0.29, 17.4, 17.9, 23.2, 36.2, 125.1, 131.2. Found: C, 60.32; H, 11.49%. Calcd for $C_8H_{18}OSi$: C, 60.69; H, 11.46%.
11. J. Eisch and J. E. Galle, J. Am. Chem. Soc., 98, 4646 (1976).
12. We are tempted to assume following reaction mechanism: (1) oxiranyl anion **14** attacks silicon of silacyclobutane to give five-coordinated silicate **16**, (2) one of methylene group of silacyclobutane migrate from silicon to epoxide carbon and this nucleophilic rearrangement give silacyclopentane **17** under epoxide ring cleavage, and (3) syn elimination of Si-O^- provides **15**. Alternatively, the reaction could proceed as follows: (1) oxiranyl anion rearranged to carbene $Ph_3Si\ddot{C}CH(R)OLi$ and (2) resulting carbene inserted into CH_2-Si bond to afford **17**.



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