

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

Inter- and Intramolecular Versions

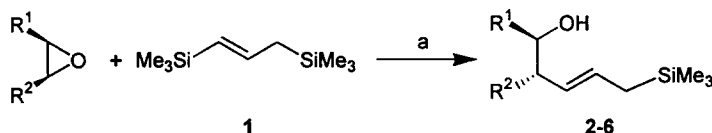
Anette Nowak, Oliver Bolte, Ernst Schaumann*

Institut für Organische Chemie, Technische Universität Clausthal, Leibnizstr. 6,
D-38678 Clausthal-Zellerfeld, Germany

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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



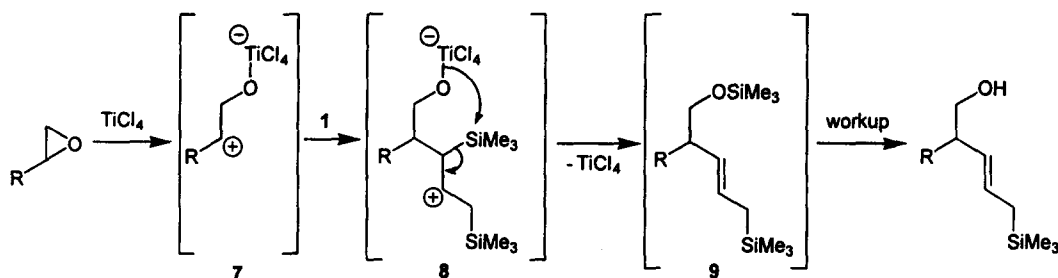
Scheme 1. - a: TiCl_4 , CH_2Cl_2 , -78°C , 19–66 %

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 ₂ H ₅	53
5		-(CH ₂) ₃ -	33
6		-(CH ₂) ₄ -	19

*Fax +49(5323)722858; e-mail: ernst.schaumann@tu-clausthal.de

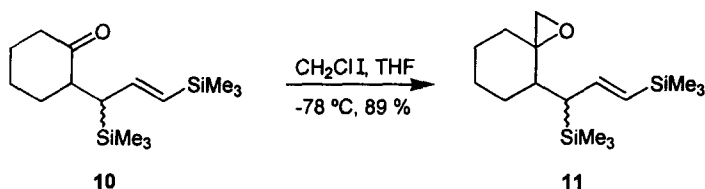
The resulting C-C double bond adopts the (E) configuration. The attack on the epoxide occurs regioselectively at the sterically hindered carbon atom. A plausible mechanism is shown in Scheme 2.



Scheme 2.

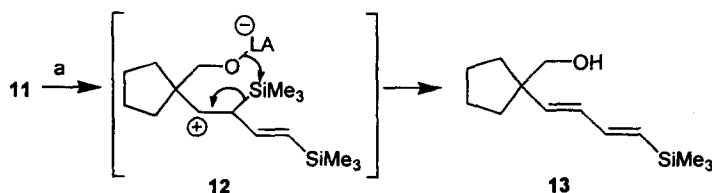
Intermediate 7 explains the S_N1 -type fashion of ring opening. The subsequent attack of the allylsilane gives species 8 with very efficient stabilization of the positive charge by the silicon β -effect.³ Migration of the more favourably oriented "inner" silyl group leads to 9.

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' 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



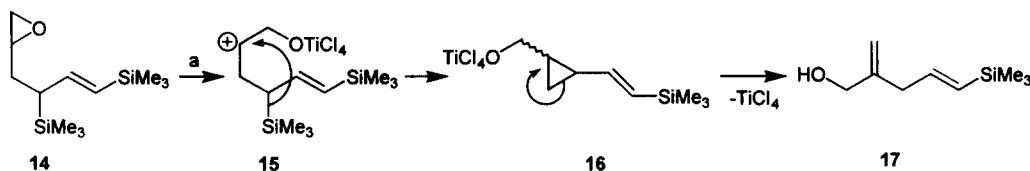
Scheme 3.

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 efficiently stabilized by silicon in 12 than in a tertiary carbocation analogous to 7 (Scheme 4).



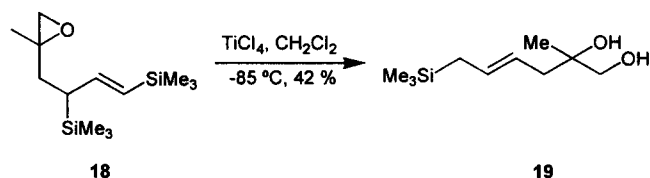
Scheme 4. - a: $TiCl_4$ (7 %) or $BF_3 \cdot OEt_2$ (48 %), CH_2Cl_2 , $-85^\circ C$

$\text{BF}_3 \cdot \text{OEt}_2$ 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 $\text{BF}_3 \cdot \text{OEt}_2$ 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; **^1H 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, $\text{CH}-\text{CH}_3$), 3.31, 3.42 (dt, each 1H, CH_2OH , $J=7.8$, 10.2 and 6.4, 10.2), 5.06 (dt, 1H, $\text{CH}-\text{CH}=\text{CH}$, $J=8.4$, 16.0), 5.50 (dt, 1H, $\text{CH}=\text{CH}-\text{CH}_2$, $J=8.4$, 16.0); **^{13}C NMR** (CDCl_3 , 100 MHz): -1.7 ($\text{Si}(\text{CH}_3)$), 17.2 (CH_3), 22.7 (CH_2Si), 40.3 ($\text{CH}-\text{CH}_3$), 67.7 (CH_2OH), 128.5, 131.0 (2C_{olef}).
- 4: **IR** (neat): 3378, 2971, 1650, 1460, 1256, 1053, 842; **^1H 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, CH_2OH), 4.96 (dd, 1H, CH_2OH , $J=8.8$, 10.4), 4.96 (dd, 1H, $\text{CH}-\text{CH}=\text{CH}$, $J=8.8$, 15.6), 5.52 (dt, 1H, $\text{CH}=\text{CH}-\text{CH}_2$, $J=8.8$, 15.6); ^{13}C NMR (CDCl_3 , 100 MHz): -2.0 (SiCH_3), 11.7 (CH_3), 23.1 (CH_2Si), 24.2 (CH_2CH_3), 48.1 (CH), 65.9 (CH_2OH), 129.4, 130.2 (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; ^1H NMR (CDCl_3 , 200 MHz): -0.05*, -0.02, 0.03*, 0.05 (s, 9H, SiCH_3), 1.42-2.64 (m, 10H, 9H $_{\text{cyclohex}}$, 1H, CHSi), 5.40*, 5.47 (d, 1H, $\text{CH}=\text{CHSi}$, $J=18.4$), 5.76*, 5.95 (dd, 1H, $\text{CH}=\text{CHSi}$, $J=10.0^*$, 18.4*, 9.6, 18.4); ^{13}C NMR (CDCl_3 , 50 MHz): -2.0, -1.9*, -1.0*, 1.3 (SiCH_3), 20.8, 24.3*, 25.5, 26.7, 28.3*, 33.4*, (3C, $\text{CH}_{2\text{cyclohex}}$), 33.9, 37.6* (CHSi), 41.8*, 41.9 ($\text{CH}_2-\text{C}=\text{O}$), 51.2*, 52.3 ($\text{CH}-\text{C}=\text{O}$), 128.8, 129.0*, 144.3, 145.8* (2C_{olef}), 213.3*, 210.8 ($\text{C}=\text{O}$)
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; ^1H NMR (CDCl_3 , 200 MHz): 0.01, 0.03 (s, 9H, SiCH_3), 1.20-2.05 (m, 10H, 9H $_{\text{cyclohex}}$, 1H, CHSi), 2.45, 2.63 (d, each 1H, CH_2epox , $J=5.0$), 5.34 (d, 1H, $\text{CH}=\text{CHSi}$, $J=18.4$), 5.83 (dd, 1H, $\text{CH}=\text{CHSi}$, $J=10.0$, 18.4); ^{13}C NMR (CDCl_3 , 50 MHz): -1.0, -1.7 (SiCH_3), 21.8, 25.5, 29.1, 31.9 ($\text{CH}_{2\text{cyclohex}}$), 38.4 (CHSi), 41.0 ($\text{CH}_{\text{cyclohex}}$), 53.2 (CH_2epox), 62.2 (C_{epox}), 126.6, 146.9 (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 CH_2Cl_2 and cooled to -85°C . 1.1 Equiv. of Lewis acid (TiCl_4 or $\text{BF}_3\cdot\text{OEt}_2$), dissolved in 20 mL / mmol of 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 NaHCO_3 solution, *n* pentane and diethyl ether (1:1:1). The organic layer was washed twice with saturated brine, dried (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; ^1H NMR (CDCl_3 , 200 MHz): 0.08 (s, 9H, SiCH_3), 1.52-1.68 (m, 8H $_{\text{cyclopent}}$), 3.44 (s, 2H, CH_2OH), 5.76 (d, 1H, CHSi , $J=15.6$), 5.80 (d, 1H, $\text{C}_{\text{quart}}-\text{CH}$, $J=18.2$), 6.13 (dd, 1H, $\text{CH}=\text{CHSi}$, $J=10.0$, 15.6), 6.52 (dd, 1H, $\text{CH}-\text{CH}=\text{CHSi}$, $J=10.0$, 18.2); ^{13}C NMR (CDCl_3 , 50 MHz): -1.3 (SiCH_3), 24.3, 34.2 ($\text{CH}_{2\text{cyclopent}}$), 50.9 (C_{quart}), 68.9 (CH_2OH), 132.1 (CHSi), 132.6 ($\text{C}_{\text{quart}}-\text{CH}$), 144.2, 140.9 (2C , $\text{CH}=\text{CH}-\text{CH}=\text{CHSi}$)
- 17: IR (neat): 3344, 2955, 1652, 1614, 1427, 1249, 1062, 992, 839; ^1H NMR (CDCl_3 , 200 MHz): 0.03 (s, 9H, SiCH_3), 1.57 (bs, 1H, OH), 2.85 (d, 2H, CH_2allyl , $J=5.9$), 4.03 (s, 2H, CH_2OH), 4.88 and 5.06 (s, each 1H, $\text{C}=\text{CH}_2$), 5.70 (d, 1H, CHSi , $J=17.8$), 6.00 (dt, 1H, $\text{HC}=\text{CHSi}$, $J=5.9$, 17.8); ^{13}C NMR (CDCl_3 , 50 MHz): -1.2 (SiCH_3), 40.6 (CH_2), 65.7 (CH_2OH), 110.5 ($\text{C}=\text{CH}_2$), 132.6 (CHSi), 143.5 ($\text{HC}=\text{CHSi}$), 147.2 (C_{quart})
- 19: IR (neat): 3389, 2955, 1657, 1453, 1406, 1249, 1154, 1047, 851; ^1H NMR (CDCl_3 , 200 MHz): 0.00 (9H, SiCH_3), 1.49 (m, 3H, CH_3 and 2H, CH_2Si), 1.67 (bs, 1H, OH), 2.05 (t, 1H, CH_2OH , $J=6.4$), 2.49 (d, 2H, CH_2 , $J=7.6$), 3.58 and 3.60 (d, each 1H, CH_2OH , $J=6.4$), 5.28 (dt, 1H, $\text{CH}=\text{CH}-\text{CH}_2\text{Si}$, $J=7.6$, 16.2), 5.53 (dt, 1H, $\text{CH}-\text{CH}_2\text{Si}$, $J=7.6$, 16.2); ^{13}C NMR (CDCl_3 , 50 MHz): -1.9 (SiCH_3), 23.0 (CH_2Si), 25.9 (CH_3), 43.9 (CH_2), 70.6 (CH_2OH), 75.4 (C_{quart}), 122.1, 131.7 (2C_{olef})
8. De Meijere, A. (Ed.) *Methods of Organic Chemistry (Houben-Weyl)*, Vol. E 17a; Thieme: Stuttgart, New York, 1997; p. 17.