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BASE-INDUCED REARRANGEMENT OF OXIRANYLSILACYCLOBUTANE INTO SILACYCLOPENTANE. APPLICATION TO STEREOSELECTIVE SYNTHESIS OF 4-ALKEN-1-OL AND 1,4,5-TRIOL

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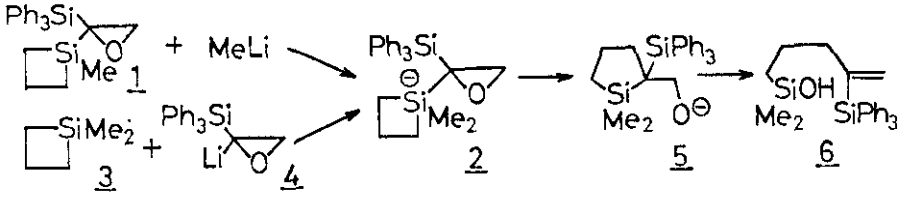
Summary: Treatment of 1-methyl-1-(cis-1,2-epoxyhexyl)-1-silacyclobutane **16a** with i-PrOLi provided erythro-1-methyl-1-isopropoxy-2-(2-hydroxypentyl)-1-silacyclopentane **17a** which was converted into (Z)-4-nonen-1-ol **18**, (E)-4-nonen-1-ol **19**, or 1,4,5-nonanetriol **20**, respectively.

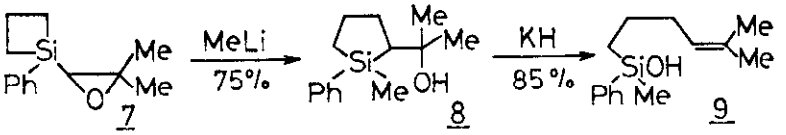
α-Trimethylsilyl epoxides undergo nucleophilic attack by dialkyl cuprate reagents[1] or lithium aluminium hydride[2] at the carbon bearing the silyl group. Nucleophiles may associate with vacant 3d orbitals of silicon and thus pentacoordinate reaction intermediates affect the regiochemistry.[3] In a previous report[4] we have shown that the reaction of 1,1-dimethyl-1-silacyclobutane **3** with triphenylsilyl-substituted oxiranyl anion **4** gave olefinic silanol **6**. We assumed an intermediacy of pentacoordinate silicate **2** in the reaction. It was anticipated that treatment of oxiranylsilacyclobutane **1** with nucleophile such as methyllithium would provide the same pentacoordinate intermediate **2** which would collapse to silacyclopentane **5** under epoxide ring opening and finally give olefinic silanol **6**. This was indeed the case as indicated by the following experiment.



Methyllithium (1.5 M ether solution, 0.37 ml, 0.55 mmol) was added to a solution of epoxy silacyclobutane **1** (0.19 g, 0.5 mmol) in THF (2.0 ml) at -78 °C under argon atmosphere. After stirring for 30 min at -78 °C, the reaction mixture was poured into 1M HCl and extracted with ethyl

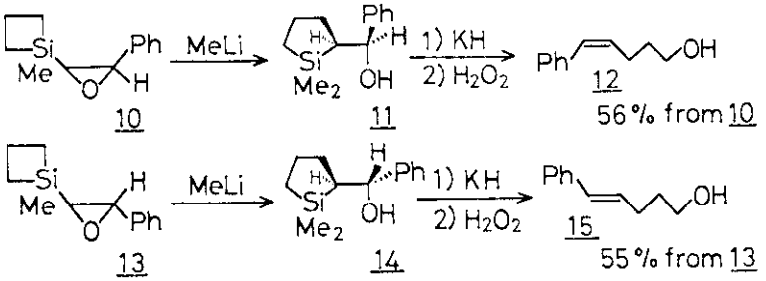
acetate (20 ml x 3). The combined organic layer was dried over anhydrous sodium sulfate and concentrated in vacuo. Purification of the product by silica-gel column chromatography gave silanol **6** (0.17 g) in 84% yield. In this case, silacyclopentane intermediate **5** was transformed into silanol **6** directly under the reaction conditions and an attempt to trap the intermediate 5 failed.

The intermediary silacyclopentane derivatives could be isolated in the reaction of other oxiranylsilacyclobutanes except **1**. For instance, quenching the reaction mixture of **7** and MeLi with methanol at -78 °C provided silacyclopentane **8**[5] in 75% yield. Further treatment of **8** with potassium hydride in THF gave silanol **9** in 85% yield.



7 8 9

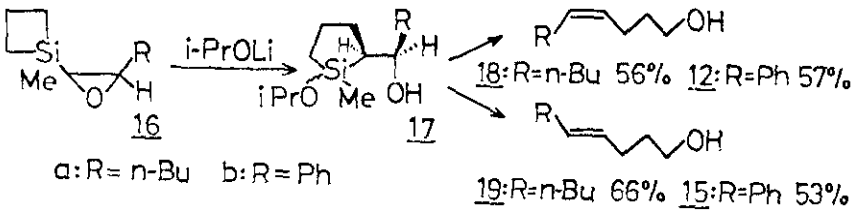
The new reaction was applied to the stereoselective synthesis of 4-alken-1-ols. An addition of methyllithium to epoxy silacyclobutane **10** gave silacyclopentane **11** as a single stereoisomer. The reaction of the alcohol **11** with potassium hydride gave (Z)-PhCH=CHCH$_2$CH$_2$CH$_2$SiMe$_2$OH which was easily converted into (Z)-5-phenyl-4-penten-1-ol upon treatment with H_2O_2-KF.[6] On the other hand, isomeric epoxy silacyclobutane **13** provided (E)-5-phenyl-4-penten-1-ol **15** selectively following the same procedure.



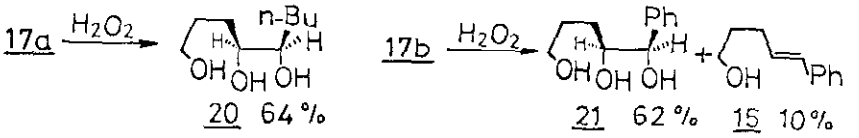
10 11 12

13 14 15

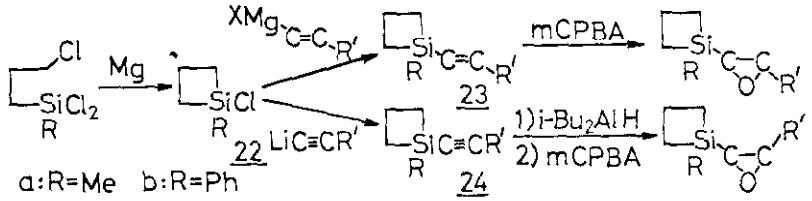
Lithium alkoxide was as effective as methyllithium for the rearrangement of oxiranylsilacyclobutane into silacyclopentane. Treatment of **16a** or **16b** with lithium isopropoxide at -78 °C gave silacyclopentane derivative **17a**[7] or **17b** in 77% or 88% yield, respectively. Exposure of the alcohol **17a** or **17b** on the one hand to (i) potassium hydride and (ii) H_2O_2-KF or to (i) boron trifluoride and (ii) H_2O_2-KF on the other led to (Z)-4-alken-1-ol (**18** or **12**) or (E)-4-alken-1-ol (**19** or **15**), respectively. The procedure provides another route to stereoselective synthesis of (Z)- and (E)-4-alken-1-ols.



The reaction was also utilized for the stereoselective synthesis of 1,4,5-triols. Oxidation of **17a** with H_2O_2-KF gave 1,4,5-triol **20**[8] in 64% yield with high stereoselectivity. In the case of the oxidation of **17b**, (E)-5-phenyl-4-penten-1-ol **15** was obtained (10%) in addition to the desired triol **21** (62%).



Epoxy silacyclobutanes were prepared as follows. Heating a THF solution of $ClCH_2CH_2CH_2SiMeCl_2$ (or $ClCH_2CH_2CH_2SiPhCl_2$) with Mg according to the reported procedure[9] afforded 1-chloro-1-methyl-1-silacyclobutane **22a** (or 1-chloro-1-phenyl-1-silacyclobutane **22b**). Then an addition of (E)-alkenylmagnesium bromide or alkynyllithium to the resulting 1-chloro-1-silacyclobutane **22** gave (E)-1-alkenyl-1-silacyclobutane **23** or 1-alkynyl-1-silacyclobutane **24** in 65-80% yield. Hydroalumination of 1-alkynyl-1-silacyclobutane **24** with i-Bu_2AlH provided (Z)-1-alkenyl-1-silacyclobutane. Epoxidation of the resulting (E)- or (Z)-1-alkenyl-1-silacyclobutanes with mCPBA provided the corresponding epoxy silacyclobutanes (60-85% yield).



References and Notes

1. P. F. Hudrlik, D. Peterson, and R. J. Rona, J. Org. Chem., **40**, 2263 (1975).
2. W. E. Fristad, T. R. Bailey, and L. A. Paquette, J. Org. Chem., **45**, 3028 (1980).
3. W. P. Weber, "Silicon Reagents for Organic Synthesis," Springer-

Verlag, Berlin, 1983, Chap 1.

4. Y. Takeyama, K. Oshima, and K. Utimoto, Tetrahedron Lett., **31**, 6059 (1990).
5. The silacyclopentane **8** consisted of two diastereomers (**8a:8b** = 45:55) which were separated by silica gel column chromatography using hexane-ethyl acetate = 10:1 as an eluant. Faster moving compound **8a**: Bp 105-110 °C (1.0 Torr, bath temp); IR (neat) 3400, 2960, 2924, 2852, 1428, 1376, 1365, 1252, 1111, 806, 783, 734, 698 cm^{-1}; ^1H NMR ($CDCl_3$) δ0.49 (s, 3H), 0.55-0.80 (m, 1H), 0.90-1.70 (m, 4H), 1.25 (s, 3H), 1.29 (s, 3H), 1.95-2.25 (m, 3H), 7.31-7.73 (m, 5H); ^{13}C NMR ($CDCl_3$) δ -2.90, 13.71, 25.58, 30.00, 30.59, 30.67, 43.34, 73.10, 127.8, 128.9, 133.8, 139.5. Found: C, 71.75; H, 9.52%. Calcd for $C_{14}H_{22}OSi$: C, 71.74; H, 9.46%. Slower moving silacyclopentane **8b**: IR (neat) 3300, 2960, 2920, 2854, 1428, 1376, 1253, 1116, 1069, 790, 734, 698 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.47 (s, 3H), 0.88-1.75 (m, 5H), 1.04 (s, 3H), 1.11 (s, 3H), 1.95-2.28 (m, 3H), 7.33-7.75 (m, 5H); ^{13}C NMR ($CDCl_3$) δ-2.58, 12.24, 24.70, 30.01, 30.14, 30.41, 45.23, 72.80, 128.1, 129.5, 135.0, 137.3. Found: C, 71.69; H, 9.48%. Calcd for $C_{14}H_{22}OSi$: C, 71.74; H, 9.46%.
6. K. Tamao, N. Ishida, T. Tanaka, and M. Kumada, Organometallics, **2**, 1694 (1983).
7. The silacyclopentane **17a** consisted of two diastereomers (**A:B** = 24:76) which were separated by silica-gel column chromatography. Faster moving compound **A**: Bp 76 °C (1.0 Torr, bath temp); IR (neat) 3298, 2954, 2930, 2856, 1728, 1459, 1381, 1369, 1351, 1254, 1172, 1124, 1029, 878, 810, 782, 750 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.26 (s, 3H), 0.60 (ddd, J = 8.2, 12.3, 14.5 Hz, 1H), 0.68-0.85 (m, 1H), 0.91 (t, J = 6.7 Hz, 3H), 1.17 (d, J = 6.0 Hz, 3H), 1.18 (d, J = 6.0 Hz, 3H), 1.25-1.73 (m, 9H), 1.80-2.08 (m, 2H), 2.93 (bs, 1H), 3.89-4.00 (m, 1H), 4.03 (sept, J = 6.1 Hz, 1H): ^{13}C NMR ($CDCl_3$) δ-1.67, 13.34, 14.13, 22.79, 23.62, 25.54, 25.63, 26.84, 28.46, 34.51, 36.35, 66.19, 71.74. Found: C, 63.77; H, 11.82%. Calcd for $C_{13}H_{28}O_2Si$: C, 63.88; H, 11.55%. Slower moving isomer **B**: IR (neat) 3286, 2956, 2930, 2858, 1731, 1460, 1382, 1369, 1254, 1174, 1124, 1095, 1052, 1021, 879, 786, 770 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.18 (s, 3H), 0.41 (ddd, J = 8.8, 12.0, 15.3 Hz, 1H), 0.80-1.05 (m, 1H), 0.92 (t, J = 7.0 Hz, 3H), 1.03-1.75 (m, 10H), 1.18 (d, J = 6.1 Hz, 6H), 1.85-2.23 (m, 2H), 3.55-3.73 (m, 1H), 4.01 (sep, J = 6.1 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ -3.07, 12.42, 14.07, 22.64, 24.19, 25.54, 25.61, 28.25, 29.76, 36.02, 38.23, 65.40, 73.74. Found: C, 63.81; H, 11.59%. Calcd for $C_{13}H_{28}O_2Si$: C, 63.88; H, 11.55%.
8. **20**: Mp 91.7-92.2 °C; IR ($CHCl_3$) 3300, 3004, 2932, 2870, 1467, 1458, 1381, 1050, 1006 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.92 (t, J = 6.8 Hz, 3H), 1.13-1.88 (m, 10H), 2.50-3.85 (bm, OH, 3H), 3.55-3.85 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 14.02, 22.73, 28.21, 28.36, 29.43, 31.24, 62.91, 74.69, 74.76. Found: C, 61.11; H, 11.56%. Calcd for $C_9H_{20}O_3$: C, 61.33; H, 11.44%.
9. J. Laane, J. Am. Chem. Soc., **89**, 1144 (1967).

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