The unimportance of inductive localized π-polarization on ^{13}C NMR chemical shifts in protonated acetophenones was first discussed by Craik and Brownlee, the orginators of the inductive localized π-polarization phenomenon.[40] However, Brown et al.[21,22,25] have attempted to use this effect as a possible explanation for the observed deviations in the application of the "tool of increasing electron demand" in the ^{13}C NMR spectroscopic study of certain carbocations. We believe that our studies emphasizes the unimportance of such effects on ^{13}C NMR chemical shifts in fully developed carbocations under superacid conditions.

Conclusion

We conclude that use of the Gassman-Fentiman tool of increasing electron demand, coupled with ^{13}C NMR, to probe for extraordinary behavior in π-conjugated cations is reliable only if the chemical shifts of *all* conjugatively related cationic carbon sites are taken into account. The attempt to correlate $^{13}C^+$ NMR chemical shifts of the arylcyclopentyl cations and the σ_{C^+} parameters derived from them with only on nominally cationic carbon of a conjugated system will give misleading results. When the representative conjugated cations described in this paper are probed considering all involved carbons, they are seen to be ordinary conjugated systems, requiring only π-delocalization. There is no evidence requiring inductive localized π-polarization.

There is, therefore, no reason to doubt the reliability of the probe to detect extraordinary behavior in cyclopropyl conjugated systems (e.g., 3-aryl-3-nortricyclyl), homoallylically conjugated systems (e.g., 5-aryl-2-norbornen-5-yl), or σ-bridged systems (e.g., 2-aryl-2-norbornyl).[7-10,42]

(41) Kelly, D. P.; Jenkins, M. J. *J. Org. Chem.* **1984**, *49*, 409.
(42) Olah, G. A.; Prakash, G. K. S.; Farnum, D. G.; Clausen, T. P. *J. Org. Chem.* **1983**, *48*, 2146.

Experimental Section

The precursor alcohols, *trans*-1-aryl-3-methylbut-1-en-3-ols (**4**), were prepared by the reaction of methyllithium with either the corresponding *trans*-benzalactones or the *trans*-ethyl cinnamate in ethereal solutions. The 4-arylpent-2-yn-4-ols (**5**) were prepared by the addition of propynyllithium to the respective substituted acetophenones in refluxing tetrahydrofuran solutions. The ^1H NMR spectral data and the physical constants of precursor alcohols are listed in Tables I and II. The ^{13}C NMR data are listed in Tables III and IV.

Carbocations. The ions were prepared by the addition of the appropriate precursor dissolved in SO_2ClF to a fivefold excess of FSO_3H:SbF_5 dissolved in SO_2ClF precooled at −78 °C so as to obtain a 15% solution of the carbocations.

NMR Spectra. The ^1H and ^{13}C NMR spectra were obtained on a Varian Associates Model XL-200 NMR spectrometer equipped with variable-temperature probes. The field lock was held by a 2.5-mm capillary containing acetone-d_6. The chemical shifts are referenced to external tetramethylsilane.

Acknowledgment. Support of our work at USC by the National Institutes of Health is gratefully acknowledged.

Registry No. 2 (X = 4-OCH_3), 96307-90-3; **2** (X = 3,4-$(CH_3)_2$), 96307-91-4; **2** (X = 4-CH_3), 96307-92-5; **2** (X = 3-CH_3), 96307-93-6; **2** (X = H), 96307-94-7; **2** (X = 3-CF_3), 96307-95-8; **2** (X = 4-CF_3), 96307-96-9; **2** (X = 3,5-$(CF_3)_2$), 96307-97-0; **3** (X = 4-OCH_3), 96307-98-1; **3** (X = 3,4-$(CH_3)_2$), 96307-99-2; **3** (X = 4-CH_3), 96308-00-8; **3** (X = 3-CH_3), 96308-01-9; **3** (X = H), 96308-02-0; **3** (X = 3-CF_3), 96308-03-1; **3** (X = 4-CF_3), 96308-04-2; **3** (X = 3,5-$(CF_3)_2$), 96308-05-3; **4** (X = 4-OCH_3), 77144-22-0; **4** (X = 3,4-$(CH_3)_2$), 96307-79-8; **4** (X = 4-CH_3), 77144-23-1; **4** (X = 3-CH_3), 96307-80-1; **4** (X = H), 57132-28-2; **4** (X = 3-CF_3), 96307-81-2; **4** (X = 4-CF_3), 96307-82-3; **4** (X = 3,5-$(CF_3)_2$), 96307-83-4; **5** (X = 4-OCH_3), 96307-84-5; **5** (X = 3,4-$(CH_3)_2$), 96307-85-6; **5** (X = 4-CH_3), 5876-72-2; **5** (X = 3-CH_3), 96307-86-7; **5** (X = H), 6712-32-9; **5** (X = 3-CF_3), 96307-87-8; **5** (X = 4-CF_3), 96307-88-9; **5** (X = 3,5-$(CF_3)_2$), 96307-89-0.

Silacyclopropylcarbinyl and Cyclopropylsilylenium Cations in the $AlCl_3$-Induced Rearrangements of (Chloromethyl)vinylsilanes[1]

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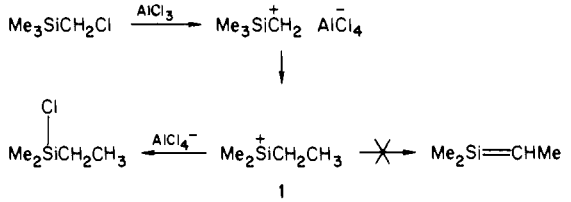
Received November 5, 1984

Abstract: Reaction of a variety of (chloromethyl)vinylsilanes and $AlCl_3$ affords cyclopropylchlorosilane products. These reactions are most economically viewed as proceeding via β-closure of the initially formed carbocation to produce silacyclopropylcarbinyl cations which either rearrange to cyclopropylsilylenium ions or can be quenched directly by chloride to yield allylic chlorosilanes. Alkyl substitution at the terminal position of the vinyl group induces a shift to allylic products consistent with stabilization of the initial silacyclopropylcarbinyl cation relative to the rearranged ion or a silacyclobutyl cation formed from γ-closure.

The first observation of $AlCl_3$-induced rearrangements of α-chloroalkylsilanes was by Whitmore,[2] who in 1947 reported that treatment of (chloromethyl)trimethylsilane with $AlCl_3$ produced ethyldimethylchlorosilane in 79% yield. It was assumed that this reaction proceeded in a fashion analogous to the $AlCl_3$-induced rearrangement of neopentyl chloride with chloride quenching of the corresponding silylenium ion **1** rather than loss of a proton to produce the then unknown silicon-carbon double bond.



1

Although the $AlCl_3$-induced rearrangement has often been employed for synthetic purposes,[3] there has been surprisingly little

(1) Presented at the VII International Symposium on Organosilicon Chemistry, Kyoto, Japan, September 11, 1984.
(2) Whitmore, F. C.; Sommer, L. H.; Gold, J. *J. Am. Chem. Soc.* **1947**, *69*, 1976.

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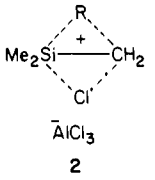
effort expended toward a mechanistic understanding. In 1965, Eaborn reported the results of a kinetic study to determine the mechanism of $AlCl_3$-catalyzed rearrangements of (chloromethyl)triorganosilanes.[4] This investigation of the rearrangement of p-$XC_6H_4Me_2SiCH_2Cl$ (X = CH_3, H, and Cl) revealed the reactions to be first order in silane, although the order with respect to $AlCl_3$ could not be determined. Since the relative reactivities [(CH_3)1.7:H(1.0):(Cl)0.02] demonstrated that the isomerization was drastically retarded by an electron-withdrawing group, it was concluded that the rearrangement was concerted, involving synchronous nucleophilic attack at silicon, migration of the organic substituent, and separation of chloride from carbon. Thus, a four-centered transition state (**2**) was proposed.

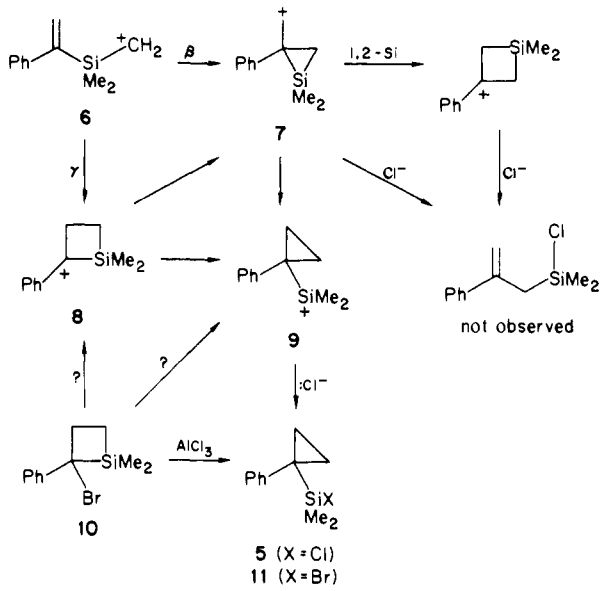


2

Later studies by Steward[5] on the migratory aptitude of various (chloromethyl)trialkylsilanes in the presence of $AlCl_3$ revealed that primary alkyl groups migrated more readily than secondary or tertiary groups. This was attributed to significant negative charge developed on the migrating group, and it was concluded that the breakdown of an intermediate resembling **2** was rate determining. However, a systematic study of the behavior of chloromethyl- and dichloromethyl-substituted disilanes in the presence of chloromethyl- and dichloromethyl-substituted disilanes in the presence of $AlCl_3$ conducted by Tamao and Kumada[6] produced a pattern of migratory ease for various silyl groups opposite that expected from the conclusions of Steward. These authors favored a mechanism involving an initial slow, rate-determining step of carbon–chlorine bond ionization, followed by a synchronous fast step of nucleophilic attack by halide on silicon and migration from silicon to carbon. This view was supported by the results of Hairston and O'Brien[7] in their study of the rearrangement of 2-(trimethylsilyl)-2-chloropropane with SbF_5 where an initially formed tertiary carbocation was directly observed by ^1H NMR.

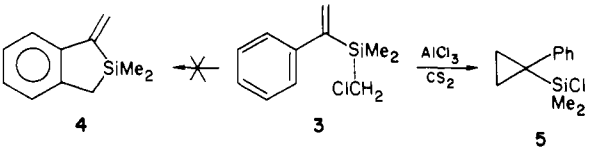
Thus, several different mechanistic proposals for these rearrangements can be found in the literature with supporting data for each. It is to be noted that since quite different systems are utilized for each of these separate studies, each proposal may be correct—for the specific systems studied. The absence of silylenium ion invocation in the post-1947 mechanistic discussions of the rearrangements can quite likely be ascribed to the complete absence of experimental evidence for such species in solution. This barrier has disappeared with the recent generation and observation of a silylenium ion by Lambert.[8] In addition to this extremely important experimental result, recent ab initio molecular orbital calculations by Hopkinson and Lien[9] reveal that there is essentially no barrier for the very favorable (ΔH = −40 kcal/mol) rearrangement of $H_3SiCH_2^+$ to $H_2Si^+CH_3$.

Scheme I



Results and Discussion

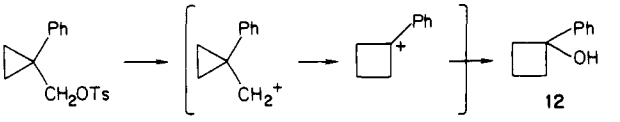
Our interest in the $AlCl_3$-induced rearrangement of chloromethylsilanes originated serendipitously when we attempted to synthesize silaindane **4** via an $AlCl_3$-catalyzed, intramolecular, Friedel–Crafts cyclization of (1-phenylvinyl)(chloromethyl)dimethylsilane (**3**). To our naive surprise, no **4** was found in the product mixture, but rather a single isomer of **3**, (1-phenylcyclopropyl)dimethylchlorosilane (**5**), had been formed in 19% yield. The structure of **5** was largely deduced from the 300-MHz ^1H NMR spectrum (δ 0.26, $SiMe_2$; 0.85 and 0.97, overlapped doublets-of-doublets of 2H each), the CMR spectrum (δ 16.4, 10.4 and 0.13), and reduction by LiAlH to the corresponding silyl hydride (ν_{SiH} 2095 cm^{-1}).



4 3 5

Formation of **5** can be rationalized by either β- or γ-attack on the vinyl group by the initially formed carbocation **6** (Scheme I). Either the silacyclopropylcarbinyl cation **7** or silacyclobutyl cation **8** could react directly with chloride to form **5** or could rearrange to the cyclopropylsilylenium ion **9** prior to reaction with chloride.

Although the data do not allow a mechanistic distinction, the possibility of **8** being on this surface was confirmed by reacting 2-bromo-2-phenyl-1,1-dimethyl-1-silacyclobutane (**10**)[10] with $AlCl_3$ under similar conditions[11] to obtain **5** (22%) and the corresponding bromide **11** (51%).[12] It must be emphasized that this result does not demand that **8** be involved in the formation of **5** from **3**; it simply suggests that **8** is capable of intersecting with the energy surface of this rearrangement. Indeed, it is quite possible that the initially formed ion from **10** is the silylenium ion **9**. It is of considerable interest to contrast this behavior with that of the analogous 1-phenylcyclopropylcarbinyl cation (generated by solvolysis of the corresponding tosylate) which affords only the cyclobutanol **12**.[13]



12

(3) Sommer, L. H.; Bailey, D. L.; Gould, J. R.; Whitmore, F. C. *J. Am. Chem. Soc.* **1954**, *76*, 801. Vdovin, V. M.; Nametkin, N. S.; Pushchevaya, K. S.; Topchiev, A. V. *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk* **1962**, *6*, 1127. Vdovin, V. M.; Nametkin, N. S.; Pushchevaya, K. S.; Topchiev, A. V. *Izv. Akad. Nauk SSR, Otd. Khim. Nauk* **1963**, *2*, 274. Nametkin, N. S.; Vdovin, V. M.; Pushchevaya, K. S.; Egorochkin, A. N. *Izv. Akad. Nauk SSR, Ser. Khim.* **1967**, *11*, 2530. Kumada, M.; Nakajima, J.; Ishikawa, M.; Yamamoto, Y. *J. Org. Chem.* **1958**, *2o*, 292. Sakurai, H.; Yamamori, H.; Kumada, M. *J. Org. Chem.* **1968**, *33*, 1527.

(4) Bott, R. W.; Eaborn, C.; Rushton, B. M. *J. Organomet. Chem.* **1965**, *3*, 455.

(5) Steward, O. W.; Uhl, W. J.; Sands, B. W. *J. Organomet. Chem.* **1968**, *15*, 329.

(6) Tamao, K.; Kumada, M. *J. Organomet. Chem.* **1971**, *30*, 339.

(7) Hairston, T. J.; O'Brien, D. H. *J. Organomet. Chem.* **1970**, *2o*, C41. Hairston, T. J.; O'Brien, D. H. *J. Organomet. Chem.* **1971**, *29*, 79.

(8) Lambert, J. B.; Schulz, W. J., Jr. *J. Am. Chem. Soc.* **1983**, *105*, 1671.

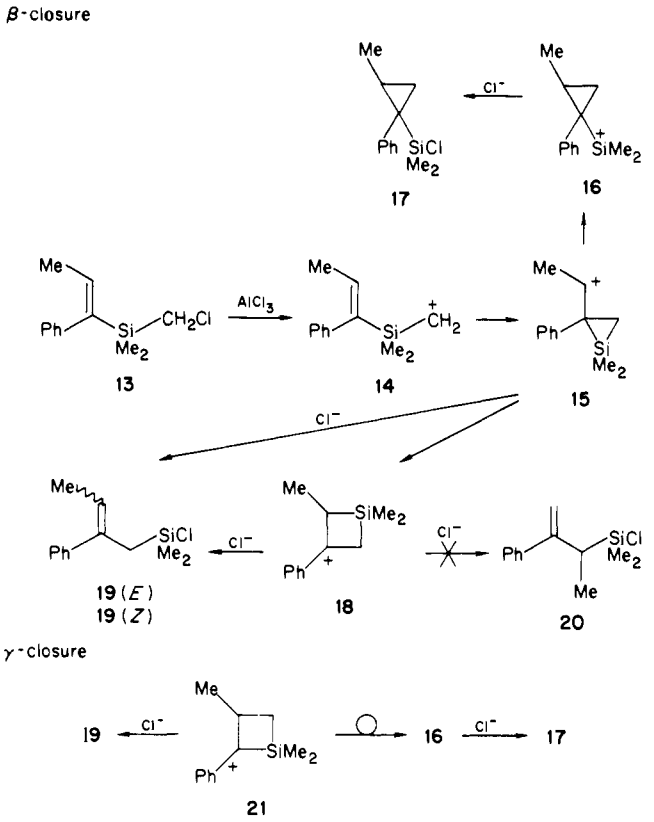
(9) Hopkinson, A. C.; Lien, M. H. *J. Org. Chem.* **1981**, *46*, 998.

(10) Valkovich, P. B.; Ito, T. I.; Weber, W. P. *J. Org. Chem.* **1974**, *39*, 3543. Valkovich, P. B.; Weber, W. P. *Tetrahedron Lett.* **1975**, *26*, 2153.

(11) All reactions with $AlCl_3$ were conducted in refluxing CS_2.

(12) The predominance of the bromide product (**11**) in this reaction is obviously suggestive of concertedness of at least an oriented tight ion pair. This point is now under investigation.

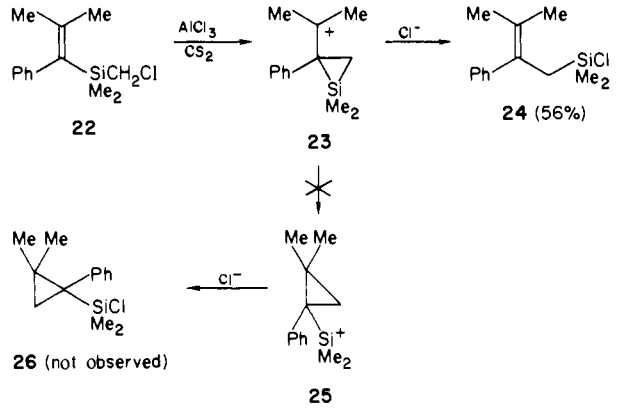
Scheme II



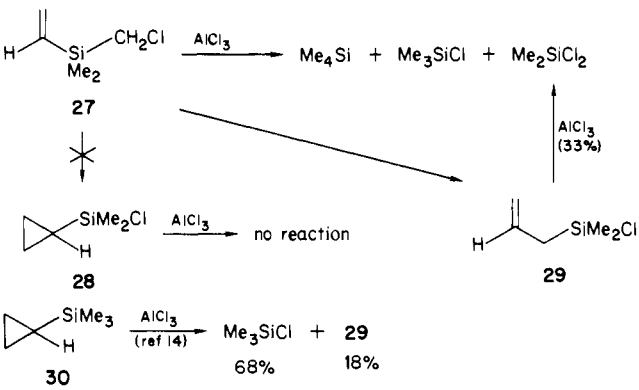
It was decided to probe this reaction by the addition of cation-stabilizing substituents at the terminal olefinic carbon. Thus, formation of the silacyclopropylcarbinyl cation would be favored and might be sufficiently stabilized (relative to the isomeric silylenium ion) to be scavenged by chloride to produce an allylic product of rearrangement. To this end (*E*)-(1-phenyl-2-methylvinyl)(chloromethyl)dimethylsilane (**13**) was synthesized and reacted with $AlCl_3$ (Scheme II). The expectation of allylic products was realized, as the *E*- and *Z*-stereoisomers of **19** were formed in a combined yield of 59%. However, cyclization was not completely thwarted as a 14% yield of the cyclopropylsilyl chloride **17** was also produced. These results are in keeping with β-closure of the initially formed carbocation **14** to form silacyclopropylcarbinyl cation **15**. The greater stability of secondary ion **15** (relative to **7**) allows chloride trapping to produce the allylsilanes **19**. Invocation of **15** is also attractive from the viewpoint of explaining the loss of stereochemical integrity in **19**, as the more direct route of **14** → **18** → **19** would be expected to proceed with retention of stereochemistry at the double bond. Another argument, somewhat weaker, against the intermediacy of **18** is the nonobservation of the less thermodynamically favored isomer **20**. Since the observed products (**17** and **19**) can again be rationalized as arising by γ-closure to silacyclobutyl cation **21**, one still cannot definitively rule out this pathway except by the inconsistent change in products brought about by the methyl substitution.

Probing of the effects of methyl substitution on the olefinic position β to silicon was completed by the synthesis and reaction with $AlCl_3$ of (1-phenyl-2,2-dimethylvinyl)(chloromethyl)dimethylsilane (**22**) (Scheme III). No cyclopropyl product (**26**) could be detected in the product mixture, but a 56% yield of the allylic silane **24** was obtained. Although it is possible to rationalize this result with initial γ-closure, certainly the most economical explanation is β-closure to a relatively stable, tertiary silacyclopropylcarbinyl cation (**23**) which is sufficiently longlived to be trapped by chloride before rearrangement to silylenium ion **25**.

Scheme III

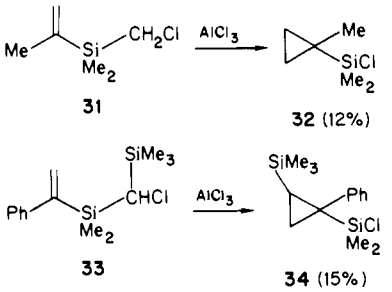


Scheme IV



Reaction of the parent system, (chloromethyl)dimethylvinylsilane (**27**), and $AlCl_3$ did not produce any cyclopropyldimethylsilyl chloride (**28**). The isolated products were Me_2SiCl_2 (25%), Me_3SiCl (4%), and Me_4Si (4%) (Scheme IV). The absence of **28** or its allylic isomer **29** could be explained by decomposition of these products under the reaction conditions. Thus, **28** was synthesized and reacted with $AlCl_3$, but no decomposition or rearrangement of **28** was observed. The lack of reactivity of **28** may appear surprising in view of Mironov's report[14] that cyclopropyltrimethylsilane (**30**) is rather cleanly converted to chlorotrimethylsilane and allylchlorodimethylsilane by $AlCl_3$. However, it is well established that the presence of a chlorine on silicon strongly deactivates the system toward rearrangement (cf., e.g., ref 15). Thus, **28** would be expected to be much less reactive toward $AlCl_3$ than would **30**. In contrast, we do find that the allylchlorosilane **29** reacts with $AlCl_3$ under our reaction conditions to afford a 33% yield of Me_2SiCl_2.

The parent system, **27**, is the only vinyl(chloromethyl)silane not possessing substituents at the β-olefinic carbon which did not afford some cyclopropyl product. Thus, reaction of $AlCl_3$ with the vinyl(chloromethyl)silanes **31** and **33** produced the respective isomeric cyclopropylsilyl chlorides **32** and **34** in small (12% and 15%) but isolable amounts. Silane **33** is the only example of a secondary α-halo silane investigated in this work.

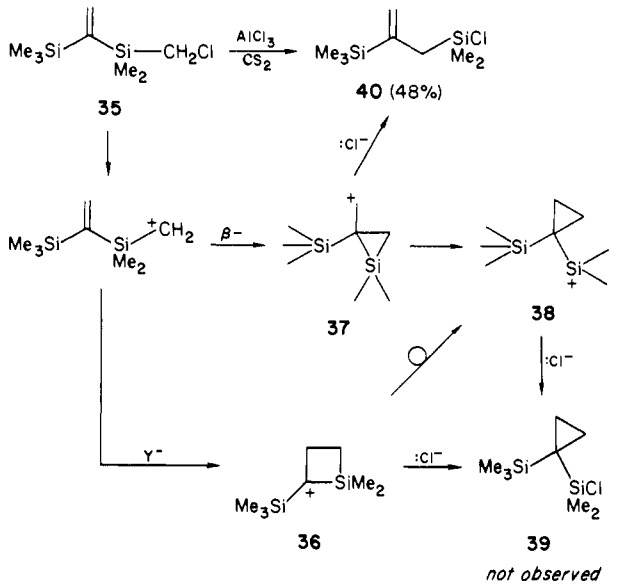


(13) Roberts, D. D. *J. Org. Chem.* **1965**, *30*, 23.

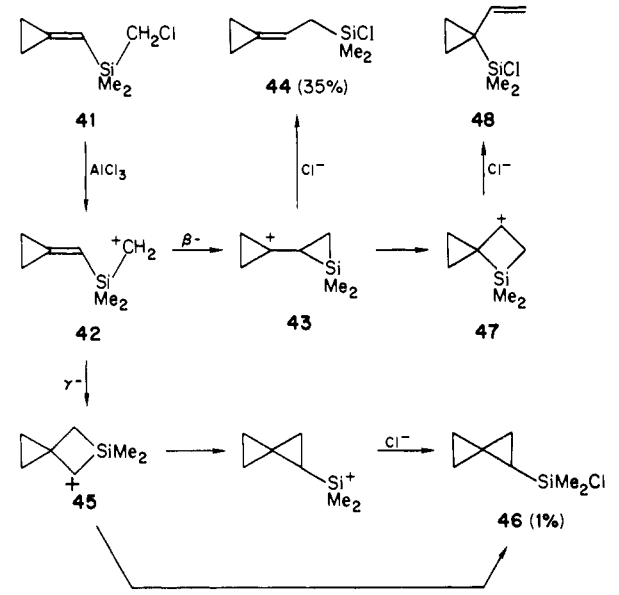
(14) Mironov, V. F.; Sheludyakov, V. D.; Shcherbinin, V. V.; Viktorov, E. A. *Zh. Obshch. Khim.* **1975**, *45*, 1796.

(15) Kumada, M.; Ishikawa, M. *J. Organomet. Chem.* **1964**, *1*, 411.

Scheme V



Scheme VI



To further probe the effects of substitution on these rearrangements, it was decided to employ the well-established ability of a silyl group to stabilize a β-carbocation.[16] To this end, (1-(trimethylsilyl)vinyl)(chloromethyl)dimethylsilane (**35**) was synthesized and reacted with $AlCl_3$. The major point of interest in this system lies in the fact that γ-closure produces a carbocation (**38**) that is α to two silicons, while β-closure yields a carbocation (**37**) that is stabilized by virtue of being β to two silicons (Scheme V). Thus, the silacyclopropylcarbinyl cation **37** is expected to be exceptionally stable and correspondingly less prone to rearrange to the cyclopropylsilylenium ion **38**. Indeed, none of the cyclopropylsilyl chloride **39** was detected in the product mixture. The only isomeric product was the allylsilyl chloride **40** (48%) as was expected from chloride attack on **37**.

To date, the most interesting and revealing system we have studied is (((1-chloromethyl)dimethylsilyl)methylene)cyclopropane (**41**). Several novel possibilities (Scheme VI) await the initially formed cation **42** as β-closure produces an ion (**43**) that in addition to being silacyclopropylcarbinyl is cyclopropyl, while γ-closure affords a cyclopropylcarbinyl cation (**45**). Reaction of **41** and $AlCl_3$ produces, as expected, the allylic silane **44** as the major product (35%). However, two minor products, both formed in 1% yield and isolated as their methyl ether derivatives, are most revealing of the intricacies of this reaction. The spirocyclic silyl chloride **46** can be formed from either β- or γ-closure and ensuring rearrangements illustrated in Scheme VI. However, it is difficult to rationalize the formation of cyclopropylsilane **48** without invoking the intermediacy of the spirocyclic cation **47** which in turn appears to require **43** as a precursor. Thus, once again, all products are easily explicable by the assumption of initial β-closure.

Table I. $AlCl_3$-Induced Rearrangement of (Chloromethyl)vinylsilanes

(chloromethyl)silanes	cyclopropyl product (%)	allylic product (%)
6	**5** (19)	
13	**17** (59)	**19** (14)
22		**24** (56)
31	**32** (12)	
33	**34** (15)	
35		**40** (48)
41	**46, 48** (1,1)	**44** (35)

In summary, all of the products found from the reactions of all the (chloromethyl)vinylsilanes investigated in this study (summarized in Table I) can be rationalized by cyclization of the initially formed carbocation, or incipient carbocation, in a β-fashion to produce a silacyclopropylcarbinyl cation. This cation can, depending upon its stability, react with chloride to produce allylchlorosilanes or rearrange to a cyclopropylsilylenium ion or (in the unique case of **47**) a β-silyl carbocation. Although the intermediacy of silacyclobutyl cations formed from initial γ-closure is not ruled out, no observed products demand them. It should be emphasized that for the sake of simplicity we have utilized only classical cationic structures in this discussion. It may well be that when more data have accumulated (especially direct spectral observation) that bridged, delocalized intermediates will emerge as favored intermediates. The situation is now similar to that of the cyclopropylmethyl cation in its infancy of the 1950's.[17]

After this manuscript was submitted for publication, a related report by Tamao[18] appeared. The authors also found that the cyclopropyl to allyl product ratio was highly dependent upon the substituents on the olefinic unit of the alkenyl(chloromethyl)silane. Unfortunately, it is difficult to compare our results with theirs as no common starting material was used, the solvents were different, the relative amounts of $AlCl_3$ were different, and the two studies were conducted at different temperatures. Nevertheless, it is of interest that Tamao found retention of the olefinic stereochemistry in the allylic products, while the sole case in which we could make a stereochemical observation (**13**) we found both *E* and *Z* products (**19**). The Japanese group does not consider the possibility of cyclopropylsilylenium ion (e.g., **9**) involvement and argues that the site of closure can be controlled by the presence of unfavorable steric interaction between a $Si-CH_3$ and a terminal substituent in the transition state leading from a (*Z*)-alkenylsilane (**47**, R^2 = H; R^3 = alkyl) to a puckered silacyclobutyl cation (**48**). Thus, they found that (*E*)-olefins (**47**; R^2 = alkyl, R^3 = H) produced mixtures of allylic and cyclopropyl products, while a (*Z*)-olefin (**47**, R^2 = H; R^3 = R) formed only allylic products, and an alkene substituted only at the internal olefinic carbon (**47**, $R^2 = R^3$ = H) yielded only the cyclopropyl product. While this explanation is certainly in keeping with all their results, one notes that this steric rational predicts that our chloromethylsilane **35** would exclusively afford cyclopropane **39** (Scheme V) instead of the observed allylic product **40**. Thus, we are still of the view that electronic factors can be dominant in control.

Experimental Section

Instrumentation. Routine ^1H NMR spectra were recorded on either a Varian Model A-60, EM-360, or EM-360L spectrometer. High-reso-

(16) Lambert, J. B.; Finzel, R. B. *J. Am. Chem. Soc.* **1982**, *104*, 2020.

(17) March, J. "Advanced Organic Chemistry"; McGraw-Hill: New York, 1977; pp 298–300.

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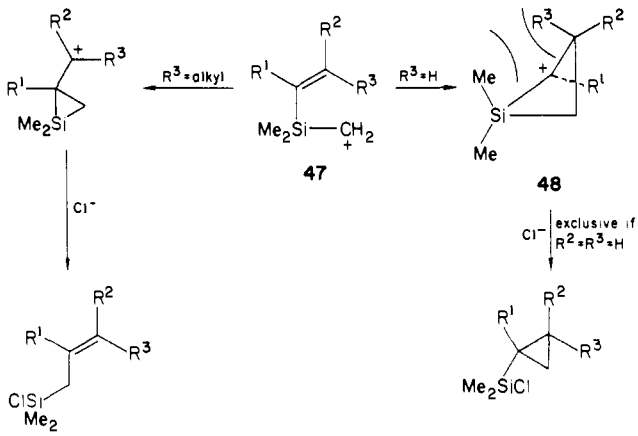

lution ^{1}H NMR was obtained on either a Bruker WM-300 or Nicolet NT-300 spectrometer. All chemical shifts are reported as ppm from Me_4Si with either Me_4Si, methylene chloride, chloroform, benzene, or 1,4-dioxane as an internal standard. ^{13}C NMR spectra were recorded on either a JEOL FX-90Q or Nicolet NT-300 spectrometer with $CDCl_3$ as an internal standard. Gas chromatograph–mass spectra (GC–MS) were recorded on a Finnigan Model 4023 mass spectrometer. Exact mass measurements were obtained on an AEI-MS-902 spectrometer. All mass spectra were recorded at 70 eV and are presented as *m/e* (% relative intensity). Elemental analyses for carbon and hydrogen were determined by Mic Anal or Galbraith Laboratories. Gas chromatographic (GC) data were obtained on a Varian-Aerograph Model 1700, 920, GOW-MAC Series 550P, Fisher/Victoreen Series 4400, or Hewlett Packard Series 5790A gas chromatograph. The Fisher/Victoreen GC was equipped with a 10 ft × $^1/_8$ in., 10% OV101 on Chromosorb W column. The Hewlett Packard GC was equipped with a 12 m × 0.25 mm capillary column coated with dimethylsilicone. All other columns will be described as used. All products were isolated by preparative GC and produced a single peak on an analytical GC. Unless otherwise stated, all GC yields were determined with internal standards and predetermined response factors. Infrared (IR) spectra were recorded on a Beckman IR-4250 spectrometer.

General Procedure for the Reaction of $AlCl_3$ with α-(Chloromethyl)-silanes. $AlCl_3$ was purified by sublimation and stored under N_2. All glassware was flame dried under a N_2 atmosphere. Addition of $AlCl_3$ was carried out in a dry, N_2-filled glove bag. The carbon disulfide used was distilled from CaH_2. The silane was added to the reaction flask via syringe as a solution in carbon disulfide, and the reaction was carried out under a N_2 atmosphere. The progress of the reaction was monitored by ^{1}H NMR of aliquots. After distillation, a considerable amount of nonvolatile material remained as pot residue.

Synthesis of (1-Phenylvinyl)(chloromethyl)dimethylsilane (3). To a stirring solution of α-bromostyrene[19] (8.2 g, 45 mmol) in 150 mL of ether at −23 °C was added 51 mL (95 mmol) of 1.76 M *tert*-butyllithium in pentane dropwise over 2 h. After the mixture was stirred for an additional 2 h at −23 °C, (chloromethyl)dimethylchlorosilane (6.4 g, 45 mmol) was added over 20 min. The mixture was allowed to warm to room temperature, precipitated salts were filtered off, solvent was removed by rotary evaporation, and remaining salts were separated by centrifugation. Distillation at 64 °C and 0.15 torr yielded 6.4 g of **3** (68%): ^{1}H NMR (CCl_4) δ 7.03 (m, 5 H), 5.72 (d, 1 H, J = 2 Hz), 5.52 (d, 1 H, J = 2 Hz), 2.70 (s, 2 H), 0.25 (s, 6 H); ^{13}C NMR ($CDCl_3$) δ 150.0, 143.8, 129.6, 128.4, 126.7, 30.0, −4.0; mass spectrum, 212 (6.1), 211 (3.1), 210 (M^+, 17), 161 (100), 159 (26), 145 (16), 135 (66), 103 (24), 93 (13), 79 (23), 77 (13), 59 (11); calculated for $C_{11}H_{15}SiCl$ 210.06316, measured 210.06250. Anal. Calcd for $C_{11}H_{15}SiCl$: C, 62.68; H, 7.17. Found: C, 62.55; H, 7.26.

Reaction of (1-Phenylvinyl)(chloromethyl)dimethylsilane (3) with $AlCl_3$. A mixture of **3** (3.955 g, 18.22 mmol) and $AlCl_3$ (0.986 g, 7.40 mmol) in 150 mL of CS_2 was stirred and heated at reflux for 1 h. After the mixture was filtered and CS_2 removed by rotary evaporation, the residue was diluted with pentane, centrifuged to remove salts, and evaporated to afford a clear, yellow, liquid sample of (1-phenylcyclopropyl)dimethylchlorosilane (**5**) (19% NMR yield). An analytical sample of **5** was obtained by preparative GC (10 ft × $^1/_4$ in., 20% SE-30, 220 °C): ^{1}H NMR (CCl_4) δ 7.20 (m, 5 H), 0.97 (m, 2 H), 0.85 (m, 2 H), 0.26 (s, 6 H); ^{13}C NMR ($CDCl_3$) δ 143.6, 130.7, 128.2, 125.9, 16.4, 10.4, 0.13; mass spectrum, 212 (3.2), 211 (1.6), 210 (M^+, 9.8), 195 (2.2), 174 (3.9), 117 ($M^+ - Me_2SiCl$, 23), 93 (100), 77 (6.4), 65 (22); calculated for $C_{11}H_{15}SiCl$ 210.06316, measured 210.06209. Anal. Calcd for $C_{11}H_{15}SiCl$: C, 62.68; H, 7.17. Found: C, 62.91; H, 7.26. Reduction of **5** with $LiAlH_4$ afforded (1-phenylcyclopropyl)dimethylsilane: NMR (CS_2) δ 7.28 (s, 5 H), 3.97 (m, 1 H, SiH), 1.00 (s, 4 H), 0.20 (d, 6 H, J = 4 Hz); ^{13}C NMR ($CDCl_3$) δ 145.9, 130.0, 128.1, 125.2, 13.6, 10.2, −5.4; IR (CCl_4) 3060, 3015, 2985, 2950, 2095 cm^{-1}; mass spectrum, 176 (M^+, 27), 161 (33), 148 (65), 135 (19), 121 (22), 72 (28), 59 (100); calculated for $C_{11}H_{16}Si$ 176.10213, measured 176.10279.

Reaction of 2-Bromo-2-phenyl-1,1-dimethylsilacyclobutane (10)[10] with $AlCl_3$. A mixture of **10** (0.423 g, 2.01 mmol) and $AlCl_3$ (0.107 g, 0.804 mmol) in 15 mL of CS_2 was stirred and heated at reflux for 45 min. After the mixture was filtered and the CS_2 removed by trap-to-trap distillation, the remaining residue consisted of **5** (22%) and **11** (51%). Yields were determined by ^{1}H NMR. Pure samples of each were obtained by preparative GC (12 ft × $^1/_4$ in., 15% SE-30, 150 °C). Spectral data of **5** were identical with those of authentic material (vide supra). **11**: ^{1}H NMR (CCl_4) δ 7.32 (s, 5 H), 1.32 (m, 4 H), 0.83 (s, 6 H); mass spectrum, 256 (13), 254 (M^+, 13), 201 (10), 200 (9.6), 174 (23), 159 (22), 139 (97), 137 (100), 117 (42), 91 (15), 77 (7.1).

Synthesis of ((*E*)-1-Phenyl-2-methylvinyl)(chloromethyl)dimethylsilane (13). To a stirring solution of α-bromo-β-methylstyrene[20] (*E*:*Z* = 9:1) (6.8 g, 35 mmol) in 100 mL of ether at −23 °C was added 1.92 M *tert*-butyllithium (36 mL, 69 mmol) dropwise. After being stirred for an additional 1 h, the solution was transferred via a double-ended needle to a solution of (chloromethyl)dimethylchlorosilane (4.5 mL, 33 mmol) in ether (10 mL) at −23 °C. The mixture was allowed to warm to room temperature, filtered, and stripped of solvent on a rotary evaporator. The remaining residue was diluted with hexane and centrifuged to precipitate the salts. Following removal of hexane, crude **13** was isolated by column chromatography (silica gel/hexane) to afford a 56% yield of **13**, which was further purified by distillation (65–69 °C, 0.2 torr) and preparative GC (10 ft × $^1/_4$ in., 20% SE-30): ^{1}H NMR (CCl_4) δ 7.03 (m, 5 H), 6.12 (q, 1 H, J = 6 Hz), 2.63 (s, 2 H), 1.55 (d, 3 H, J = 6 Hz), 0.17 (s, 6 H); ^{13}C NMR ($CDCl_3$) δ 142.2, 141.3, 138.6, 128.3, 127.8, 125.7, 29.9, 16.1, −4.75; mass spectrum, 226 (4.0), 225 (2.0), 224 (M^+, 11), 175 (61), 135 (100), 115 (14), 105 (5.2), 91 (10), 79 (19), 59 (20); calculated for $C_{12}H_{17}SiCl$ 224.07904, measured 224.07894. Anal. Calcd for $C_{12}H_{17}SiCl$: C, 64.11; H, 7.62. Found: C, 64.42; H, 7.68.

Reaction of ((*E*)-1-Phenyl-2-methylvinyl)(chloromethyl)dimethylsilane (13) with $AlCl_3$. A mixture of **13** (0.52 g, 2.3 mmol), $AlCl_3$ (0.078 g, 0.58 mmol), and 15 mL of CS_2 was stirred and heated at reflux for 1 h. The reaction mixture was filtered under vacuum, and a majority of CS_2 was removed by trap-to-trap distillation. The remaining solution was diluted with acetone and centrifuged to precipitate salts. Acetone was removed by trap-to-trap distillation to afford (1-phenyl-2-methylcyclopropyl)dimethylchlorosilane (**17**, 14%) and (*Z*)- and (*E*)-(2-phenyl-3-methylallyl)dimethylchlorosilane (**19**-*Z*, 34%; **19**-*E*, 25%). The stereochemical assignments of **19**-*E* and **19**-*Z* were made solely on the basis of the relative chemical shifts of the single olefinic protons. The analogous (*E*)- and (*Z*)-β-methylstyrenes have olefinic absorptions at δ 6.25 and 5.78, respectively. **17**: ^{1}H NMR ($CDCl_3$) δ 7.06 (m, 5 H), 1.15 (m, 2 H), 0.725 (d, 3 H, J = 6 Hz), 0.534 (t, 1 H), 0.158 (s, 3 H), 0.126 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 139.7, 131.3, 128.0, 125.7, 21.6, 17.8, 15.9, 15.4, 0.39, 0.001; mass spectrum, 226 (2.9), 225 (1.5), 224 (M^+, 8.7), 188 (7.6), 155 (10), 131 (82), 115 (15), 92 (100), 77 (13), 65 (26); calculated for $C_{12}H_{17}SiCl$ 224.07881, measured 224.07904. Anal. Calcd for $C_{12}H_{17}SiCl$: C, 64.11; H, 7.62. Found: C, 64.28; H, 7.72. **19**-*Z*: ^{1}H NMR ($CDCl_3$) δ 7.33 (m, 5 H), 5.78 (q, 1 H, J = 6 Hz), 2.37 (s, 2 H), 1.79 (d, 3 H, J = 6 Hz), 0.22 (s, 6 H); ^{13}C NMR ($CDCl_3$) δ 143.9, 136.0, 128.7, 128.3, 126.8, 126.5, 23.1, 15.0, 2.28; mass spectrum, 226 (2.8), 225 (1.6), 224 (M^+, 8.4), 195 (2.4), 117 (8.5), 93 (100), 77 (6.1), 65 (15); calculated for $C_{12}H_{17}SiCl$ 224.07881, measured 224.07849. Anal. Calcd for $C_{12}H_{17}SiCl$: C, 64.11; H, 7.62. Found: C, 64.48; H, 7.81. **19**-*E*: ^{1}H NMR ($CDCl_3$) δ 7.25 (m, 5 H), 5.51 (q, 1 H, J = 7 Hz), 2.19 (s, 2 H), 1.62 (d, 3 H, J = 7 Hz), 0.19 (s, 6 H); ^{13}C NMR ($CDCl_3$) δ 147.0, 128.7, 128.4, 128.3, 126.8, 126.5, 31.8, 15.0, 1.8; mass spectrum, 226 (2.8), 225 (1.5), 224 (M^+, 8.6), 117 (8.6), 93 (100), 77 (6.6), 65 (16); calculated for $C_{12}H_{17}SiCl$ 224.07881, measured 224.07850. Anal. Calcd for $C_{12}H_{17}SiCl$: C, 64.11; H, 7.62. Found: C, 64.28; H, 7.72.

Synthesis of α-Bromo-β,β-dimethylstyrene. A solution of Br_2 in CS_2 was added dropwise to a stirring solution of β,β-dimethylstyrene[21] (9.8 g, 74 mmol) in 50 mL of CS_2 at −78 °C until an excess of Br_2 had been added. After the mixture was stirred for an additional 2 h at −78 °C and warmed to room temperature, DBU (13 g, 85 mmol) was added dropwise. CS_2 was removed by rotary evaporation, and the remaining residue

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was diluted with ether and extracted with H_2O, 0.1 N HCl, and saturated NaCl. The organic phase was dried over $MgSO_4$, and ether was removed by rotary evaporation. Distillation (50–65 °C, 0.1 torr) afforded 6.1 g (39%) of α-bromo-β,β-dimethylstyrene: ^1H NMR ($CDCl_4$) δ 7.12 (s, 5 H), 1.97 (s, 3 H), 1.65 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 141.3, 133.5, 129.4, 128.2, 127.7, 116.9, 25.3, 22.0; mass spectrum, 212 (24), 210 (M^+, 25), 131 (100), 129 (15), 116 (29), 115 (42), 91 (59); calculated for $C_{10}H_{11}Br$ 210.00441, measured 210.00498.

Synthesis of (1-Phenyl-2,2-dimethylvinyl)(chloromethyl)dimethylsilane (22). To a stirring solution of α-bromo-β,β-dimethylstyrene (6.1 g, 29 mmol) in 100 mL of ether at −23 °C was added 1.92 M *tert*-butyllithium (34 mL, 65 mmol) dropwise. The procedure is essentially that of Seebach.[22] After the mixture was stirred for an additional 2 h at −23 °C, (chloromethyl)dimethylchlorosilane (5.0 mL, 38 mmol) was added, and the solution was allowed to warm to room temperature. The salts were filtered off and the solvent removed by rotary evaporation. Crude **22** (14%) was isolated by distillation (50–70 °C, 0.3 torr). Preparative GC (10 ft × $^1/_4$ in., 15% SE-30, 230 °C) or column chromatography (silica gel/hexane) was used to obtain pure **22**: ^1H NMR (CCl_4) δ 7.20 (m, 5 H), 2.83 (s, 2 H), 2.14 (s, 3 H), 1.70 (s, 3 H), 0.40 (s, 6 H); ^{13}C NMR ($CDCl_3$) δ 147.5, 144.88 134.8, 128.2, 125.3, 31.3, 24.7, 23.3, −2.34; mass spectrum, 240 (4.0), 239 (2.2), 238 (M^+, 12), 189 (75), 135 (100); calculated for $C_{13}H_{19}SiCl$ 238.09446, measured 238.09523. Anal. Calcd for $C_{13}H_{19}SiCl$: C, 65.38; H, 8.02. Found: C, 65.60; H, 8.21.

Reaction of (1-Phenyl-2,2-dimethylvinyl)(chloromethyl)dimethylsilane (22) with $AlCl_3$. A mixture of **22** (2.44 g, 102 mmol) and $AlCl_3$ (0.73 g, 54 mmol) in 100 mL of CS_2 was stirred at reflux for 40 min. Solids were removed by filtration, and CS_2 was stripped off on a rotary evaporator. The remaining residue was diluted with pentane to precipitate the salts, which were then removed by centrifuging. Pentane was stripped off by rotary evaporation to afford clear, orange liquid **24** in 56% yield: ^1H NMR (CCl_4) δ 7.17 (m, 5 H), 2.27 (s, 2 H), 1.87 (s, 3 H), 1.67 (s, 3 H), 0.24 (s, 6 H); ^{13}C NMR ($CDCl_3$) δ 144.1, 129.6, 129.2, 128.0, 126.8, 126.2, 28.1, 22.2, 21.3, 2.36; mass spectrum, 240 (3.1), 239 (1.7), 238 (M^+, 9.2), 145 (14), 129 (33), 93 (100), 77 (7.7), 65 (19); calculated for $C_{13}H_{19}SiCl$ 238.09446, measured 238.09468. Anal. Calcd for $C_{13}H_{19}SiCl$: C, 65.38; H, 8.02. Found: C, 65.53; H, 8.09.

Reaction of (Chloromethyl)dimethylvinylsilane (27) with $AlCl_3$. A mixture of **27** (Petrarch Chemical Co.) (0.60 g, 4.5 mmol), $AlCl_3$ (0.180 g, 1.35 mmol), and 10 mL of CS_2 was stirred and heated at 46 °C for 1.5 h. The mixture was trap-to-trap distilled to afford dimethyldichlorosilane (29%), trimethylchlorosilane (4%), and tetramethylsilane (4%).

Synthesis of Cyclopropyldimethylchlorosilane (28). Cyclopropyldimethylsilane was prepared in a 50% yield from cyclopropyllithium and dimethylchlorosilane by a procedure analogous to that described by Seyferth and Cohen for the synthesis of cyclopropyltrimethylsilane.[23] Cyclopropyldimethylchlorosilane was prepared from cyclopropyldimethylsilane and triphenylmethyl chloride in a 24% yield. The procedure followed was analogous to that described by Corey and West for the synthesis of triphenylsilyl chloride.[24]

Reaction of Cyclopropyldimethylchlorosilane (28) with $AlCl_3$. A mixture of **28** (0.118 g, 0.880 mmol), $AlCl_3$ (0.032 g, 0.24 mmol), and 1 mL of CS_2 was heated at 50 °C in a sealed NMR tube for 7 h and then allowed to stand at room temperature for 14 h. ^1H NMR indicated that no reaction had occurred. The contents of the NMR tube were transferred to a flask, and an additional 0.03 g of $AlCl_3$ was added. Suspension was stirred and heated at reflux for 7 h; however, no reaction was observed by ^1H NMR.

Reaction of Allyldimethylchlorosilane (29) with $AlCl_3$. A mixture of 0.40 g (3.0 mmol) of **29** (Petrarch), $AlCl_3$ (0.117 g, 0.878 mmol), and 10 mL of CS_2 was stirred and heated at 46 °C for 1.5 h. Trap-to-trap distillation afforded starting material and dimethyldichlorosilane (39%). Dimethyldichlorosilane and allyldimethylchlorosilane were identified by comparison with ^1H NMR and mass spectra of authentic samples.

Synthesis of (1-Methylvinyl)(chloromethyl)dimethylsilane (31). To a solution of 2-bromopropene (8.16 g, 67.4 mmol) in 250 mL of ether at −78 °C was added 1.95 M *tert*-butyllithium (69 mL, 130 mmol) dropwise over 2.5 h. After the mixture was stirred for an additional 1 h at −78 °C, the anion was transferred via a double-ended needle to a stirring solution of (chloromethyl)dimethylchlorosilane (10 mL, 76 mmol) in 50 mL of ether at −78 °C. The solvent was removed on a rotary evaporator, and the remaining residue was diluted with hexane and centrifuged to precipitate the salts. Hexane was removed by rotary evaporation, followed by distillation (67 °C, 33 torr), to afford **31** in a 49% yield: ^1H NMR (CCl_4) δ 5.61 (d of t, 1 H), 5.29 (d of t, 1 H), 2.85 (s, 2 H), 1.96 (t, 3 H), 0.42 (s, 6 H); ^{13}C NMR ($CDCl_3$) δ 144.2, 127.1, 29.6, 22.5, −5.20; mass spectrum, 148 (M^+, 0.02), 133 (2.9), 105 (6.1), 99 (100), 93 (17), 79 (24), 73 (80), 59 (26); calculated for $C_6H_{13}SiCl$ 148.04751, measured 148.04817. Anal. Calcd for $C_6H_{13}SiCl$: C, 48.46; H, 8.81. Found: C, 48.55; H, 8.98.

Reaction of (1-Methylvinyl)(chloromethyl)dimethylsilane (31) with $AlCl_3$. A mixture of **31** (0.423 g, 2.86 mmol), $AlCl_3$ (0.105 g, 0.788 mmol), and 10 mL of CS_2 was stirred and heated at reflux for 75 min. Following vacuum filtration, all volatiles were isolated by trap-to-trap distillation. The two products present in the distillate were identified as dimethyldichlorosilane (18%) and (1-methylcyclopropyl)dimethylchlorosilane (**32**, 12%). Both products were isolated by preparative GC (10 ft × $^1/_4$ in., 15% SE-30). **32**: ^1H NMR ($CDCl_3$) δ 1.06 (s, 3 H), 0.56 (m, 4 H), 0.33 (s, 6 H); ^{13}C NMR ($CDCl_3$) δ 20.9, 10.7, 2.5, −0.45; mass spectrum, 150 (1.7), 149 (0.62), 148 (M^+, 5.0), 133 (4.7), 113 (3.7), 105 (13), 93 (100), 79 (18), 65 (26); calculated for $C_6H_{13}SiCl$ 148.04751, measured 148.04791. Anal. Calcd for $C_6H_{13}SiCl$: C, 48.46; H, 8.81. Found: C, 48.33; H, 8.92.

Synthesis of ((Trimethylsilyl)chloromethyl)dimethylchlorosilane. To a stirring solution of (chloromethyl)trimethylsilane (12.4 g, 100 mmol) and 200 mL of THF at −78 °C was added 1.43 M *sec*-butyllithium (71 mL, 100 mmol) dropwise. This procedure is the same as that of Magnus except for the absence of TMEDA.[25] After the mixture was stirred for an additional 2 h, 200 mL of THF was added. The α-silyl carbonion mixture was slowly transferred via a double-tipped needle to a stirring solution of dimethyldichlorosilane (50 mL, 400 mmol) and 200 mL of THF at −78 °C. THF was removed by distillation, and the crude chlorosilane product was also isolated by distillation (43–50 °C, 2 torr). ((Trimethylsilyl)chloromethyl)dimethylchlorosilane (13%) was purified by preparative GC (10 ft × $^1/_4$ in., 15% SE-30): ^1H NMR (CCl_4) δ 2.63 (s, 1 H), 0.66 (s, 3 H), 0.63 (s, 3 H), 0.30 (s, 9 H); mass spectrum, 216 (0.24), 214 (M^+, 0.35), 199 (1.8), 149 (0.82), 106 (19), 73 (100), 59 (31). The spectral data match those previously reported for this compound by Fritz.[26]

Synthesis of (1-Phenylvinyl)((trimethylsilyl)chloromethyl)dimethylsilane (33). To a stirring solution of α-bromostyrene (2.4 g, 13 mmol) and ether (40 mL) at −23 °C was added 1.95 M *tert*-butyl-butyllithium (13.5 mL, 26.3 mmol) dropwise. After being stirred for an additional 1 h, the anion solution was transferred dropwise via a double-tipped needle to a stirring solution of ((trimethylsilyl)chloromethyl)dimethylchlorosilane (2.5 g, 13 mmol) and ether (15 mL) at −23 °C. The mixture was allowed to warm to room temperature, and the solvent was largely removed on a rotary evaporator. The salts were removed by centrifuging and the product isolated by distillation (72–105 °C, 0.15 torr) to afford **33** in a 43% yield. Analytically pure **33** was obtained by column chromatography (silica gel/hexane): ^1H NMR (CCl_4) δ 7.25 (m, 5 H), 5.95 (d, 1 H, J = 3 Hz), 5.73 (d, 1 H, J = 3 Hz), 2.58 (s, 1 H), 0.40 (s, 3 H), 0.34 (s, 3 H), 0.17 (s, 9 H); ^{13}C NMR ($CDCl_3$) δ 151.2, 144.1, 129.5, 128.3, 127.0, 126.6, 35.1 −1.06, −1.98, −2.52; mass spectrum, 282 (M^+, 5.6), 267 (4.2), 231 (13), 174 (38), 161 (100), 145 (25), 135 (51), 103 (28), 73 (73), 65 (33), 59 (37); calculated for $C_{14}H_{23}Si_2Cl$ 282.10269, measured 282.10317. Anal. Calcd for $C_{14}H_{23}SiCl$: C, 59.43; H, 8.19. Found: C, 59.83; H, 8.53.

Reaction of (1-Phenylvinyl)((trimethylsilyl)chloromethyl)dimethylsilane (33) with $AlCl_3$. A mixture of **33** (0.553 g, 1.95 mmol), $AlCl_3$ (0.108 g, 0.810 mmol), and 15 mL of CS_2 was stirred and heated at 46 °C for 10 h. Solid material was removed by filtration under vacuum, and CS_2 was removed by trap-to-trap distillation. The remaining residue was treated with acetone, followed by centrifuging, to precipitate the salts. A 15% yield of (1-phenyl-2-(trimethylsilyl)cyclopropyl)dimethylchlorosilane (**34**) was obtained along with trimethylchlorosilane (17%). Preparative GC (10 ft × $^1/_4$ in., 20% SE-30, 230 °C) was used to isolate pure **34**. **34**: ^1H NMR ($CDCl_3$) δ 7.11 (s, 5 H), 1.08 (d of d, 1 H, J = 4 and 10 Hz), 0.85 (d of d, 1 H, J = 4 and 7 Hz), 0.18 (s, 3 H), 0.13 (s, 3 H), 0.095 (d of d, 1 H, J = 7 and 10 Hz), −0.42 (s, 9 H); ^{13}C NMR ($CDCl_3$) δ 131.0, 130.7, 128.0, 126.0, 21.6, 12.7, 9.7, 0.45, −0.17, −1.40; mass spectrum, 284 (0.06), 282 (0.62), 267 (0.93), 174 (78), 159 (52), 145 (6.2), 135 (23), 93 (17), 73 (100); calculated for $C_{14}H_{23}Si_2Cl$ 282.10269, measured 282.10217. Anal. Calcd for $C_{14}H_{23}Si_2Cl$: C, 59.43; H, 8.19. Found: C, 59.67; H, 8.18.

Synthesis of (1-Bromovinyl)trimethylsilane. Bromine was added dropwise to vinyltrimethylsilane[27] (19.0 g, 190 mmol) with stirring at −78 °C until an excess of bromine was present. Distillation (80 °C, 8 torr) afforded 19.1 g (39% yield) of (1,2-dibromoethyl)trimethylsilane: ^1H

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NMR (CCl_4) δ 3.7 (m, 3 H), 0.43 (s, 9 H). (1-Bromovinyl)trimethylsilane was prepared in a 59% yield from (1,2-dibromoethyl)trimethylsilane and diethylamine according to the procedure of Ottolenghi and co-workers.[27]

Synthesis of ((1-Trimethylsilyl)vinyl)(chloromethyl)dimethylsilane (35). To a solution of 4.30 g (24.1 mmol) of (1-bromovinyl)trimethylsilane and 200 mL of ether at −78 °C was added dropwise 25 mL (49 mmol) of 1.95 M *tert*-butyllithium. After addition of *tert*-butyllithium was completed, stirring at −78 °C was continued for 2 h. The anion solution was transferred via a double-ended needle to a stirring solution of 3.8 mL (29 mmol) of (chloromethyl)dimethylchlorosilane in 20 mL of ether at −78 °C. After being stirred an additional 1 h at −78 °C, the mixture was allowed to warm to room temperature, and the salts were filtered off. Ether and pentane were distilled, and 2.65 g of **35** (49% yield) was isolated by distillation (48–57 °C, 2.2 torr): ^1H NMR (CCl_4) δ 6.73 (s, 2 H), 2.93 (s, 2 H), 0.26 (s, 6 H), 0.15 (s, 9 H); ^{13}C NMR ($CDCl_3$) δ 150.9, 142.4, 30.8, −0.32, −3.4; mass spectrum, 193 (14), 192 (6.2), 191 ($M^+ - CH_3$, 36), 163 (8.3e, 157 (55), 107 (6.9), 97 (24), 83 (49), 73 (100), 59 (34); calculated for $C_8H_{19}Si_2Cl$ 206.07139, measured 206.07169. Anal. Calcd for $C_8H_{19}Si_2Cl$: C, 46.45; H, 9.26. Found: C, 46.15; H, 9.36.

Reaction of ((1-Trimethylsilyl)vinyl)(chloromethyl)dimethylsilane (35) with $AlCl_3$. A mixture of 0.440 g (2.13 mmol of **35**, 0.102 g, (0.765 mmol) of $AlCl_3$, and 15 mL of CS_2 was stirred and heated at reflux for 75 min. The liquid layer was decanted off, and all volatiles were isolated by trap-to-trap distillation (50 °C, 0.5 torr). CS_2 was removed by distillation and ((2-trimethylsilyl allyl)dimethylchlorosilane (**40**, 48% yield) was isolated pure by preparative GC (10 ft × 1/4 in., 15% SE-30, 155 °C): ^1H NMR (CS_2) δ 5.50 (m, 1 H), 5.29 (m, 1 H), 1.89 (m, 2 H), 0.39 (s, 6 H), 0.10 (s, 9 H); ^{13}C NMR ($CDCl_3$) δ 146.9, 125.2, 26.9, 2.15, −1.36; mass spectrum, 208 (1.5), 207 (0.69), 206 (3.5), 191 (34), 165 (10), 151 (5.4), 98 (61), 93 (18), 83 (22), 73 (100), 59 (10); calculated for $C_8H_{19}Si_2Cl$ 206.07139, measured 206.07121. Anal. Calcd for $C_8H_{19}Si_2Cl$: C, 46.45; H, 9.26. Found: C, 46.56; H, 9.40.

Synthesis of (((Chloromethyl)dimethylsilyl)methylene)cyclopropane (41). To a stirring solution of 4.252 g (31.97 mmol) of (bromomethylene)cyclopropane[28] and 100 mL of ether at −23 °C was added 33 mL (64 mmol) of 1.92 M *tert*-butyllithium dropwise. After addition was complete, the mixture was stirred for an additional 2 h at −23 °C and then transferred via a double-ended needle to a stirring solution of (chloromethyl)dimethylchlorosilane (4.54 g, 32.0 mmol) and 100 mL of ether at −23 °C. The mixture was allowed to warm to room temperature, salts were filtered off, and pentane and ether were removed by distillation. The remaining suspension was centrifuged and distilled (30–37 °C, 0.25 torr) to afford **41** in a 39% yield: ^1H NMR (CCl_4) δ 5.90 (m, 1 H), 2.75 (s, 2 H), 1.07 (m, 4 H), 0.24 (s, 6 H); ^{13}C NMR ($CDCl_3$) δ 143.6, 113.0, 30.8, 3.97, 2.93 −3.84; mass spectrum, 147 (1.9), 146 (0.55), 145 ($M^+ - CH_3$, 5.2), 132 (2.6), 117 (8.1), 111 (52), 107 (26), 93 (44), 83 (76), 79 (100), 63 (18), 59 (14), 53 (15); calculated for $C_6H_{10}SiCl$ ($M^+ - CH_3$) 145.02403, measured 145.02373. Anal. Calcd for $C_7H_{13}SiCl$: C, 52.31; H, 8.15. Found: C, 52.36; H, 8.25.

Reaction of (((Chloromethyl)dimethylsilyl)methylene)cyclopropane (41) with $AlCl_3$. A mixture of 0.389 g (2.43 mmole of **41**, 0.116 g (0.872 mmol) of $AlCl_3$, and 30 mL of CS_2 was stirred and heated at reflux for 2 h. The liquid phase was decanted off, and all volatiles were isolated by trap-to-trap distillation. The distillate was composed of CS_2, **44**, **46**, and **48** (from GCMS). A solution of 0.092 g (2.87 mmol) of methanol and 0.226 g (2.87 mmol) of pyridine was added to the distillate and stirred for 8 h. The salts were precipitated out of solution by centrifuging, and CS_2 was removed via distillation to afford a mixture of the methoxysilanes corresponding to **44**, **46**, and **48** in yields of 35%, 1%, and 1%, respectively. Compounds **44**, **46**, and **48** could not be completely separated by preparative GC (8 ft × 1/4 in. 15% SE-30, 135 °C); however, the methoxy derivatives were isolated pure via preparative GC (8 ft × 1/4 in., 15% SE-30, 135 °C). **44**: ^1H NMR ($CDCl_3$) δ 5.75 (m, 1 H), 1.92 (d, 2 H, J = 8 Hz), 1.09 (m, 2 H), 1.00 (m, 2 H), 0.40 (s, 6 H); ^{13}C NMR ($CDCl_3$) δ 122.3, 111.7, 24.2, 3.19, 2.15, 1.50; mass spectrum, 162 (0.41), 161 (0.09), 160 (M^+, 1.4), 145 (1.4), 132 (1.2), 118 (5.1), 109 (4.0), 93 (100), 79 (4.4), 65 (15); calculated for $C_7H_{13}SiCl$ 160.04751, measured 160.04756. **46**: mass spectrum, 145 ($M^+ - CH_3$, 3.3), 132 (7.6), 109 (6.8), 93 (100), 79 (7.7), 75 (45), 65 (16); calculated for $C_7H_{13}SiCl$ 160.04751, measured 160.04778. **48**: ^1H NMR ($CDCl_3$) δ 5.9 (m, 1 H), 5.1 (m, 2 H), 0.78 (m, 2 H), 0.68 (m, 2 H), 0.39 (s, 6 H); ^{13}C NMR ($CDCl_3$) δ 140.1, 115.2, 32.7, 10.3, 0.09; mass spectrum, 162 (0.85), 161 (0.21), 160 (M^+, 2.6), 145 (4.8), 132 (1.5), 124 (2.7), 118 (6.4), 109 (9.7), 93 (100), 79 (7.7), 65 (15); calculated for $C_7H_{13}SiCl$ 160.04751, measured 160.04703. **44**-OME: ^1H NMR ($CDCl_3$) δ 5.74 (m, 1 H), 3.43 (s, 3 H), 1.71 (m, 2 H), 0.98 (m, 4 H), 0.097 (s, 6 H); ^{13}C NMR ($CDCl_3$) δ 120.2, 113.1, 50.5, 21.3, 3.06, 1.94, −2.60; mass spectrum, 156 (M^+, 0.09) 141 (1.1), 126 (0.49), 109 (3.5), 89 (100e, 75 (8.7), 59 (89). Anal. Calcd for $C_8H_{16}SiO$: C, 61.47; H, 10.32. Found: C, 61.69; H, 10.51. **46**-OMe: ^1H NMR ($CDCl_3$) δ 3.42 (s, 3 H), 1.06 (d of d, 1 H, J = 3 and 9 Hz), 0.72 (m, 5 H), 0.26 (d of d, 1 H, J = 6 and 9 Hz), 0.049 (s, 3 H), 0.016 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 50.4, 12.2, 9.7, 6.0, 5.3, 3.6, −3.0, −3.2; mass spectrum, 143 (0.17), 142 (0.95), 141 ($M^+ - CH_3$, 8.4), 113 (12), 109 (5.1), 89 (100), 75 (32), 59 (67). Anal. Calcd for $C_8H_{16}SiO$: C, 61.47; H, 10.32. Found: C, 61.68; H, 10.50. **48**-OMe: ^1H NMR ($CDCl_3$) δ 5.9 (M, 1 H), 5.0 (M, 2 H), 3.46 (s, 3 H), 0.65 (M, 2 H), 0.55 (M, 2 H), 0.06 (s, 6 H); ^{13}C NMR ($CDCl_3$) δ 142.3, 113.4, 50.7, 28.0, 9.7, −4.4; mass spectrum, 156 (M^+, 0.26), 141 (2.6), 126 (0.87), 109 (6.4), 89 (100), 75 (7.9), 59 (62). There was insufficient **48**-OMe for elemental analysis.

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Registry No. 3, 96430-36-3; **5**, 96430-38-5; **6**, 96430-39-6; **10**, 56892-25-2; **11**, 96430-40-9; **13**, 96430-41-0; **17**, 96430-42-1; **19**-*E*, 96430-43-2; **19**-*Z*, 96430-44-3; **22**, 96430-45-4; **24**, 96430-46-5; **27**, 16709-86-7; **28**, 57522-83-5; **29**, 4028-23-3; **31**, 18148-06-6; **32**, 96430-47-6; **33**, 96430-48-7; **34**, 96430-49-8; **35**, 96430-50-1; **40**, 81500-78-9; **41**, 96430-51-2; **44**, 96444-66-5; **44**-OMe, 96430-52-3; **46**, 96430-53-4; **46**-OMe, 96430-54-5; **48**, 96430-55-6; **48**-OMe, 96430-56-7; $AlCl_3$, 7446-70-0; Me_2SiCl_2, 75-78-5; Me_3SiCl, 75-77-4; Me_4Si, 75-76-3; (chloromethyl)dimethylchlorosilane, 1719-57-9; α-bromostyrene, 98-81-7; (1-phenylcyclopropyl)dimethylsilane, 96430-37-4; (*E*)-α-bromo-β-methylstyrene, 31076-47-8; (*Z*)-α-bromo-β-methylstyrene, 31026-78-5; β,β-dimethylstyrene, 768-49-0; α-bromo-β,β-dimethylstyrene, 5912-93-6; cyclopropyldimethylsilane, 57522-87-9; triphenylmethyl chloride, 76-83-5; 2-bromopropene, 557-93-7; ((trimethylsilyl)chloromethyl)dimethylchlorosilane, 18140-01-7; (chloromethyl)trimethylsilane, 2344-80-1; vinyltrimethylsilane, 754-05-2; (1,2-dibromoethyl)trimethylsilane, 18146-08-2; (1-bromovinyl)trimethylsilane, 13683-41-5; (bromomethylene)cyclopropane, 33745-37-8.

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