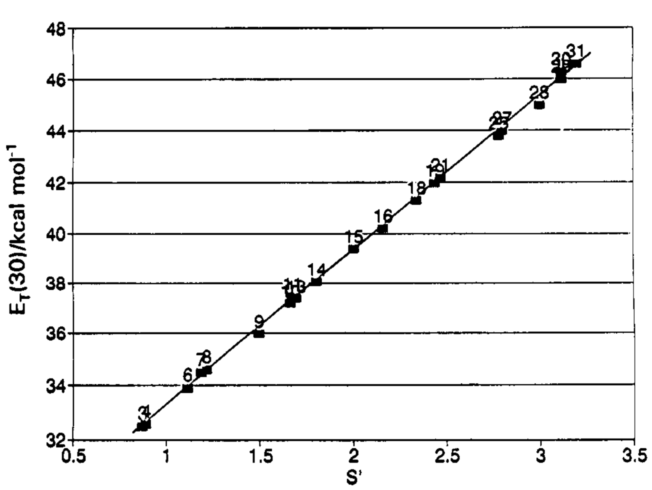

Figure 3. Comparison of the nonspecific solvation parameters, S', with Dimroth–Reichardt's $E_T(30)$ scale (kcal mol^{-1}).

solvents, chlorinated aliphatic solvents, CH_3NO_2, CH_3CN, and $(CH_3)_2CO$ lead to a good correlation of $E_T(30)$ and π^*. The excellent correlation of $E_T(30)$ and S' for all these systems, shown in Figure 3, suggests that the problems lie with π^*.

The β–π^* analysis attributes differences in the β parameters for N-alkyl-3-nitroaniline and 3-nitroaniline to the existence of 2:1 donor–acceptor adducts in the former.[5b,c] If some of the strong donor solvents formed 2:1 complexes with 3-nitroaniline and medium donor-strength solvents did not, the data would not fit E and C. With such a low K for the 1:1 adduct of dioxane and with the large size of *N,N*-dimethylacetamide, it is highly unlikely that any 2:1 adduct would form in these solvents. Furthermore, both the decrease in partial positive charge and probability considerations would lead to a very low K for a 2:1 adduct.

A very significant difference in ECS′ and β–π^* arises in those cases where correlations to β–π^* give rise to family-dependent properties, i.e., different linear plots for C=O, ether, amine, etc. families of compounds. The concept of families is foreign to the EC approach and was shown to occur with β–π^* when the property correlated had larger contributions from covalency than those used to derive the parameters.[19] This was subsequently recognized,[20,21] and an additional term was added to β–π^*. The analysis in this paper suggests this modification of β–π^* will only provide additional opportunity to average in effects not related to specific and nonspecific solvation. The enthalpy-based data set, which includes donors and acceptors of widely varying covalent and electrostatic bonding contributions, fixes the E_B and C_B values and prevents this from happening in E and C analyses. This is evidenced by the fact that the weak donor systems in this article cannot be averaged into $E_A{}^*$ and $C_A{}^*$ for the nitroaniline probes.

In conclusion, the β–π^* and the ECS′ approaches are very different. The wider range of donor–acceptor systems that are accurately correlated in the latter is its main advantage. A broad data base does not permit deviant systems to be averaged in, but identifies them as involving unusual effects. It is hoped that this analysis will stimulate further research to determine which of these two very different interpretations is correct. Is incomplete complexation an incorrect proposal or does the limited data set for β–π^* average in deviant systems introducing errors in the parameters? Using both approaches in data analyses may reveal patterns consistent with those reported here and provide more details about the subtle, important, interesting chemistry occurring in solution.

Registry No. *p*-$NO_2C_6H_4OH$, 100-02-7; *p*-$NO_2C_6H_4NH_2$, 100-01-6; *p*-$NO_2C_6H_4NHMe$, 100-15-2; *p*-$NO_2C_6H_4NHEt$, 3665-80-3; *m*-$NO_2C_6H_4NH_2$, 99-09-2; *m*-$NO_2C_6H_4NHEt$, 4319-19-1; 3,5-$(NO_2)_2C_6H_3NH_2$, 618-87-1.

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Rearrangements of Organosilicon Compounds Using Organoaluminum Reagents. Conversion of Phenyl- and Alkenyl(chloromethyl)silanes to Benzyl- and Allylsilanes

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Received June 16, 1992

Various (chloromethyl)silanes undergo Wagner–Meerwein-type rearrangements using a catalytic amount of $EtAlCl_2$ in dichloromethane. The resulting chlorosilanes have been converted to alkyl(or aryl)silanes with RMgX and/or to fluorosilanes with NH_4HF_2. In this way phenyl-, alkenyl-, and allyl(chloromethyl)silanes were converted to benzyl-, allyl-, and homoallylsilanes, respectively. Attempted rearrangements of methyl-, alkynyl-, and furyl(chloromethyl)silanes under these conditions were not successful.

In general, nucleophilic displacements at silicon in R_3SiX are considerably more facile than those at carbon in RX. We have therefore initiated a program to explore the possibility of making carbon–carbon bonds by first attaching two organic groups (which might be difficult to join by conventional methods) to silicon and forming the carbon–carbon bond in an intramolecular process. The silicon, having served as a template, could subsequently be removed, or used as a site for further useful reactions.

Rearrangements of α-substituted organosilicon com-

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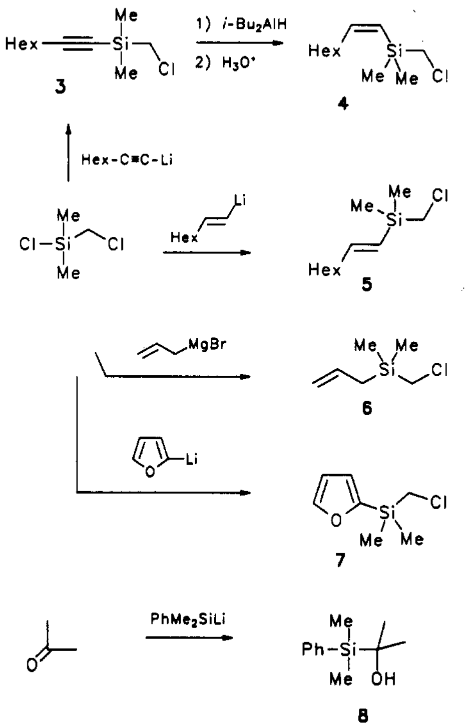
Scheme I



pounds, with migration of an organic group from silicon to carbon, have been known for some time, but have been studied very little from a synthetic point of view.[1] These rearrangements have been found to take place under the influence of acids,[2–5] nucleophiles,[6] and heat.[7] Initially we decided to investigate the scope, limitations, and possible synthetic utility of the acid-induced processes. We have found that rearrangements of some simple (chloromethyl)silanes can be carried out conveniently under mild conditions using a catalytic amount of $EtAlCl_2$ in methylene chloride at room temperature and can be used for the synthesis of some benzyl- and allylsilanes.[8,9]

The acid-induced rearrangements of α-substituted organosilicon compounds are formally analogous to the Wagner–Meerwein rearrangements in carbon systems. The first example, reported by Whitmore and co-workers in 1947,[2a] was the reaction of (chloromethyl)trimethylsilane with $AlCl_3$ to give a product in which a methyl group had migrated from silicon to the adjacent carbon. A number of similar rearrangements of other α-halosilanes have been reported,[2] as well as analogous rearrangements of α-hydroxysilanes[3,4] and isopropenylsilanes.[5]

Rearrangements of α-halosilanes have generally been carried out with strong Lewis acids such as anhydrous $AlCl_3$ or SbF_5. Our initial objectives were to develop milder reaction conditions, and to explore the utility of these reactions in the synthesis of carbon-functional organosilicon compounds. Sublimed aluminum chloride[2h,r–t] has been particularly effective for these rearrangements. Since this is somewhat inconvenient (as well as harsh), our first objective was to investigate other reagents.

As substrates for these reactions, we have used compounds **1**–**8**. $PhMe_2SiCH_2Cl$ (**1**) and Me_3SiCH_2Cl (**2**) are commercially available, and compounds **3**–**8** were prepared as shown in Scheme I. We have studied the reaction of $PhMe_2SiCH_2Cl$ (**1**) with a variety of Lewis acids. In most cases, either no reaction or formation of uncharacterized products was observed.[11] We then studied the use of

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(1) For reviews, see: (a) Eaborn, C. *Organosilicon Compounds*; Butterworths, London, 1960; especially pp 434–439. (b) Bažant, V.; Chvalovský, V.; Rathouský, J. *Organosilicon Compounds*; Academic Press: New York, NY, 1965; Vol. 1, especially pp 325–328. (c) Eaborn, C.; Bott, R. W. In *Organometallic Compounds of the Group IV Elements*; MacDiarmid, A. G., Ed.; Marcel Dekker: New York, NY, 1968; Volume 1 ("The Bond to Carbon"), Part I, pp 105–536, especially pp 443–450. (d) O'Brien, D. H.; Hairston, T. J. *Organomet. Chem. Rev. A* **1971**, *7*, 95–157. (e) Brook, A. G.; Bassindale, A. R. In *Rearrangements in Ground and Excited States*; de Mayo, P., Ed.; Academic Press: New York, NY, 1980; Vol. 2, pp 149–227, especially pp 190–191. For gas-phase experiments, with theoretical discussion and an extensive bibliography, see: (f) Bakhtiar, R.; Holznagel, C. M.; Jacobson, D. B. *J. Am. Chem. Soc.* **1992**, *114*, 3227–3235.

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(5) Isopropenylsilanes: (a) Sommer, L. H.; Evans, F. J. *J. Am. Chem. Soc.* **1954**, *76*, 1186–1187. (b) Kumada, M.; Naka, K.; Ishikawa, M. *J. Organomet. Chem.* **1964**, *2*, 136–145. (c) Kumada, M.; Ishikawa, M.; Maeda, S.; Ikura, K. *J. Organomet. Chem.* **1964**, *2*, 146–153. (d) Hudrlik, P. F.; Kulkarni, A. K. *Tetrahedron Lett.* **1985**, *26*, 1389–1390.

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(7) For leading references, see the following: (a) Bassindale, A. R.; Brook, A. G.; Jones, P. F.; Lennon, J. M. *Can. J. Chem.* **1975**, *53*, 332–337. (b) Larson, G. L.; Klesse, R.; Cartledge, F. K. *Organometallics* **1987**, *6*, 2250–2252. (c) Buynak, J. D.; Strickland, J. B.; Lamb, G. W.; Khasnis, D.; Modi, S.; Williams, D.; Zhang, H. *J. Org. Chem.* **1991**, *56*, 7076–7083.

(8) Portions of this work were presented at the following meetings: (a) Hudrlik, P. F. 19th Organosilicon Symposium, Baton Rouge, Louisiana, April 26, 1985. (b) Hudrlik, P. F.; Abdallah, Y. M.; Hudrlik, A. M. 21st Organosilicon Symposium, McGill University, Montreal, Canada, June 3, 1988.

(9) After this work was substantially complete, Tamao and co-workers[2s] and Barton and co-workers[2t] reported independent studies of rearrangements of alkenyl(chloromethyl)silanes to allylsilanes (and cyclopropylsilanes) using sublimed $AlCl_3$. Allylsilanes have also been prepared from alkynyl(chloromethyl)silanes by hydroalumination followed by in situ treatment with either excess MeLi at room temperature (stereoselective) or Me_3Al in refluxing heptane (isomeric mixtures).[10] Reactions of phenyl-, vinyl-, and allyl(chloromethyl)silanes with sublimed $AlCl_3$ followed by distillation of the reaction mixtures have been reported to give products of Si–C bond cleavage and "resinification" (with small amounts of dimethyl(*o*-tolyl)chlorosilane from $PhMe_2SiCH_2Cl$): Zhun', V. I.; Ustinova, O. L.; Sheludyakov, V. D.; Turkel'taub, G. N.; Slyusarenko, T. F.; Tandura, S. N.; Androsenko, S. I. *J. Gen. Chem. USSR* **1990**, *60*, 986–990.

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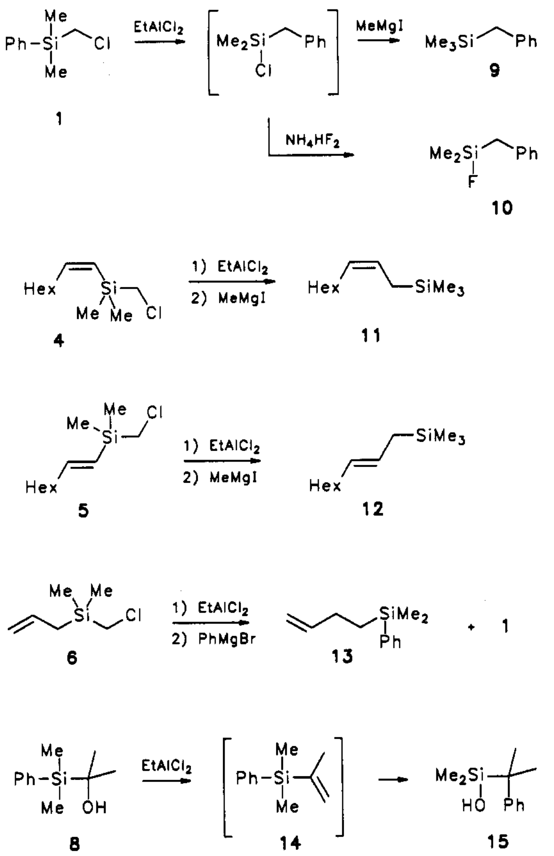
Scheme II



commercially available solutions of organoaluminum reagents.[12] Preliminary experiments using Me_3Al or Me_2AlCl resulted in no reaction. However, treatment of **1** with 1.5 equiv of methylaluminum sesquichloride ($Me_2AlCl{\cdot}Cl_2AlMe$) in toluene at room temperature resulted in the formation of benzyltrimethylsilane (**9**) in 61% yield. This product may be considered to result from the desired rearrangement of phenyl from silicon to carbon followed by alkylation at silicon by the aluminum reagent. Attempts to extend this procedure to the *trans*-alkenyl substrate **5** gave a mixture of uncharacterized products.

We found that the conversion of **1** to **9** could also be carried out by using 0.1 equiv of methylaluminum sesquichloride (as a toluene solution) in methylene chloride at room temperature (giving presumably a chlorosilane) followed by treatment with MeMgI (81% yield). We also found that the rearrangement could be carried out with 0.1 equiv of $EtAlCl_2$ (as a hexanes solution) in methylene chloride (followed by MeMgI, 71% yield). The latter procedure is more convenient since $EtAlCl_2$ is commercially available as a solution in hexanes, while the sesquichloride is available in the higher boiling toluene.[13]

We have treated substrates **2**–**8** with 0.1 equiv of $EtAlCl_2$ in methylene chloride at room temperature. Some of the results are shown in Scheme II. The cis and trans substrates **4** and **5** were transformed (after treatment of the initially formed chlorosilanes with MeMgI) to *cis*- and *trans*-allylsilanes **11** and **12**, respectively, and with essentially complete retention of double bond stereochemistry. The *trans*-allylsilane **12** was formed together with about 20% of another compound believed to be an isomeric cyclopropyl compound (74% total yield) from the NMR spectrum of the mixture and by analogy to the work of Tamao et al.[2s] who found the reaction of **5** with freshly sublimed $AlCl_3$ (followed by MeMgBr) gave a 78:22 mixture of **12** and 1-(trimethylsilyl)-2-hexylcyclopropane. Treatment of the allyl substrate **6** with 0.1 equiv of $EtAlCl_2$ in methylene chloride, followed by PhMgBr led to the homoallylsilane **13**. A minor product (about 20%), shown to be $PhMe_2SiCH_2Cl$ (**1**), was also observed, apparently resulting from cleavage of the allyl group.

Attempts to induce a rearrangement reaction of the alkynyl substrate **3** with $EtAlCl_2$ under a variety of conditions led to no reaction or to uncharacterized products. Attempts to induce a rearrangement of the furyl substrate **7** led to no reaction (0.1 equiv of $EtAlCl_2$/3 days/room temperature) or disappearance of starting material with no products observed (1.0 equiv of $EtAlCl_2$/room temperature/3 h) (both reactions in CH_2Cl_2 with dodecane as internal standard).

We have also briefly investigated the preparation of fluorosilanes by in situ treatment of the initially formed chlorosilanes (from the rearrangements) with NH_4HF_2.[14] Thus treatment of $PhMe_2SiCH_2Cl$ (**1**) with 0.1 equiv of $EtAlCl_2$ in methylene chloride followed by NH_4HF_2 in ether or in DMF led to benzyldimethylfluorosilane (**10**) in 67% and 71% yields, respectively. And in preliminary experiments, the *cis*- and *trans*-vinyl substrates **4** and **5** similarly led to fluorosilanes.

Substrates having a hydroxyl leaving group were also investigated, since such substrates can be readily prepared from addition of a silylmetallic reagent to an aldehyde or ketone,[15] and substrates having the leaving group at a secondary or tertiary center should be easily available. In preliminary experiments, treatment of (1-hydroxyethyl)phenyldimethylsilane with $EtAlCl_2$ led to uncharacterized products. Treatment of the tertiary hydroxy substrate **8** with 0.1 equiv of $EtAlCl_2$ in methylene chloride for 30 min led to no reaction; however, similar treatment with 1.0 equiv of $EtAlCl_2$ for 1 h (followed by aqueous workup) led to rearrangement product **15** in 74% yield. Investigation of the product mixture from a similar reaction after only 15 min at room temperature revealed the presence of phenyl(isopropenyl)dimethylsilane (**14**), product of dehydration.[16]

In these rearrangement reactions, the migratory aptitudes of phenyl, alkenyl, and allyl appear (not surprisingly) to be greater than that of methyl.[17] We have also studied the reaction of Me_3SiCH_2Cl (**2**) with $EtAlCl_2$ to see if methyl would migrate if there was no competition from better migrating groups. Treatment of **2** with $EtAlCl_2$ in methylene chloride (either 0.1 equiv or 1.0 equiv, with decane as internal standard) showed no reaction after 2 days at room temperature.

The lack of reactivity of the furyl substrate **7** to conditions which caused rearrangement of the analogous phenyl substrate (**1**) is interesting and may be due to complexation of the Lewis acid at the furyl oxygen. A

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[11] Among those tried were $BF_3{\cdot}Et_2O$, $SnCl_4$, $TiCl_4$ (in both CCl_4 and CH_2Cl_2), $SbCl_5/CH_2Cl_2$, and various silver salts in CH_2Cl_2, MeCN, or $MeNO_2$. (We also tried $AlCl_3$ from a freshly opened bottle.)

[12] Alkylaluminum halides are Lewis acids which are also Brønsted bases, and thus remove water or HCl. For a discussion, see: Snider, B. B.; Rodini, D. J.; Karras, M.; Kirk, T. C.; Deutsch, E. A.; Cordova, R.; Price, R. T. *Tetrahedron* 1981, *37*, 3927–3934.

[13] Some reactions using toluene as a solvent gave mixtures of products. Snider and co-workers[12] advise against using toluene because of the possibility of Friedel–Crafts reactions.

[14] For the use of NH_4HF_2 for the preparation of fluorosilanes from silyl sulfates, see refs 5b and 5c.

[15] For leading references to the preparation of α-hydroxysilanes, see ref 1c (pp 180–187) and ref 3b.

[16] Brook and co-workers (ref 3b) found that $Ph_3Si(CHOHMe)$ failed to react with BF_3, and that $Ph_3Si(CMe_2OH)$ underwent dehydration.

[17] Migratory aptitudes are discussed in refs 1f, 2c, 2g, 2h, 2k, 2n, 4a, 5c, 6b, and 7c.

similar lack of reactivity in Lewis acid-promoted rearrangement reactions in substrates having heteroatoms such as O or N, was observed by Corey and co-workers.[2q,r,6a] The fact that the dehydration product **14** is at least in part an intermediate in the rearrangement reaction of the tertiary hydroxy substrate **8** suggests that further rearrangement and loss of stereochemistry might result in more complicated systems. It is, however, particularly noteworthy that (1) the reagents used to induce the rearrangements are easily handled and commercially available and (2) allylsilanes were prepared in high stereochemical purity from vinylsilanes. Many methods have been reported for preparing stereochemically pure vinylsilanes,[18] and allylsilanes are of considerable synthetic importance.[19,20]

Rearrangements of groups from silicon to carbon are also known to occur under nucleophilic conditions. We have found that rearrangements of this type can be used to overcome some of the limitations of the acid-promoted process, and this work will be the subject of future reports.

Experimental Section

General. All reactions were carried out under nitrogen or argon. The verb "concentrated" refers to removal of solvent using a rotary evaporator. Kugelrohr distillation refers to bulb-to-bulb distillation in a Kugelrohr apparatus; the temperature following in parentheses refers to the oven temperature. GC (gas chromatography) analyses were carried out on Hewlett-Packard 5880 or Varian Aerograph model 90P instruments; in some cases, the retention time of a hydrocarbon standard under the given conditions is included. Proton NMR spectra were obtained on Hitachi Perkin-Elmer R-600 (60 MHz), Nicolet NT-200 (200 MHz), or General Electric QE-300 (300 MHz) spectrometers. The spectra were referenced to CH_2Cl_2 (δ 5.30) for compounds with aromatic hydrogens and to $CHCl_3$ (δ 7.26) for other compounds. Mass spectra were obtained on a Finnigan MAT 4500 GC/mass spectrometer. High-resolution mass spectra (HRMS) were determined by the Midwest Center for Mass Spectrometry, University of Nebraska.

Anhydrous ether was distilled from sodium/benzophenone. Methylene chloride was distilled from calcium hydride.

(Chloromethyl)dimethylchlorosilane and phenyl(chloromethyl)dimethylsilane (**1**) were purchased from Petrarch Systems (now Hüls America, Inc). Solutions or organoaluminum compounds were purchased from Aldrich Chemical Co.

1-Octynyl(chloromethyl)dimethylsilane (**3**) was prepared by treatment of 1-octyne with *n*-BuLi followed by $ClMe_2SiCH_2Cl$, and (*Z*)-1-octenyl(chloromethyl)dimethylsilane (**4**) was prepared by reduction of **3** with *i*-Bu_2AlH, in procedures similar to those in refs 2s and 10.[21] (*E*)-1-Octenyl(chloromethyl)dimethylsilane (**5**) was prepared by treatment of (*E*)-1-octenyl iodide[18b] with *tert*-butyllithium followed by $ClMe_2SiCH_2Cl$ in a procedure similar to that of ref 2s. Allyl(chloromethyl)dimethylsilane (**6**) was prepared from $ClMe_2SiCH_2Cl$ and allylmagnesium bromide.[22] Phenyl(1-hydroxy-1-methylethyl)dimethylsilane (**8**) was prepared from (phenyldimethylsilyl)lithium and acetone.[23] A comparison sample of phenyl(isopropenyl)dimethylsilane (**14**) was prepared by treatment of phenyldimethylchlorosilane with isopropenylmagnesium bromide.[24]

2-Furyl(chloromethyl)dimethylsilane (7). To 1.5 g (22 mmol) of furan in 30 mL of anhydrous ether was added dropwise 10 mL (19.4 mmol) of *n*-BuLi (1.94 M in hexanes). The resulting mixture was stirred for 3 h at room temperature and then added *via* cannula to an ice cooled solution of 2.0 g (14 mmol) of $ClMe_2SiCH_2Cl$ in 20 mL of anhydrous ether. The resulting mixture was stirred for 2 h at 0 °C and then worked up by slow addition of saturated aqueous $NaHCO_3$. The aqueous layer was extracted with ether, and the combined organic layers dried ($MgSO_4$), concentrated, and distilled (bp 50–55 °C, 35 mm) to give 1.76 g (72% yield) of **7** as a colorless liquid: IR (film) 2965, 1552, 1455, 1254, 1008, 818, 749 cm^{-1}; NMR ($CDCl_3$, 300 MHz) δ 0.41 (s), 2.96 (s, CH_2Cl), 6.42 (m), 6.76 (m), 7.68 (m), and small peaks at 0.22 (s), 0.54 (s), and 2.75 (s) (impurity); mass spectrum *m/z* (tentative assignment, relative intensity) 176 ($M^+[^{37}Cl]$, 3.6), 174 ($M^+[^{35}Cl]$, 8.2), 161 ($[M - Me]^+[^{37}Cl]$, 0.1), 159 ($[M - Me]^+[^{35}Cl]$, 0.4), 139 ($[M - Cl]^+$, 0.4), 125 ($[M - CH_2Cl]^+$, 100); HRMS calcd for $C_7H_{11}OSiCl$ 174.0268, found 174.0265. GC analysis[25a] showed one single peak at 4.48 min.

Conversion of Phenyl(chloromethyl)dimethylsilane (1) to Benzyltrimethylsilane (9). To 0.3 g (1.62 mmol) of $PhMe_2SiCH_2Cl$ (**1**) in 20 mL of methylene chloride was added 0.17 mL (0.17 mmol) of $EtAlCl_2$ (1.0 M in hexanes), and the resulting mixture was stirred for 20 min at room temperature. The mixture was then cooled in ice, a solution of methylmagnesium iodide in ether (from 0.5 g MeI, 20 mL ether, and 0.15 g Mg) was added, and the resulting mixture was stirred for 1 h at 0 °C and 1 h at room temperature. The mixture was cooled to 0 °C, saturated aqueous NH_4Cl was added, and the aqueous layer was extracted twice with ether. The combined organic layers were dried ($MgSO_4$) and concentrated. Kugelrohr distillation (65–70 °C, 7 mm) gave 0.19 g (71% yield) of **9** as a colorless liquid. GC analysis[25a] showed one single peak at 4.89 min. The IR and NMR spectra and GC retention time were essentially identical to those of a commercial sample of benzyltrimethylsilane.

Conversion of (*Z*)-1-Octenyl(chloromethyl)dimethylsilane (4) to (*Z*)-2-Nonenyltrimethylsilane (11). To 0.188 g (0.86 mmol) of (*Z*)-1-octenyl(chloromethyl)dimethylsilane (**4**) (containing ≤4% *E* isomer **5** by GC) in 2 mL of methylene chloride was added 0.09 mL (0.09 mmol) of $EtAlCl_2$ (1.0 M in hexanes). The resulting mixture was stirred for 30 min at room temperature. A solution of 10 mL of methylmagnesium iodide in ether (from 3.5 g MeI, 25 mL ether, 0.6 g Mg) was added, and the resulting mixture was heated at reflux for 2 h. The mixture was cooled to room temperature and added to cooled saturated aqueous NH_4Cl and ether. The aqueous layer was extracted twice with ether, and the combined organic layers were washed ($NaHCO_3$), dried ($MgSO_4$), and concentrated. Kugelrohr distillation (70–80 °C), oil pump vacuum) gave 0.105 g (61.6% yield) of **11** as a colorless liquid: IR (film) 2958, 2928, 1249, 854 cm^{-1}. The NMR spectrum was equivalent to that reported[10b,26] for this compound. GC analysis[25a] ($C_{12}H_{26}$ = 6.87 min) showed peaks at 7.25 min (4.1%, **12**) and 7.43 min (95.9%, **11**). The GC/mass spectrum showed a major and minor peak in the GC having very similar mass spectra differing only slightly in peak intensities. The mass spectrum of the major peak showed *m/z* (tentative assignment, relative intensity) 198 (M^+, 7.3), 183 ($[M - Me]^+$, 1.7), 99 (2.3), 73 (Me_3Si^+, 100).

Conversion of (*E*)-1-Octenyl(chloromethyl)dimethylsilane (5) to (*E*)-2-Nonenyltrimethylsilane (12). To a solution of 0.208 g (0.95 mmol) of (*E*)-1-octenyl(chloromethyl)dimethylsilane (**5**) in 2 mL of methylene chloride was added 0.1 mL (0.1 mmol) of $EtAlCl_2$ (1.0 M in hexanes), and the resulting mixture was stirred for 30 min at room temperature. A solution of 20 mL of methylmagnesium iodide in ether (from 7.2 g of MeI, 50 mL of ether, and 2.0 g of Mg) was added, and the resulting mixture was

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[18] For leading references, see: (a) Chan, T. H.; Fleming, I. *Synthesis* 1979, 761–786. (b) Hudrlik, P. F.; Kulkarni, A. K.; Jain, S.; Hudrlik, A. M. *Tetrahedron* 1983, *39*, 877–882.

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[20] Furthermore, as Tamao and co-workers have demonstrated,[2s] halosilanes can be readily oxidized to alcohols.

[21] We carried out the *i*-Bu_2AlH reduction in ether and obtained a mixture of **4** and the corresponding Me_3Si compound from which a pure sample of **4** was obtained by distillation (see also ref 2s). Utimoto and co-workers[10b] carried out the same reduction in heptane and obtained a good yield of the chloromethyl compound **4**.

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[25] (a) GC analysis was carried out on the Hewlett-Packard instrument, using a 25-m cross-linked polymethyldisiloxane capillary column with the following temperature program: 50 °C for 1 min, then 10 °C/min to 250 °C, and 250 °C for 5 min. (b) GC analysis was carried out on the Varian instrument at 100 °C, using a 10-ft × 0.25-in. aluminum column packed with 10% SE-30 on 60/80 mesh Chromosorb W.

[26] Another NMR spectrum reported[2s] for **11** is not equivalent to ours.

stirred at room temperature for 1 h and at reflux for 2 h. The reaction mixture was added to saturated aqueous NH_4Cl and ether, and the aqueous layer was extracted twice with ether. The combined organic layers were washed ($NaHCO_3$), dried ($MgSO_4$), and concentrated. Kugelrohr distillation (60–70 °C, oil pump vacuum) gave 0.14 g (74% yield as **12**) of a colorless liquid having an IR spectrum consistent with that reported[10b] for **12**. The NMR spectrum ($CDCl_3$, 200 MHz) contained the peaks reported[2a,10b] for **12** and in addition small peaks from δ –0.08 to +0.35 and a very small broad peak centered about –0.7 (may be due to a cyclopropyl compound; see ref 2a) and 2.75 (m, probable impurity). GC analysis[25a] ($C_{12}H_{26}$ = 6.87 min) showed the major peaks at 6.92 min (19%) and 7.25 min (73%); under these conditions, the cis compound (**11**) came at 7.43 min; <3% was visible. The mass spectrum of the major peak (**12**) in the GC of the GC/mass spectrum showed *m/z* (tentative assignment, relative intensity) 198 (M^+, 8.2), 183 ($[M - Me]^+$, 1.4), 99 (2.2), 73 (Me_3Si^+, 100). The mass spectrum of the second largest peak (tentatively assigned as a cyclopropylsilane) showed 198 (M^+, not visible), 183 ($[M - Me]^+$, 0.6), 99 (3.1), 85 (2.2), 73 (Me_3Si^+, 100).

Conversion of Allyl(chloromethyl)dimethylsilane (6) to Phenyl(homoallyl)dimethylsilane (13) and Phenyl(chloromethyl)dimethylsilane (1). To 1.0 g (6.7 mmol) of allyl(chloromethyl)dimethylsilane (**6**) in 15 mL of methylene chloride was added 0.7 mL (0.7 mmol) of $EtAlCl_2$ (1.0 M in hexanes), and the resulting mixture was stirred at room temperature for 30 min. The reaction mixture was cooled in ice, and 25 mL of PhMgBr in ether (from 6.28 g of bromobenzene, 40 mL of ether, and 1.2 g of Mg) was added. The resulting mixture was heated at reflux for 3 h, cooled, and added to ice-cooled 20% NH_4Cl. The aqueous layer was extracted with ether; the combined organic layers were washed ($NaHCO_3$), dried ($MgSO_4$), and concentrated. Kugelrohr distillation (80–90 °C, 1 mm) followed by chromatography (to remove biphenyl) on 30 g of silica gel (petroleum ether) gave 0.86 g of a mixture of **13**[27] and **1** as a colorless liquid. GC analysis[25a] ($C_{12}H_{26}$ = 6.75 min) showed the major peaks at 7.20 min (17.3%, **1**), 7.74 min (70.3%, **13**), and 8.90 min (6.5%, PhPh). The NMR spectrum ($CDCl_3$), 60 MHz) showed δ 0.31 (s, SiMe of **13**), 0.45 (s, SiMe of **1**), m centered at 0.94 (CH_2Si of **13**), m centered at 2.11 (allyl), 2.99 (s, CH_2Cl), 4.85, 5.03, and 5.16 (terminal vinyl, appearing as three multiplets), 5.81 (center of multiplet, internal proton of vinyl), 7.46 (m, Ph). The GC/MS showed three peaks in the GC, assigned as compound **1**, compound **13** [*m/z* (tentative assignment, relative intensity) 190 (M^+, 6.8), 175 ($[M - Me]^+$, 14.2), 162 (12.2), 149 ($[M - allyl]^+$, 3.5), 135 ($PhMe_2Si^+$, 100), 121 ($PhMeSiH^+$, 22.7), 105 ($C_6H_5Si^+$, 9.4)], and biphenyl.

Conversion of Phenyl(1-hydroxy-1-methylethyl)dimethylsilane (8) to (1-Phenyl-1-methylethyl)dimethylsilanol (15). To 0.5 g (2.6 mmol) of silyl alcohol **8** in 20 mL of methylene chloride was added 2.6 mL (2.6 mmol) of $EtAlCl_2$ (1.0 M in hexanes), and the resulting mixture was stirred 1 h at room temperature. Saturated aqueous $NaHCO_3$ and ether were added, the aqueous layer was extracted twice with ether, and the combined organic layers were dried ($MgSO_4$), concentrated, and Kugelrohr distilled (85–90 °C, 0.7 mm), giving 0.37 g (74% yield) of **15** as a yellowish liquid: IR (film) 3340, 2963, 2867, 1601, 1494, 1473, 1254, 855, 828, 780, 699 cm^{-1}; NMR ($CDCl_3$, 60 MHz) δ 0.04 (s, 6 H), 1.41 (s, 6 H), 1.66 (small m which disappears upon addition of D_2O, 1 H), 7.28 (br s, 5 H) plus 1.0–1.4 (impurity, 3 H); mass spectrum *m/z* (tentative assignment, relative intensity) 194 (M^+, 16.5), 179 ($[M - Me]^+$, 0.7), 137 ($PhMeSiOH^+$, 2.8), 118 (13.5), 103 (1.9), 91 ($C_7H_7^+$, 6.3), 75 (Me_2SiOH^+, 100); HRMS calcd for $C_{11}H_{18}OSi$ 194.1127, found 194.1135. GC analysis[25a] showed a single peak at 8.31 min.

In a similar experiment [97 mg (0.5 mmol) of **8**, 2 mL of methylene chloride, 0.5 mL (0.5 mmol) of $EtAlCl_2$ (1.0 M in hexanes), 15 min at room temperature] the GC analysis[25a] showed a major peak at 6.20 min (24%), identified as phenyl(isopropenyl)dimethylsilane (**14**) by comparison of IR, NMR, GC, and GC/MS of the product mixture with those of an authentic sample of **14**.[24]

Conversion of Phenyl(chloromethyl)dimethylsilane (1) to Benzyldimethylfluorosilane (10). To 925 mg (5.01 mmol) of phenyl(chloromethyl)dimethylsilane (**1**) in 10 mL of methylene chloride was added 0.5 mL (0.5 mmol) of $EtAlCl_2$ (1.0 M in hexanes), and the resulting mixture was stirred at room temperature for 30 min. Then 20 mL of anhydrous ether was added, followed by 1.425 g (25 mmol) of NH_4HF_2, and the resulting mixture was stirred at room temperature for 2 h. Water (10 mL) was added, and the aqueous layer was extracted twice with ether. The combined organic layers were washed ($NaHCO_3$), dried ($MgSO_4$), concentrated, and Kugelrohr distilled (75–80 °C, oil pump vacuum) to furnish 562 mg (67% yield) of **10** as a colorless liquid. The IR[28] and NMR[29] spectra were equivalent to those reported. GC analysis[25b] ($C_{10}H_{22}$ = 1.7 min) showed the major peak at 2.0 min (94%).

In a similar reaction using DMF/NH_4HF_2 (0.36 mL, 2 mmol) of $PhMe_2SiCH_2Cl$, 4 mL of CH_2Cl_2, 0.2 mL (0.2 mmol) of $EtAlCl_2$ (1.0 M in hexanes), 30 min/room temperature; followed by 10 mL of DMF and 575 mg (10 mmol) of NH_4HF_2, ca. 18 h/room temperature), fluorosilane **10** was obtained in 71% yield.

Acknowledgment. We thank the National Science Foundation (CHE-8607561 and CHE-9007879) and NIGMS (SO6GM08016) for support of this work. We also thank the National Science Foundation (RII-8804636) for financial support for the purchase of a 300-MHz NMR spectrometer.

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