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A HIGHLY STEREOSELECTIVE ROUTE TO 2-ALKENYLTRIMETHYLSILANES

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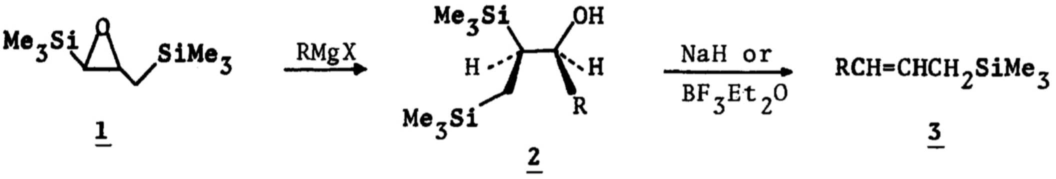
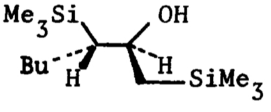
1,2-Epoxy-1,3-bis(trimethylsilyl)propane reacts with various Grignard reagents (RMgX) to give 1-R-2,3-bis(trimethylsilyl)-1-propanols which upon olefination with NaH or with BF_3Et_2O give the corresponding (Z) or (E)-2-alkenyltrimethylsilanes in moderate to good yields, respectively.

Allylsilanes are versatile synthetic reagents and can be prepared by several methods including silylation of allyl-metal species, Wittig olefination, and catalytic hydrosilylation or reductive silylation of 1,3-dienes.$^{1)}$ These methods, however, often show poor stereoselectivity yielding a mixture of (E) and (Z) stereoisomers which are not easily separable from each other. We report here another route which is useful for stereoselective synthesis of 2-alkenyltrimethylsilanes using 1,2-epoxy-1,3-bis(trimethylsilyl)propane (**1**).

The requisite substrate (E)-**1** [bp 75–76 °C/1600 Pa; IR 1255, 870, and 840 cm^{-1}; NMR (CCl_4) δ 0.03 (s, 9H), 0.05 (s, 9H), 0.58 (dd, J=14 and 7.5 Hz, 1H), 1.15 (dd, J=14 and 5.5 Hz, 1H), 1.71 (d, J=3.2 Hz, 1H) and 2.62 (m, 1H)] was prepared in 68% yield by oxidation of (E)-1,3-bis(trimethylsilyl)propene$^{2)}$ with m-chloroperbenzoic acid (0 °C in CH_2Cl_2). Alkylation of **1** with $(n\text{-}Bu)_2CuLi$ occurred slowly in ether (-40 °C, 24 h) affording an expected alcohol **4** in 75% yield, whereas **1** reacted rapidly with various Grignard reagents in ether at room temperature to give Si-rearranged alcohols **2** in good yields, except for the alkylation with a bulky reagent t-BuMgBr where the major product was in fact an enol silyl ether **6**.$^{3)}$ The results are listed in Table 1. A magnesium salts-induced rearrangement$^{4)}$ of **1** to an aldehyde **5** probably explains the formation of **2** and **6**.





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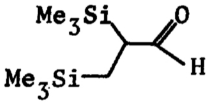

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$Me_3SiCH_2CH=CH(OSiMe_3)$

6

Table 1. Reaction of 1 with organometallic reagents and subsequent olefination[a]

	2[b,c]	3, Yield/%[c,d]	
Reagent	Yield/%	Method A[e]	Method B[f]
MeMgI	89	58[g] (89% Z)	92[g] (92% E)
i-PrMgBr	87	45[g] (> 99% Z)	93[g] (> 99% E)
n-BuMgBr	85	73[g] (98% Z)	90 (94% E)
t-BuMgBr	20[g]	50[g] (> 99% Z)	75[g] (> 99% E)
c-C_6H_{11}MgCl	86	55 (> 99% Z)	96 (> 99% E)
PhMgBr	92	90[h] (94% Z)	88 (> 99% E)
(n-Bu)$_2$CuLi	75 (as 4)[i]	80 (> 99% E)	88 (52% Z)

a) The products were characterized by microanalytical and/or spectral data. The stereochemical assignment for 3 was chiefly based on the finding that the E-isomer showed a C=C stretching frequency by 5–15 cm^{-1} higher than that of the Z-isomer. b) 1 was added to an ethereal solution of a Grignard reagent (2 equiv.) at room temperature (30 min). c) Isolated yield unless otherwise noted. d) Isomeric purity was determined by GLC and NMR. e) Refluxed for 3–5 h in 1,2-dimethoxyethane with NaH (1–2 equiv.). f) Mixed with boron trifluoride etherate (2 equiv.) in ether at room temperature for 30 min. g) Determined by GLC. h) Refluxed for 20 min; prolonged heating gave 1-phenyl-1-propene. i) At -40 °C for 24 h.

The alcohol 4 gave (E)-2-heptenyltrimethylsilane (3; R=n-Bu) stereospecifically upon olefination with NaH (Method A), but with BF$_3$Et$_2$O (Method B) an isomeric mixture of the product without significant selectivity (E/Z=48/52). On the other hand, the olefination reaction of 2 by either method A or B was highly stereoselective and gave (Z) or (E)-2-alkenyltrimethylsilanes 3 in moderate to good yields, respectively, as shown in Table 1. Relatively low stereospecificity in the olefination of an alcohol 2 with R=Me may arise from the contamination of a wrong diastereoisomer of the alcohol.

Further study on stereoselective synthesis of disubstituted allylsilanes from 2 is in progress.

References

1) E. W. Colvin, "Silicon in Organic Synthesis," Butterworths, London (1981); W. P. Weber, "Silicon Reagents for Organic Synthesis," Springer-Verlag, Berlin, Heidelberg (1983).
2) (E)-1,3-Bis(trimethylsilyl)propene can be prepared from allyltrimethylsilane [for example, see J. Dunoguès, R. Calas, N. Ardoin, and C. Biran, J. Organomet. Chem., 32, C31 (1971); R. Corriu and J. Massee, ibid., 57, C5 (1973); H. O. House, P. C. Gaa, J. H. C. Lee, and D. VanDerveer, J. Org. Chem., 48, 1670 (1983)], but we obtained it more economically from 1,3-dichloropropene (E/Z=55/45) by in situ coupling reaction with Me$_3$SiCl (2.5 equiv.) in the presence of excess magnesium in THF in 61% yield.
3) The stereochemistry of the alcohols 2 and 4 was deduced from the fact that NaH-promoted β-elimination occurs in a syn fashion (see Ref. 1).
4) P. F. Hudrlik, R. N. Misra, G. P. Withers, A. M. Hudrlik, R. J. Rona, and J. P. Arcoleo, Tetrahedron Lett., 1976, 1453.

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