

other nucleophiles including CO, NO, SO₂, CO₂, and CH₃CN, as well as other substituted carbonyls into a Zr-C bond of (η⁵-C₅H₅)₂Zr(CH₂Si(CH₃)₂CH₂).

Acknowledgment. We wish to thank the National Science Foundation (Grant No. ISP-8011453) for the financial support of this research. Computer time for the analysis of the X-ray diffraction data was provided by the

West Virginia Network for Educational Telecomputing.

Registry No. (η⁵-C₅H₅)₂Zr(OCH₂CH₂Si(CH₃)₂CH₂), 91798-56-0; (η⁵-C₅H₅)₂Zr(CH₂Si(CH₃)₂CH₂), 89530-31-4; OCH₂, 50-00-0.

Supplementary Material Available: Tables of refined thermal parameters, hydrogen bond distances and angles, and observed and calculated structure factors (12 pages). Ordering information is given on any current masthead page.

Silafunctional Compounds in Organic Synthesis. 25.¹ The Aluminum Chloride Catalyzed Rearrangement of Alkenyl(chloromethyl)silanes to Allyl- and Cyclopropylsilanes

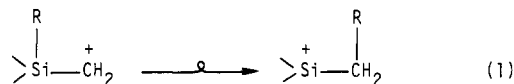
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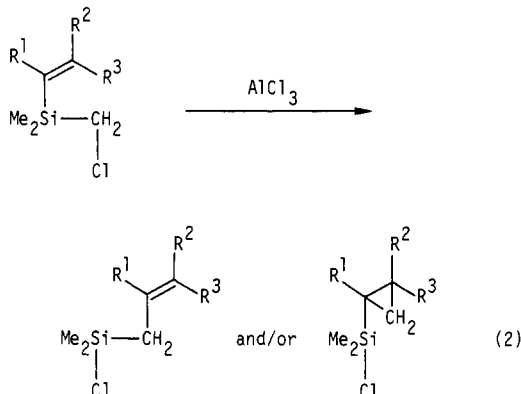
Received May 9, 1984

Alkenyl(chloromethyl)dimethylsilanes undergo the aluminum chloride catalyzed rearrangement to form the corresponding allyl- and/or cyclopropylchlorosilanes, depending upon the structure of the alkenyl group. The reaction courses appear to be determined primarily by the stability of the α- or β-silyl carbocation species. The synthetic utility of the rearrangement products has been shown by their conversion to alcohols via the hydrogen peroxide oxidation of the carbon-silicon bond.

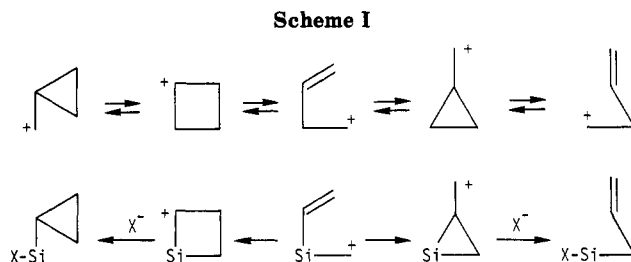
The Wagner-Meerwein type rearrangement involving migration of an organic group from silicon to the α-carbon atom has been recognized as one of the typical cationic rearrangements of organosilicon compounds (eq 1).²



However, there has been no report dealing with the migration of an alkenyl group. We describe herein the aluminum chloride catalyzed rearrangement of alkenyl(chloromethyl)dimethylsilanes to allyl- and/or cyclopropylsilanes (eq 2). The present rearrangement may be re-



garded as a silicon version of the well-known rearrangement among homoallyl, cyclopropylcarbinyl, and cyclo-



butyl carbocations,³ as shown in Scheme I.

This paper reports electronic and steric factors that determine the reaction courses and synthetic utilities of the rearranged silafunctional compounds.

Results and Discussion

AlCl₃-Catalyzed Rearrangement. Six representative compounds 1-6, listed in Table I, were examined in this study. The rearrangement was carried out in dry dichloromethane (1 mL/1 mmol) at room temperature. Upon addition of freshly sublimed AlCl₃ (ca. 10 mol %), a slightly exothermic reaction occurred and was completed in 5-25 min. The rearrangement products allyl- and/or cyclopropylchlorosilanes were methylated with the methyl Grignard reagent and characterized.

The results are summarized in Table I, in which the starting materials are listed in the order of decreasing allyl/cyclopropyl ratios. The reaction courses are highly dependent upon the structure of the alkenyl group. The characteristic features are summarized as follows. (1) A (*Z*)-1-alkenylsilane gives an allylsilane exclusively. (2) An (*E*)-1-alkenylsilanes affords an allylsilane predominantly, together with a cyclopropylsilane as a minor product. (3) An α-substituted vinylsilane forms a cyclopropylsilane

(1) For part 24 see: Tamao, K.; Kanatani, R.; Kumada, M. *Tetrahedron Lett.* 1984, 25, 1913.

(2) (a) Whitmore, F. C.; Sommer, L. H.; Gold, J. J. *Am. Chem. Soc.* 1947, 69, 1976. (b) Eaborn, C.; Bott, R. W. In "Organometallic Compounds of the Group IV Elements"; MacDiarmid, A. G., Ed.; Marcel Dekker: New York, 1968; Vol. 1, Part 1, pp 443-448. (c) Brook, A. G.; Bassindale, A. R. In "Rearrangements in Ground and Excited States"; de Mayo, P., Ed.; Academic Press: New York, 1980; Vol. 2, pp 149-227.

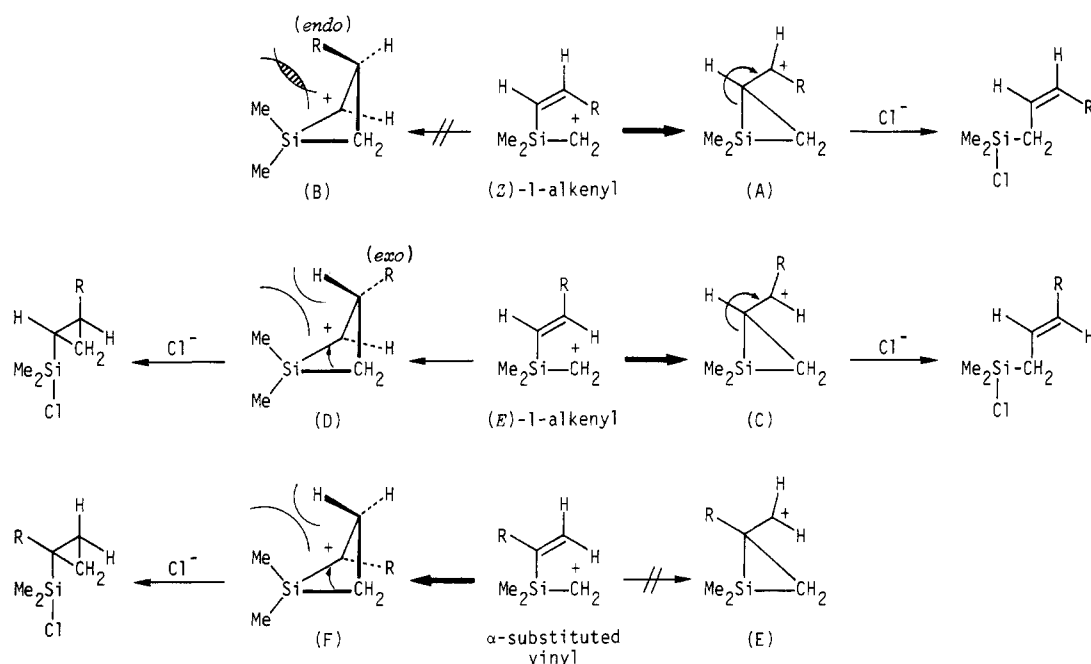
(3) Breslow, R. In "Molecular Rearrangements"; de Mayo, P., Ed.; Interscience: New York, 1963; Part 1, Chapter 4, pp 259-276.

Table I. AlCl_3 -Catalyzed Rearrangement of Alkenyl(chloromethyl)silanes^a

alkenyl(chloromethyl)silane	rearrangement product(s) ^b		yield, ^c %	allyl/cyclopropyl ratio ^d
			89	100/0
			83	93/7
			65	87/13
			58	78/22
			93	77/23
			44	0/100

^a Carried out in dry CH_2Cl_2 at room temperature in the presence of AlCl_3 (10 mol %) for 5–25 min. ^b After methylation. ^c Isolated yield. ^d Determined by ^1H NMR.

Scheme II



selectively. (4) The alkene geometry is retained in all cases.

Although the exact mechanism is not clear yet, the following seem to be most consistent with the observed structure–reactivity relationship.

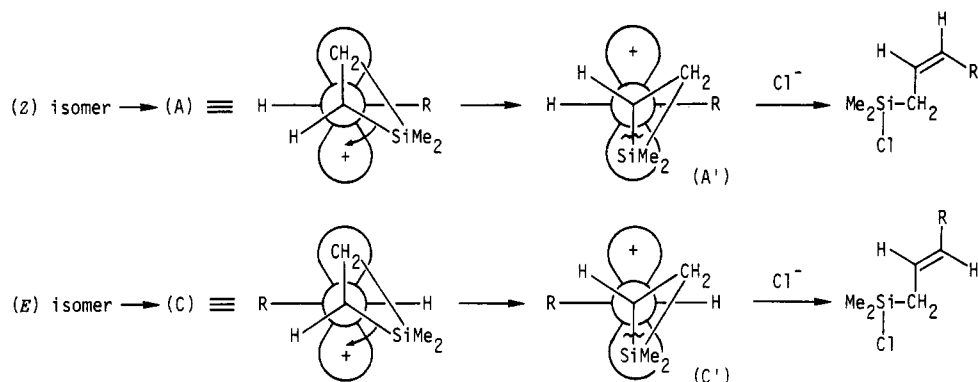
The reaction courses seem to be primarily determined by the stability balance between α -silyl and β -silyl carbocations.⁴ The initially formed silylmethyl cation may attack either the α -olefinic carbon atom to form a

“silacyclopentylcarbonyl cation”, the cationic center being β to silicon, or the β -olefinic carbon atom to form a “silacyclobutyl cation”, the cationic center being α to silicon.

In Scheme II, all of the possible carbocation species are shown for three typical cases, i.e., (*Z*)- and (*E*)-1-alkenylsilanes and α -substituted vinylsilanes. It seems convenient to consider the (*E*)-alkenyl case first. The β -silyl secondary alkyl cation C should be more stable than the α -silyl secondary alkyl cation D, since the former may be stabilized by the σ - π conjugation.⁴ Therefore, the allyl-

(4) Colvin, E. “Silicon in Organic Synthesis”; Butterworths: London, 1981; pp 15–20.

Scheme III



silane is formed preferentially, together with the cyclopropylsilane as a minor product.

In the case of the *(Z)*-alkenylsilane, a steric factor arises additionally on the route to the puckered silacyclobutyl α -silyl carbocation B more seriously than to the β -silyl carbocation A. Thus, at the initial stage of the interaction of the silylmethyl cation with the π -orbital of the β -carbon, the β -substituent (R group) inevitably becomes endo to experience a serious steric repulsion with one methyl group on silicon. This should be compared with the R group being exo disposed in cation D from the *(E)*-alkenylsilane, mentioned above. Consequently, the *(Z)*-alkenylsilane may take only the course to A, resulting in the formation of the allylsilane exclusively.

In the case of the α -substituted alkenylsilane, the β -silyl carbocation E is primary, while the α -silyl carbocation F is tertiary. Furthermore, no steric constraint is present in the latter, similar to D. Therefore, the course to F might be much more favorable than that to E, resulting in the exhaustive formation of the cyclopropylsilane.

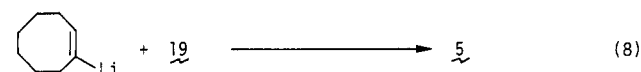
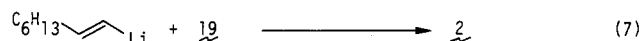
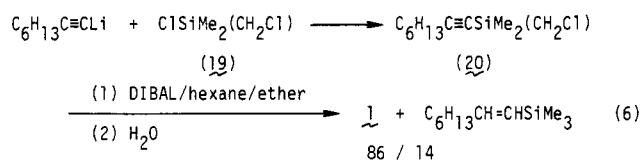
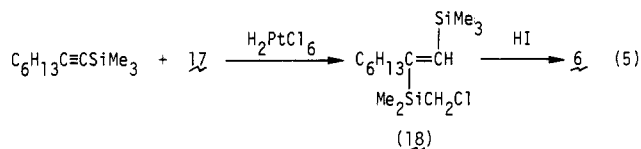
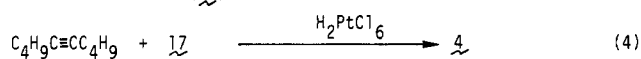
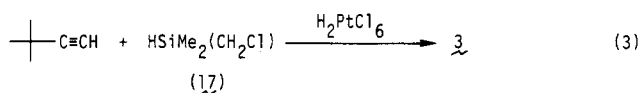
Retention of the geometry of the migrating alkenyl group is consonant with the known stereochemistry of many intermolecular electrophilic cleavage reactions of alkenylsilanes⁵ and may be visualized by Scheme III. In the "silacyclopropylcarbonyl cations", A from the *Z* isomer and C from the *E* isomer, rotation about the developing carbon-carbon single bond should occur to the direction that permits the maximum overlap of the silicon-carbon single-bond orbital with the carbocation vacant orbital to form the conformers A' and C', respectively. The cleavage of the silicon-carbon bond results in the formation of allylsilanes with retention of configuration of the double bond. Retention of the configuration in the cyclopropylsilane formation may be readily visualized by the intermediacy of the silacyclobutyl cation species D shown in Scheme II.⁶

Preparation of Starting Materials and Characterization of Products. Several methods were employed for preparation of the starting materials. Compounds 3 and 4 were readily prepared by the H_2PtCl_6 -catalyzed hydrosilylation of the corresponding acetylenes with $\text{HSiMe}_2(\text{CH}_2\text{Cl})$ (17) in a regio- and stereoselective fashion (eq 3 and 4).

1-Octen-2-ylsilane (6) was prepared in two steps: regioselective hydrosilylation of octynyltrimethylsilane⁷ with

17 followed by cleavage of the trimethylsilyl group,⁸ as shown in eq 5.

(Z)-Octenyl derivative (1) was prepared by hydroalumination of 1-octynyl(chloromethyl)dimethylsilane (20),⁹ with reduction of the chloromethyl group also taking place in some extent (eq 6). *(E)*-Octenylsilane (2) was obtained by coupling of an *(E)*-octenyllithium reagent¹⁰ with $\text{ClSiMe}_2(\text{CH}_2\text{Cl})$ (19) (eq 7), while hydrosilylation of 1-octyne with 17 gave a regioisomeric mixture of 2 and 6 in the ratio of 81:19. Cyclooctenyl derivative 5 was also prepared by the similar coupling reaction (eq 8).



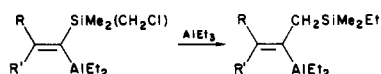
These compounds, 1-6, and synthetic intermediates 18 and 20 exhibited consistent ^1H NMR spectral data (Table II) and elemental analysis (Table III).

^1H NMR spectral data of the rearrangement products (after methylation) are also listed in Table II. The single products 7 and 16 respectively from 1 and 6 were readily characterized by ^1H NMR data. The latter product 16 showed an A_2B_2 pattern characteristic of an unsymmetrically 1,1-disubstituted cyclopropane ring. ^{13}C NMR data are also consistent with the structure (Table II).

In those cases where both of the allyl- and cyclopropylsilane were formed, the characterization of the latter (minor products) was not so simple, since the two products

(5) Reference 4; pp 44-82.

(6) K. Utimoto and his co-workers, Kyoto University, have recently observed the following interesting rearrangement of (aluminum-substituted alkenyl)chloromethylsilanes to the corresponding allylsilanes promoted by AlEt_3 (private communication).



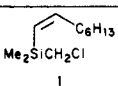
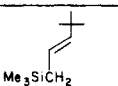
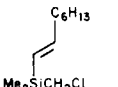
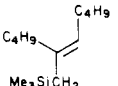
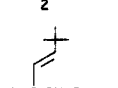
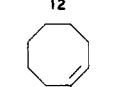
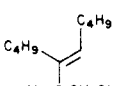
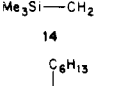
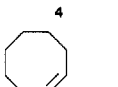
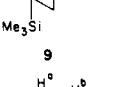
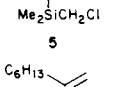
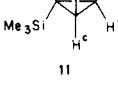
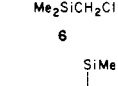
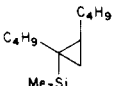
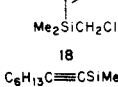
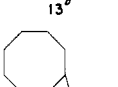
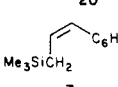
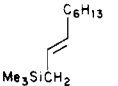
(7) Hudrlik, P. F.; Schwartz, R. H.; Hogan, J. C. *J. Org. Chem.* **1979**, *44*, 155.

(8) Utimoto, K.; Kitai, M.; Nozaki, H. *Tetrahedron Lett.* **1975**, 2825.

(9) (a) Eisch, J. J.; Damasevitz, G. A. *J. Org. Chem.* **1976**, *41*, 2214. (b) Uchida, K.; Utimoto, K.; Nozaki, H. *Ibid.* **1976**, *41*, 2215.

(10) Newmann, H.; Seebach, D. *Chem. Ber.* **1978**, *111*, 2785.

Table II. ¹H NMR Spectral Data of Alkenyl(chloromethyl)dimethylsilanes, Allyltrimethylsilanes, and Cyclopropyltrimethylsilanes^a

compd	¹ H NMR (Me ₄ Si), ppm	compd	¹ H NMR (Me ₄ Si), ppm
	0.24 (s, 6 H), 0.77-1.01 (m, 3 H), 1.19-1.54 (m, 8 H), 1.96-2.24 (m, 2 H), 2.74 (s, 2 H), 5.39 (d, <i>J</i> = 14 Hz, 1 H), 6.32 (dt, <i>J</i> = 7 and 14 Hz, 1 H)		-0.04 (s, 9 H), 0.98 (s, 9 H), 1.29-1.42 (m, 2 H), 5.18-5.32 (m, 2 H)
	0.08 (s, 6 H), 0.67-0.93 (m, 3 H), 1.06-1.47 (m, 8 H), 1.84-2.17 (m, 2 H), 2.61 (s, 2 H), 5.55 (d, <i>J</i> = 18 Hz, 1 H), 6.07 (dt, <i>J</i> = 6 and 18 Hz, 1 H)		(400 MHz) -0.01 (s, 9 H), 0.881-0.929 (m, 6 H), 1.279-1.364 (m, 8 H), 1.445 (d, <i>J</i> = 0.7 Hz, 2 H), 1.928-2.004 (m, 4 H), 4.911 (t, <i>J</i> = 7.2 Hz, 1 H)
	0.15 (s, 6 H), 0.99 (s, 9 H), 2.67 (s, 2 H), 5.67 (d, <i>J</i> = 19 Hz, 1 H), 6.08 (d, <i>J</i> = 19 Hz, 1 H)		-0.05 (s, 9 H), 1.29-1.57 (m, including singlet at 1.39, 2 H, total 10 H), 1.84-2.06 (m, 4 H), 5.09 (t, <i>J</i> = 8 Hz, 1 H)
	0.15 (s, 6 H), 0.76-0.99 (m, 6 H), 1.11-1.49 (m, 8 H), 1.88-2.20 (m, 4 H), 2.70 (s, 2 H), 5.73 (t, <i>J</i> = 7 Hz, 1 H)		(400 MHz) -0.753 to -0.695 (m, 1 H), -0.088 (s, 9 H), 0.235-0.280 (m, 1 H), 0.302-0.346 (m, 1 H), 0.529-0.574 (m, 1 H), 0.852-0.886 (m, 3 H), 1.200-1.361 (m, 10 H)
	0.21 (s, 6 H), 1.28-1.67 (m, 8 H), 1.99-2.39 (m, 4 H), 2.74 (s, 2 H), 6.04 (t, <i>J</i> = 7 Hz, 1 H)		(400 MHz) -0.567 (ddd, H ^a), -0.082 (s, 9 H), 0.177 (ddd, possibly H ^c), 0.392 (ddd, possibly H ^b), 0.524 (ddd, H ^d), 0.906 (s, 9 H) (<i>J</i> _{ab} = 10.1, <i>J</i> _{ac} = 6.9, <i>J</i> _{ad} = 6.9, <i>J</i> _{bc} = 3.9, <i>J</i> _{bd} = 5.1, <i>J</i> _{cd} = 7.8 Hz)
	0.14 (s, 6 H), 0.69-0.94 (m, 3 H), 1.05-1.47 (m, 8 H), 1.88-2.19 (m, 2 H), 2.69 (s, 2 H), 5.29-5.39 (m, 1 H), 5.54-5.64 (m, 1 H)		(400 MHz) -0.075 (dd, <i>J</i> = 3.7 and 5.1 Hz, 1 H), -0.062 (s, 9 H), 0.532 (dd, <i>J</i> = 3.7 and 7.9 Hz, 1 H), 0.575-0.641 (m, 1 H), 0.861-0.929 (m, 6 H), 1.220-1.459 (m, 12 H)
	0.14 (s, 9 H), 0.22 (s, 6 H), 0.79-1.01 (m, 3 H), 1.15-1.53 (m, 8 H), 1.97-2.37 (m, 2 H), 2.74 (s, 2 H), 6.01 (s, 1 H)		(400 MHz) -0.212 (dd, <i>J</i> = 3.7 and 4.9 Hz, 1 H), -0.019 (s, 9 H), 0.511 (dd, <i>J</i> = 3.6 and 7.9 Hz, 1 H), 0.572-0.641 (m, 1 H), 0.851-1.259 (m, 3 H), 1.389-1.526 (m, 5 H), 1.609-1.701 (m, 2 H), 2.004-2.182 (m, 2 H)
	0.23 (s, 6 H), 0.77-1.01 (m, 3 H), 1.14-1.69 (m, 8 H), 2.08-2.29 (m, 2 H), 2.74 (s, 2 H)		-0.09 (s, 9 H), 0.08-0.20 and 0.20-0.35 (A ₂ B ₂ symmetrical m, total 4 H), 0.71-0.94 (m, 3 H), 1.08-1.47 (m, 10 H)
	-0.01 (s, 9 H), 0.74-0.99 (m, 3 H), 1.08-1.51 (m, 10 H), 1.75-2.06 (m, 2 H), 3.97-4.43 (m, 2 H)		
	(400 MHz) -0.029 (s, 9 H), 0.852-0.886 (m, 3 H), 1.200-1.361 (m, 8 H), 1.382 (dd, <i>J</i> = 0.9 and 7.9 Hz, 2 H), 1.953 (q, <i>J</i> = 6.7 Hz, 2 H), 5.224 (dt, <i>J</i> = 6.7 and 15.1 Hz, 1 H)		

^a Unless otherwise stated, 100-MHz NMR data are given. Solvent was CCl₄ for 100 MHz and CDCl₃ for 400 MHz. s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet. ^b Authentic sample. ^c ¹³C NMR data: -2.24 (q, SiMe₃), 5.57 (s), 9.35 (t), 14.16 (q), 22.79 (t), 29.08 (t), 30.07 (t), 32.01 (t), 38.52 ppm (t).

appeared as a single peak on the GLC column and could not be separated in pure states. The structures were deduced by careful examination of 400-MHz ¹H NMR spectra of the mixture of products. 1-Silyl-2-alkylcyclopropanes **9** and **11** showed diagnostic high-field signals around δ -0.6 due to the methine proton on the silyl group bearing carbon atom. 1-Silyl-1,2-dialkylcyclopropanes **13** and **15** were identified by comparison of the ¹H NMR spectra with those of the authentic samples that were prepared by methylenation¹¹ of the corresponding alkenylsilanes (*E*)-1-octenyl- and 1-cyclooctenyltrimethylsilane, respectively. The spectral coincidence also gave strong evidence for the *E* configuration of **13**. Similarly, the *E* configuration of **9** and **11** has been tentatively assigned.

Alcohol Synthesis from the Rearrangement Products. Since the rearrangement products have a chlorine atom on silicon, the carbon-silicon bond therein should be oxidatively cleaved by the action of hydrogen peroxide to form the corresponding alcohols.^{1,12} A typical example

Table III. Elemental Analysis of Organosilicon Compounds Prepared in This Study

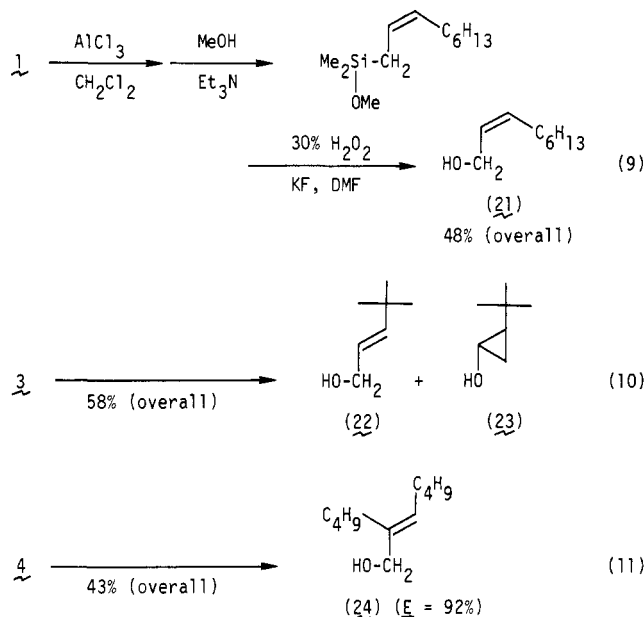
compd	formula	found (calcd)	
		C	H
1	C ₁₁ H ₂₃ SiCl	60.17 (60.37)	10.65 (10.59)
2	C ₁₁ H ₂₃ SiCl	60.11 (60.37)	10.76 (10.59)
3	C ₉ H ₁₉ SiCl	56.53 (56.66)	10.29 (10.04)
4	C ₁₃ H ₂₇ SiCl	^a	
5	C ₁₁ H ₂₁ SiCl	60.83 (60.93)	9.92 (9.76)
6	C ₁₁ H ₂₃ SiCl	60.26 (60.37)	10.54 (10.59)
7	C ₁₂ H ₂₆ SiCl	72.46 (72.64)	13.50 (13.21)
8 and 9 ^b	C ₁₀ H ₂₀ Si	^c	
10 and 11 ^b	C ₁₀ H ₂₂ Si	70.37 (70.50)	12.97 (13.02)
12 and 13 ^b	C ₁₄ H ₃₀ Si	74.22 (74.25)	13.50 (13.35)
14 and 15 ^b	C ₁₂ H ₂₄ Si	73.61 (73.39)	12.39 (12.32)
16	C ₁₂ H ₂₆ Si	72.46 (72.64)	13.50 (13.21)
18	C ₁₄ H ₃₁ Si ₂ Cl	57.69 (57.78)	10.98 (10.74)
20	C ₁₁ H ₂₁ SiCl	61.12 (60.93)	10.02 (9.76)

^a High-resolution mass: found, 246.1561; calcd, 246.1569. ^b Isomeric mixture. ^c High resolution mass: found, 198.1791; calcd, 198.1802.

is given for the conversion of **1** to (*Z*)-2-nonen-1-ol (**21**) (eq 9). Further examples shown in eq 10 and 11 were also

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obtained under similar conditions. These results provide a new method for the transformation of alkenyl(chloromethyl)silanes into the stereo-defined alcohols.



Experimental Section

General Remarks. ^1H NMR spectra were determined with a JEOL JNM-MH 100 spectrometer and JNM-GX 400 (400 MHz) spectrometer. ^{13}C NMR spectra were recorded by using a Hitachi R-900 ^{13}C spectrometer. Chemical shifts (δ) are recorded in parts per million downfield from Me_2Si . Infrared spectra were obtained on a Hitachi EPI-G3 grating infrared spectrometer. Mass spectra were measured on a JEOL JMS-D300 mass spectrometer connected with a JEOL LGC-20K gas chromatograph, equipped with a 1-m glass column packed with OV-17 (3%) on Chromosorb B, and a JMA-2000 data processing system. Ionization voltage was 24 eV for all compounds. GLC analyses and preparative purification were performed on a Shimadzu GC-4B gas chromatograph, equipped with a 3-m column packed with 30% Silicone DC550 on Celite 545.

Materials. 3,3-Dimethyl-1-butyne¹³ and 1-cyclooctenyl bromide¹⁴ were prepared by the published procedure. (*E*)-1-Octenyl bromide and (*E*)- and (*Z*)-5-bromo-5-decene were prepared by the vinylsilane routes.¹⁵ (Chloromethyl)dimethylsilane (17) was prepared by reduction of (chloromethyl)dimethylchlorosilane (19).¹⁶ 1-Octyne and 5-decyne were purchased from Farhan Labs, OH. Dichloromethane was dried with CaCl_2 , distilled on to Molecular Sieves 4A, and kept under nitrogen. Hexane, diethyl ether, and THF were dried over LiAlH_4 and distilled under nitrogen before use.

Preparation of Alkenyl(chloromethyl)dimethylsilanes. (*Z*)-1-Octenyl(chloromethyl)dimethylsilane (1). (*A*) 1-Octenyl(chloromethyl)dimethylsilane (20). 1-Octyne (9.82 g, 94 mmol) in dry THF (50 mL) was treated with a hexane solution of *n*-BuLi (1.59 M, 67 mL, 103 mmol) at 0 °C, and the mixture was stirred at room temperature for 2 h. (Chloromethyl)dimethylchlorosilane (19, 14.9 g, 104 mmol) was added dropwise at 0 °C. After the solution was stirred at room temperature for 12 h, usual workup gave 16.1 g (79% yield) of 20: bp 82 °C (24 mmHg).

(*B*) Hydroalumination of 20. To a solution of diisobutylaluminum hydride (DIBAL) (2.0 mL, 11 mmol) in hexane (8 mL) and diethyl ether (4 mL) was added dropwise 20 (1.95 g, 9.0 mmol) at 0 °C with stirring. After 6 h of stirring at 0 °C, the mixture was hydrolyzed and separated. The aqueous layer was extracted twice with ether. The combined organic layer was washed with water, dried over sodium sulfate, and distilled to give 1.76 g of distillate boiling up to 70 °C (7 mmHg) (bath temperature). GLC analysis of the distillate showed the formation of 1 and 1-octenyltrimethylsilane in the ratio of 86:14. A pure sample of 1 was obtained in ca. 20% yield by repeated bulb-to-bulb distillation.

(*E*)-1-Octenyl(chloromethyl)dimethylsilane (2). To a solution of (*E*)-1-octenyl bromide (1.8 g, 16 mmol) in dry ether (30 mL) was added dropwise a solution of *t*-BuLi in pentane (2.15 M, 15 mL, 33 mmol) at 0 °C. After 2.5 h of stirring, 19 (4.7 mL, ca. 35 mmol) was added at 0 °C and the mixture was stirred at room temperature overnight. Hydrolysis, extraction with ether, drying over sodium sulfate and distillation gave 0.81 g (23% yield) of 2: bp 65–75 °C (8 mmHg) (bath temperature).

(*E*)-3,3-Dimethyl-1-butenyl(chloromethyl)dimethylsilane (3). To a mixture of 3,3-dimethyl-1-butyne (1.81 g, 22.1 mmol), (chloromethyl)dimethylsilane (17) (2.98 g, 27.5 mmol), and dry THF (60 mL) was added ca. 10 μL of a 0.1 M solution of $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ in isopropyl alcohol. An exothermic reaction started and was controlled by cooling with an ice bath. The progress of the reaction was monitored by GLC. After the reaction was completed (6 h), the mixture was distilled to give 3.08 g (73% yield) of pure 3: bp 85 °C (15 mmHg) (bath temperature).

(*E*)-5-Decenyl(chloromethyl)dimethylsilane (4). In a 50-mL two-necked flask, equipped with a stirring bar, a reflux condenser, and a dropping funnel, was placed ca. 10 μL of the Pt catalyst solution (vide supra). A small amount (several drops) of a mixture of 5-decyne (8.60 g, 62 mmol) and 17 (8.06 g, 74 mmol) was added to the catalyst. The mixture was heated with a heat gun for a few minutes to initiate the reaction. To the resulting dark brown mixture was added dropwise the remaining mixture of the two reactants. The hydrosilylation proceeded highly exothermically and was controlled by intermittent cooling with an ice bath. After the addition was completed, the mixture was distilled under reduced pressure to give 13.6 g (89% yield) of 4: bp 90–105 °C (10 mmHg).

1-Cyclooctenyl(chloromethyl)dimethylsilane (5). To a mixture of 1-bromo-1-cyclooctene (7.24 g, 38.3 mmol) in diethyl ether (30 mL) was added *t*-BuLi in pentane (2.1 M, 40 mL, 84 mmol) at –78 °C over 2 min. At the same temperature, 19 (6.04 g, 42.2 mmol) was added to the mixture. The mixture was allowed to warm to room temperature and stirred for 4 h. Usual workup gave 4.43 g (53% yield) of 5: bp 90 °C (4 mmHg) (bath temperature).

1-Octen-2-yl(chloromethyl)dimethylsilane (6). To a mixture of 1-(trimethylsilyl)-1-octyne (5.0 g, 27.4 mmol) and a Pt catalyst solution (ca. 10 μL) was added dropwise 17 (4.5 g, 41.2 mmol) with stirring. An exothermic vigorous reaction started and was controlled by intermittent cooling with an ice bath. Distillation gave 6.16 g (77% yield) of (*E*)-1-(trimethylsilyl)-2-[(chloromethyl)dimethylsilyl]-1-octene (18): bp 85 °C (4 mmHg).

A mixture of the hydrosilylation product 18 (18.7 g, 64.4 mmol), benzene (100 mL), and 57% HI solution (4.5 mL) was stirred at room temperature for 4 h. The mixture was separated, washed with 10% $\text{Na}_2\text{S}_2\text{O}_3$ solution three times, saturated sodium bicarbonate solution once, and water, and then dried over sodium sulfate. Distillation gave 8.35 g (59% yield) of 6: bp 105 °C (5 mmHg).

Aluminum Chloride Catalyzed Rearrangement of Alkenyl(chloromethyl)dimethylsilanes. Typical Procedure. All reactions were carried out under nitrogen. To a solution of 1 (481 mg, 2.20 mmol) in dry dichloromethane (2 mL) was added freshly sublimed AlCl_3 (ca. 30 mg, 0.2 mmol, 10 mol %) with stirring at room temperature (around 25 °C). A slightly exothermic reaction occurred. After 10 min of stirring, an excess amount of methylmagnesium bromide in ether (1.8 M, 6 mL, 10.8 mmol) was added to the mixture at 0 °C. After 2 h of reflux, the mixture was hydrolyzed with dilute hydrochloric acid. The aqueous layer was extracted with ether three times. The organic layer and ether extracts were combined, washed with water and saturated sodium bicarbonate solution, and then dried over sodium sulfate.

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Bulb-to-bulb distillation gave 388 mg (89% yield) of pure (*Z*)-2-nonenyltrimethylsilane (7) boiling at 110 °C (22 mmHg) (bath temperature).

Preparation of Authentic Cyclopropyltrimethylsilane. According to the published procedure,¹¹ (*E*)-5-decenytrimethylsilane (320 mg, 1.5 mmol) and diiodomethane (0.21 mL, ca. 2 mmol) were added to a mixture of CuCl (340 mg, 3.4 mmol), zinc powder (210 mg, 3.2 mmol), and dry diethyl ether (3 mL). The mixture was refluxed for 22 h. The yield of the desired cyclopropane derivative was only several percent. The product 13 was isolated by GLC and analyzed by ¹H NMR (Table II). The authentic sample of 15 was also prepared under similar conditions.

Hydrogen Peroxide Oxidation of Rearrangement Products. Typical Procedure. The AlCl₃-catalyzed rearrangement of 1 (297 mg, 1.36 mmol) was carried out as described above. To the reaction mixture were added dry diethyl ether (5 mL), methanol (0.17 mL, ca. 4 mmol), and triethylamine (0.57 mL, ca. 4 mmol). After being stirred at room temperature for 1 h, the mixture was poured into water and extracted with ether three times. The combined organic layer was dried over sodium sulfate, and the solvent was evaporated. To the remaining oil, which should be mainly (*Z*)-2-nonyldimethylmethoxysilane, were successively added DMF (5 mL), potassium fluoride (250 mg, 4.3 mmol), and 30% H₂O₂ (2.1 mL, 21 mmol). The mixture was heated at 60 °C for 6 h with stirring, poured into water, and extracted with ether five times. The combined ether layer was washed once with 10% NaHSO₃ solution and twice with saturated sodium bicarbonate solution and then dried over sodium sulfate. After evaporation of the solvent bulb-to-bulb distillation gave 94 mg (48% overall yield) of (*Z*)-2-nonen-1-ol (21): bp 110 °C (22 mmHg) (bath temperature); ¹H NMR (CCl₄) δ 0.76–1.01 (m, 3 H), 1.11–1.58 (m, 9 H, including a singlet at 1.44 due to OH), 1.85–2.19 (m, 2 H), 4.07 (d, *J* = 5 Hz, 2 H), 5.26–5.67 (m, 2 H).

Other results have been obtained in a similar manner. Compound 3 gave a mixture of 4,4-dimethyl-2-penten-1-ol (22) and 2-(1,1-dimethylethyl)-1-cyclopropanol (23) in the ratio of 87:13 (48% total yield): bp 80 °C (110 mmHg) (bath temperature); IR (liquid film) 962 cm⁻¹ (trans olefin). ¹H NMR (400 MHz, CDCl₃):

compound 22, δ 1.023 (s, 9 H), 1.531 (s, 1 H), 4.104 (dd, *J* = 1.3 and 5.9 Hz, 2 H), 5.548 (dt, *J* = 5.9 and 15.6 Hz, 1 H), 5.711 (dt, *J* = 1.3 and 15.6 Hz, 1 H); compound 23, δ 0.451–0.500 (m, 1 H), 0.563–0.611 (m, 1 H), 0.830 (s, 9 H), 0.842–0.919 (m, 1 H), 1.531 (s, 1 H), 2.130–2.190 (m, 1 H). Anal. Found: C, 73.53; H, 12.59. Calcd for C₇H₁₄O: C, 73.63; H, 12.36.

Compound 4 formed (*E*)-2-butyl-2-hepten-1-ol (24), together with the *Z* isomer as a minor product in the ratio of 92:8 (43% total yield): bp 85 °C (13 mmHg) (bath temperature). These isomers were also compared with authentic samples that were prepared via lithiation¹⁰ of (*E*)- and (*Z*)-5-bromo-5-decene and the subsequent treatment with formaldehyde. ¹H NMR (100 MHz, CCl₄): *E* isomer, δ 0.54–1.06 (m, 6 H), 1.06–1.64 (m, 9 H, including OH), 1.88–2.19 (m, 4 H), 3.89 (s, 2 H), 5.27 (t, *J* = 7 Hz, 1 H); *Z* isomer (authentic sample), δ 0.54–1.10 (m, 7 H, including OH), 1.10–1.54 (m, 8 H), 1.74–2.18 (m, 4 H), 3.97 (s, 2 H), 5.06 (t, *J* = 7 Hz, 1 H).

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Registry No. 1, 91898-55-4; 2, 91898-56-5; 3, 91898-57-6; 4, 91898-58-7; 5, 91898-59-8; 6, 91898-60-1; 7, 63922-75-8; 8, 63922-74-7; 9, 91928-37-9; 10, 91898-61-2; 11, 71814-09-0; 12, 91898-62-3; 13, 91898-63-4; 14, 91898-64-5; 15, 91898-65-6; 16, 91898-66-7; 17, 3144-74-9; 18, 91928-38-0; 19, 1719-57-9; 20, 91898-67-8; 21, 41453-56-9; 22, 64081-43-2; 23, 91898-68-9; (*E*)-24, 91898-69-0; (*Z*)-24, 91898-70-3; 1-octyne, 629-05-0; (*E*)-1-octenyl bromide, 51751-87-2; 3,3-dimethyl-1-butene, 917-92-0; 5-decyne, 1942-46-7; 1-bromo-1-cyclooctene, 4103-11-1; 1-(trimethylsilyl)-1-octyne, 15719-55-8.

Enamines of Acylsilanes: An Easy Access from α -Siloxy Nitriles¹

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Reductive silylation of α -siloxy nitriles (O-silylated cyanohydrins) by Me₃SiCl/lithium in THF at 0 °C afforded an easy access to enamines of acylsilanes, a potentially interesting class of compounds in organic and organosilicon syntheses. Concurrently, the reaction led to the formation of α -siloxy silanes by substitution of the cyano group in the starting molecules.

Enamines have proven to be very useful intermediates in organic synthesis.^{2,3} Moreover, organosilylated derivatives are becoming increasingly useful as reagents in this field.^{4,5} In following up our continuing interest in acyl-

silanes,⁶ we have focused our attention on enamines 2 derived from these peculiar carbonyl compounds, with the hope they could serve as efficient and versatile synthetic tools.

(1) This has been the subject of poster sessions at the 6th International Symposium on Organosilicon Chemistry, Budapest, Hungary, 1981, and at the "Journées de Chimie Organique, Société Chimique de France", Palaiseau, France, 1981.

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