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Lewis Acid Supported Reactions of 1,3-Bis(silyl)allyl Compounds with Epoxides — Inter- and Intramolecular Versions

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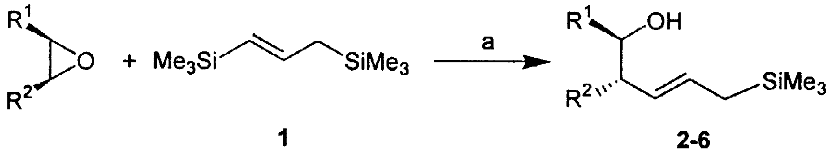
Abstract: Easily available 1,3-bis(silyl)allyl compounds react with epoxides under Lewis acid catalysis to give interesting synthetic building blocks. The course of reaction depends on the stabilization of cationic intermediates by the silicon β-effect. © 1998 Elsevier Science Ltd. All rights reserved.

Ring opening of epoxides by 1,3-bis(silyl)-substituted allyl anions is known to give 3,5-bis(silyl)-4-alkenols, i. e. bis-silylated bishomoallyl alcohols.[1] However, the analogous Lewis acid catalyzed reaction has so far not been reported. In fact, the reactivity of the weak Lewis acids zinc chloride diethyl ether complex, tin tetrachloride or boron trifluoride diethyletherate are not sufficient to effect a reaction. However, we have now found that the stronger Lewis acid titanium tetrachloride allows to isolate in moderate to good yields 5-silyl-3-alkenols, i. e. derivatives of homoallyl alcohols as single diastereomers. Monosubstituted epoxides give better yields than 1,2-disubstituted examples (Scheme 1, Table 1).[2]



Scheme 1. - a: $TiCl_4$, CH_2Cl_2, -78 °C, 19-66 %

Table 1. Lewis Acid Supported Reactions of **1** with Epoxides.

Compound	R^1	R^2	Yield [%]
2	H	H	66
3	H	CH_3	61
4	H	C_2H_5	53
5	-$(CH_2)_3$-		33
6	-$(CH_2)_4$-		19

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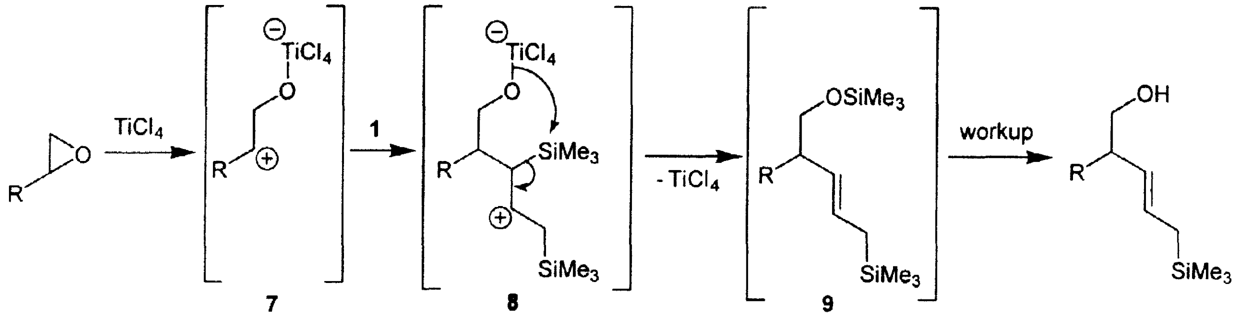
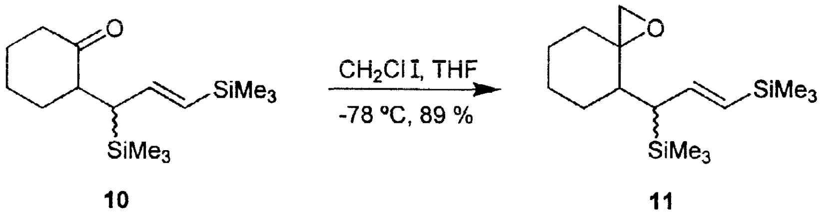
The resulting C-C double bond adopts the (E) configuration. The attack on the epoxide occurs regioselectively at the sterically hindered carbon atom. A plausible mechanism is shown in Scheme 2.



Scheme 2.

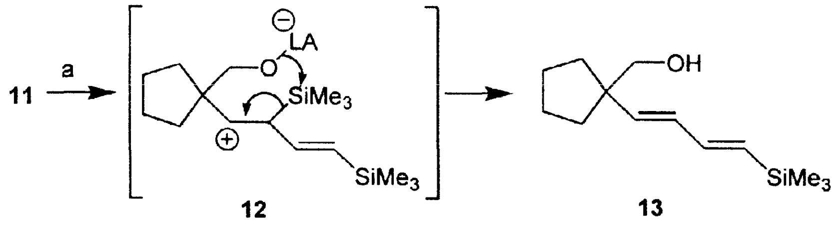
Intermediate **7** explains the S_N1-type fashion of ring opening. The subsequent attack of the allylsilane gives species **8** with very efficient stabilization of the positive charge by the silicon β-effect.[3] Migration of the more favourably oriented "inner" silyl group leads to **9**.

Considering the successful formation of **2-6**, the corresponding intramolecular reaction of bis(silyl)-substituted epoxides **11, 14, 18** is of particular interest. Precursor of epoxide **11** is ketone **10**,[4] which is obtained from cyclohexene oxide by addition of lithiated **1**[1] and subsequent oxidation with PDC under standard conditions (69 %). Ketone **10** is then treated with chloro(iodo)methane and *n* BuLi giving **11** in good yield (Scheme 3).[5] The synthesis of silyl-substituted epoxides **14** and **18** has been reported previously.[6]



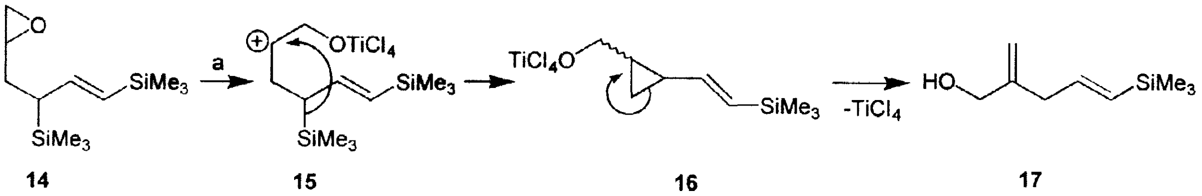
Scheme 3.

Treatment of epoxides **11, 14, 18** with Lewis acids reveals the possibility of different reaction pathways.[7] Dienol **13** is isolated from the reaction of epoxide **11** in the presence of $TiCl_4$ (7 %) or, more efficiently, of $BF_3{\cdot}OEt_2$ (48 %). The observed ring contraction demonstrates that the positive charge is more effficiently stabilized by silicon in **12** than in a tertiary carbocation analogous to **7** (Scheme 4).



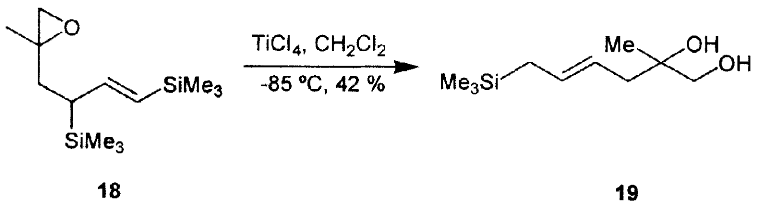
Scheme 4. - a: $TiCl_4$ (7 %) or $BF_3{\cdot}OEt_2$ (48 %), CH_2Cl_2, -85 °C

$BF_3 \cdot OEt_2$ leads to polymerization of epoxide **14**, but reaction with $TiCl_4$ gives olefin **17** in 45 % yield. We assume that, after initial epoxide opening, 1,3-cycloelimination of the silyl group give cyclopropane **16**; under the reaction conditions, this is then isomerized to product **17** (Scheme 5).[8]



Scheme 5. - a: $TiCl_4$, CH_2Cl_2, -85 °C, 45 %

Treatment of epoxide **18** with $BF_3 \cdot OEt_2$ also leads to polymerization. However, reaction with $TiCl_4$ gives diol **19**. Obviously, the additional methyl group prevents ring closure of type **15**→**16**. Instead, the intermediate of type **15** is hydrolyzed on workup with concomitant protodesilylation (Scheme 6).



Scheme 6.

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REFERENCES AND NOTES

1. Schaumann, E.; Kirschning, A.; Narjes, F. J. Org. Chem. **1991**, 56, 717-723.
2. **General Procedure for Lewis Acid Catalyzed Reaction of 1 with Epoxides**: A solution of **1** (5 mmol, 0.93 g) and the epoxide (6 mmol) in 1.6 mL / mmol of dry CH_2Cl_2 was stirred at -78 °C. $TiCl_4$ (5.5 mmol, 0.6 mL), dissolved in 1 mL / mmol of CH_2Cl_2 and cooled to -78 °C, was transferred into this solution. After the completion of the reaction, the solution was poured into a mixture of saturated aqueous $NaHCO_3$ solution, ice and diethyl ether. The organic layer was separated, washed twice with saturated brine, dried (Na_2SO_4) and concentrated in vacuo. The crude product was purified by column chromatography (PE / EE).

   2: see Hiemstra, H.; Sno, M.; Vijn, R. J.; Speckamp, W. N. J. Org. Chem. **1985**, 50, 4014-4020.

   3: **IR** (neat): 3350, 2940, 1650, 1240, 1150, 845; ^{1}**H NMR** ($CDCl_3$, 400 MHz): -0.03 (s, 9H, $SiCH_3$), 0.95 (d, 3H, CH_3, *J*=6.8), 1.43 (d, 2H, CH_2Si, *J*=8.0), 1.54 (bs, 1H, OH), 2.27 (m, 1H, $C\underline{H}$-CH_3), 3.31, 3.42 (dt, each 1H, $C\underline{H_2}OH$, *J*=7.8, 10.2 and 6.4, 10.2), 5.06 (dt, 1H, CH-$C\underline{H}$=CH, *J*=8.4, 16.0), 5.50 (dt, 1H, CH=$C\underline{H}$-CH_2, *J*=8.4, 16.0); ^{13}**C NMR** ($CDCl_3$, 100 MHz): -1.7 ($Si(CH_3)$), 17.2 (CH_3), 22.7 (CH_2Si), 40.3 ($\underline{C}H$-CH_3), 67.7 (CH_2OH), 128.5, 131.0 ($2C_{olef.}$)

   4: **IR** (neat): 3378, 2971, 1650, 1460, 1256, 1053, 842; ^{1}**H NMR** ($CDCl_3$, 400 MHz): 0.01 (s, 9H, $SiCH_3$), 0.84-0.96 (m, 5H, C_2H_5) , 1.46 (d, 2H, CH_2Si, *J*=3.0), 1.58 (bs, 1H, OH), 2.05 (m, 1H, CH), 3.49 (m, 1H, $\mathrm{C\underline{H}_2OH}$), 4.96 (dd, 1H, $\mathrm{C\underline{H}_2OH}$, *J*=8.8, 10.4), 4.96 (dd, 1H, $\mathrm{CH\text{-}C\underline{H}{=}CH}$, *J*=8.8, 15.6), 5.52 (dt, 1H, $\mathrm{CH{=}C\underline{H}\text{-}CH_2}$, *J*=8.8, 15.6); ^{13}**C NMR** ($\mathrm{CDCl_3}$, 100 MHz): -2.0 ($\mathrm{SiCH_3}$), 11.7 ($\mathrm{CH_3}$), 23.1 ($\mathrm{CH_2Si}$), 24.2 ($\mathrm{\underline{C}H_2CH_3}$), 48.1 (CH), 65.9 ($\mathrm{CH_2OH}$), 129.4, 130.2 ($\mathrm{2C_{olef.}}$)

5, **6**: see Nishiyama, H.; Narimatsu, S.; Itoh, K. Tetrahedron Lett. **1981**, 22, 5289-5292.

3. Lambert, J. B. Tetrahedron **1990**, 46, 2677-2689.
4. **10** (mixture of 2 diastereomers, 3.1:1*): **IR** (neat): 2953-2863, 1712, 1600, 1450, 1247, 838; ^{1}**H NMR** ($\mathrm{CDCl_3}$, 200 MHz): -0.05*, -0.02, 0.03*, 0.05 (s, 9H, $\mathrm{SiCH_3}$), 1.42-2.64 (m, 10H, $\mathrm{9H_{cyclohex}}$, 1H, CHSi), 5.40*, 5.47 (d, 1H, $\mathrm{CH{=}C\underline{H}Si}$, *J*=18.4), 5.76*, 5.95 (dd, 1H, $\mathrm{C\underline{H}{=}CHSi}$, *J*=10.0*, 18.4*, 9.6, 18.4); ^{13}**C NMR** ($\mathrm{CDCl_3}$, 50 MHz): -2.0, -1.9*, -1.0*, 1.3 ($\mathrm{SiCH_3}$), 20.8, 24.3*, 25.5, 26.7, 28.3*, 33.4*, (3C, $\mathrm{CH_{2cyclohex}}$), 33.9, 37.6* (CHSi), 41.8*, 41.9 ($\mathrm{\underline{C}H_2\text{-}C{=}O}$), 51.2*, 52.3 ($\mathrm{\underline{C}H\text{-}C{=}O}$), 128.8, 129.0*, 144.3, 145.8* ($\mathrm{2C_{olef.}}$), 213.3*, 210.8 (C=O)
5. **Method**: see Barluenga, J.; Baragana, B.; Concellon, J. M. J. Org. Chem. **1995**, 60, 6696-6699.

   11: **IR** (neat): 3034, 2942, 1599, 1247, 1151, 1091, 922, 840; ^{1}**H NMR** ($\mathrm{CDCl_3}$, 200 MHz): 0.01, 0.03 (s, 9H, $\mathrm{SiCH_3}$), 1.20-2.05 (m, 10H, $\mathrm{9H_{cyclohex}}$, 1H, CHSi), 2.45, 2.63 (d, each 1H, $\mathrm{CH_{2epox.}}$, *J*=5.0), 5.34 (d, 1H, $\mathrm{CH{=}C\underline{H}Si}$, *J*=18.4), 5.83 (dd, 1H, $\mathrm{C\underline{H}{=}CHSi}$, *J*=10.0, 18.4); ^{13}**C NMR** ($\mathrm{CDCl_3}$, 50 MHz): -1.0, -1.7 ($\mathrm{SiCH_3}$), 21.8, 25.5, 29.1, 31.9 ($\mathrm{CH_{2cyclohex}}$), 38.4 (CHSi), 41.0 ($\mathrm{CH_{cyclohex}}$), 53.2 ($\mathrm{CH_{2epox.}}$), 62.2 ($\mathrm{C_{epox.}}$), 126.6, 146.9 ($\mathrm{2C_{olef}}$)
6. Narjes, F.; Bolte, O.; Icheln, D.; König, W. A.; Schaumann, E. J. Org. Chem. **1993**, 58, 626-632.
7. **General Procedure for Reaction of Epoxides 11, 14, 18 with Lewis Acids:** The epoxide was dissolved in 20 mL / mmol of dry $\mathrm{CH_2Cl_2}$ and cooled to -85 °C. 1.1 Equiv. of Lewis acid ($\mathrm{TiCl_4}$ or $\mathrm{BF_3{\bullet}OEt_2}$), dissolved in 20 mL / mmol of $\mathrm{CH_2Cl_2}$ and cooled to -85 °C, was transferred into the epoxide solution. After 0.5-1.5 h (reaction was monitored by TLC) at this temperature, the solution was poured into a mixture of saturated aqueous $\mathrm{NaHCO_3}$ solution, *n* pentane and diethyl ether (1:1:1). The organic layer was washed twice with saturated brine, dried ($\mathrm{Na_2SO_4}$) and concentrated in vacuo. The residue was purified by column chromatography (PE / EE).

   13: **IR** (neat): 3375, 2869, 1637, 1579, 1248, 1047, 1002, 866, 837; ^{1}**H NMR** ($\mathrm{CDCl_3}$, 200 MHz): 0.08 (s, 9H, $\mathrm{SiCH_3}$), 1.52-1.68 (m, $\mathrm{8H_{cyclopent}}$), 3.44 (s, 2H, $\mathrm{C\underline{H}_2OH}$), 5.76 (d, 1H, CHSi, *J*=15.6), 5.80 (d, 1H, $\mathrm{C_{quart}\text{-}CH}$, *J*=18.2), 6.13 (dd, 1H, $\mathrm{C\underline{H}{=}CHSi}$, *J*=10.0, 15.6), 6.52 (dd, 1H, $\mathrm{C\underline{H}\text{-}CH{=}CHSi}$, *J*=10.0, 18.2); ^{13}**C NMR** ($\mathrm{CDCl_3}$, 50 MHz): -1.3 ($\mathrm{SiCH_3}$), 24.3, 34.2 ($\mathrm{CH_{2cyclopent}}$), 50.9 ($\mathrm{C_{quart}}$), 68.9 ($\mathrm{CH_2OH}$), 132.1 (CHSi), 132.6 ($\mathrm{C_{quart}\text{-}\underline{C}H}$), 144.2, 140.9 (2C, $\mathrm{CH{=}\underline{C}H\text{-}\underline{C}H{=}CHSi}$)

   17: **IR** (neat): 3344, 2955, 1652, 1614, 1427, 1249, 1062, 992, 839; ^{1}**H NMR** ($\mathrm{CDCl_3}$, 200 MHz): 0.03 (s, 9H, $\mathrm{SiCH_3}$), 1.57 (bs, 1H, OH), 2.85 (d, 2H, $\mathrm{CH_{2allyl}}$, *J*=5.9), 4.03 (s, 2H, $\mathrm{C\underline{H}_2OH}$), 4.88 and 5.06 (s, each 1H, $\mathrm{C{=}CH_2}$), 5.70 (d, 1H, CHSi, *J*=17.8), 6.00 (dt, 1H, $\mathrm{\underline{H}C{=}CHSi}$, *J*=5.9, 17.8); ^{13}**C NMR** ($\mathrm{CDCl_3}$, 50 MHz): -1.2 ($\mathrm{SiCH_3}$), 40.6 ($\mathrm{CH_2}$), 65.7 ($\mathrm{CH_2OH}$), 110.5 ($\mathrm{C{=}\underline{C}H_2}$), 132.6 (CHSi), 143.5 ($\mathrm{H\underline{C}{=}CHSi}$), 147.2 ($\mathrm{C_{quart}}$)

   19: **IR** (neat): 3389, 2955, 1657, 1453, 1406, 1249, 1154, 1047, 851; ^{1}**H NMR** ($\mathrm{CDCl_3}$, 200 MHz): 0.00 (9H, $\mathrm{SiCH_3}$), 1.49 (m, 3H, $\mathrm{CH_3}$ and 2H, $\mathrm{CH_2Si}$), 1.67 (bs, 1H, OH), 2.05 (t, 1H, $\mathrm{CH_2O\underline{H}}$, *J*=6.4), 2.49 (d, 2H, $\mathrm{CH_2}$, *J*=7.6), 3.58 and 3.60 (d, each 1H, $\mathrm{C\underline{H}_2OH}$, *J*=6.4), 5.28 (dt, 1H, $\mathrm{C\underline{H}{=}CH\text{-}CH_2Si}$, *J*=7.6, 16.2), 5.53 (dt, 1H, $\mathrm{C\underline{H}\text{-}CH_2Si}$, *J*=7.6, 16.2); ^{13}**C NMR** ($\mathrm{CDCl_3}$, 50 MHz): -1.9 ($\mathrm{SiCH_3}$), 23.0 ($\mathrm{CH_2Si}$), 25.9 ($\mathrm{CH_3}$), 43.9 ($\mathrm{CH_2}$), 70.6 ($\mathrm{CH_2OH}$), 75.4 ($\mathrm{C_{quart}}$), 122.1, 131.7 ($\mathrm{2C_{olef}}$)
8. De Meijere, A. (Ed.) Methods of Organic Chemistry (Houben-Weyl), Vol. E 17a; Thieme: Stuttgart, New York, 1997; p. 17.