Heteroatom Chemistry
Volume 5, Number 3, 1994

Rearrangements of (Chloromethyl)organylsilanes Induced by Lewis Acids or by Lewis Bases: Regioselective Methylenation of Allylic Systems

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Received 9 March 1994

ABSTRACT

In order to study the scope and mechanisms of the migration of organyl groups from silicon to its adjacent methylene carbon, a series of derivatives of the type $R–SiMe_2–CH_2–Cl$ *were synthesized, where R is vinyl, benzyl, methallyl, phenylethynyl, aryloxy, and N-methylanilino. Attempts were then undertaken to induce such Si → C shifts by either the Lewis acid, methylaluminum dichloride, or the Lewis base, potassium fluoride. Under Lewis acidic conditions, only the benzyl and methylallyl groups could be induced to migrate; clearly, in the case of benzyl (and probably in the case of methallyl), migration was accompanied by allylic rearrangement to produce the o-tolyl group. Under the agency of KF, all the groups investigated underwent rearrangement to produce* $F–SiMe_2–CH_2–R$*. By a crossover experiment, it was shown that, when R = aryloxy, the rearrangement occurs intermolecularly. Experimental evidence indicates that all KF-induced migrations are probably intermolecular and all* $MeAlCl_2$*-induced migrations considered here are intramolecular. The advantages for organosilicon synthesis of utilizing so-called "relay substitution reactions" with the* $Cl–SiR_2–CH_2–Cl$ *system are discussed:*

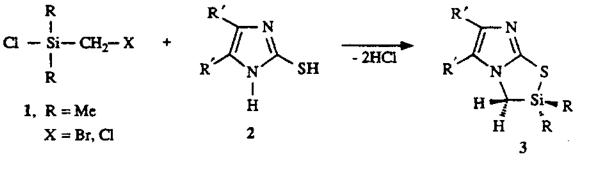
$$Cl–SiR_2–CH_2Cl \xrightarrow[-Cl]{Nu} Nu–SiR_2–CH_2Cl$$

$$\xrightarrow[\text{or } KF]{MeAlCl_2} X–SiR_2–CH_2–Nu$$

With unsymmetrical allylic systems, regioselective methylenation now becomes possible, simply by inducing the Si → C rearrangement by $MeAlCl_2$ *or by KF.*

INTRODUCTION

Halomethyl(diorganyl)silyl chlorides (**1**) are versatile intermediates in organosilicon synthesis, because both the silicon and the methylene carbon centers are prone to nucleophilic attack. Such dual reactivity is reflected, for example, in the formation of *sila*-substituted nitrogen heterocycles (**3**) from 2-mercaptoimidazoles (**2**, Equation 1) [1]. Yet a further advantage for synthesis is the greater reactivity of the silicon-chlorine



Dedicated to Prof. Adrian Gibbs Brook on the occasion of his seventieth birthday.

Part 19 of *Organosilicon Compounds with Functional Groups Proximate to Silicon*. These data were taken from the doctoral dissertation of C.S. Chiu, SUNY-Binghamton, 1990. Previous part: J.J. Eisch and C.S. Chiu, *J. Organomet. Chem., 358*, 1988, C1.

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bond, which permits highly selective nucleophilic substitution at silicon, as exemplified by the preparatively useful conversions in Equations 2 and 3 [2,3]. Finally, such products of kinetically controlled nucleophilic substitution, **4** and **5**, can be induced under thermodynamic control to transfer their substituent from silicon to methylene carbon by either Lewis acids (Equation 4 [4]) or Lewis bases (Equation 5 [5]).

$$\underset{\mathbf{4}}{\mathrm{Ph_3Si{-}CH_2{-}Cl}} \xleftarrow[\substack{\text{eq. 2}\\ \mathrm{R{=}Cl}}]{\mathrm{3PhMgBr}} \underset{\mathbf{1}}{\mathrm{Cl{-}SiR_2{-}CH_2{-}Cl}}$$

$$\xrightarrow[\substack{\text{eq. 3}\\ \mathrm{R{=}Me}}]{\mathrm{PhOH}} \underset{\mathbf{5}}{\mathrm{PhO{-}SiMe_2{-}CH_2{-}Cl}}$$

$$\underset{\mathbf{4}}{\mathrm{Ph_3Si{-}CH_2{-}Cl}} \xrightarrow{\mathrm{MeAlCl_2}} \underset{\mathbf{6}}{\mathrm{Cl{-}SiPh_2{-}CH_2{-}Ph}} \qquad (4)$$

$$\underset{\mathbf{5}}{\mathrm{PhO{-}SiMe_2{-}CH_2{-}Cl}} \xrightarrow{\mathrm{KF}} \underset{\mathbf{7}}{\mathrm{F{-}SiMe_2{-}CH_2{-}OPh}} \qquad (5)$$

Such successive substitution reactions at silicon and its adjacent carbon, as embodied by the reaction pairs, Equations 2 + 4 and Equations 3 + 5, can be termed *relay substitution reactions of organosilanes*. The nucleophilic version of such relay substitution reactions (Equation 5) has been utilized by us for preparing either the Si-substituted or the C-substituted aryloxy and arylamino derivatives from chloromethyl(diorganyl)silyl chlorides (**1**, R = Me, Equations 6 and 7) [3]. The electrophilic relay substitution (Equation 4) has been found to be particularly readily induced by MeAlCl$_2$, a Lewis acid freely soluble both in halocarbons and in hydrocarbons [6].

$$\underset{\mathbf{1},\ \mathrm{R\,=\,Me}}{\mathrm{Cl{-}SiMe_2{-}CH_2{-}Cl}} \xrightarrow[\substack{\text{eq. 6}\\ \mathrm{E\,=\,O,\,NR}}]{\mathrm{ArEH}}$$

$$\mathrm{ArE{-}SiMe_2{-}CH_2{-}Cl} \xrightarrow[\text{eq. 7}]{\mathrm{KF}} \mathrm{F{-}SiMe_2{-}CH_2{-}EAr}$$

In the present study, a series of Si-substituted triorganylsilylmethyl chlorides, R′–SiMe$_2$–CH$_2$Cl (**8**), have been prepared by the kinetically controlled attack of various nucleophiles on Cl–Si-Me$_2$CH$_2$–Cl. These derivatives were then treated, alternatively, with the Lewis acid, methylaluminum dichloride (**9**), or the Lewis base, potassium fluoride (**10**) to learn the following: (1) whether the substituent R′ could be transferred to the adjacent methylene carbon; (2) whether R′ would undergo any intragroup rearrangement; and (3) whether such 1,2 silicon-carbon shifts involved intramolecular or intermolecular pathways (Equations 8 and 9). Because extensive studies of such rearrangements of **8** have already been reported, where R′ is vinylic [4], aryl [4a], and alkyl [5a], we have chosen to examine neglected or little studied [4a] examples of **8**, where R′ is allylic, benzylic, 1-alkynyl, aryloxy, and arylamino. In so doing, we have found that there are significant advantages for organic synthesis in inducing such Si → C shifts by MeAlCl$_2$ or by KF.

$$\underset{\mathbf{10}}{\mathrm{Cl{-}SiMe_2{-}CH_2{-}R'}} \xleftarrow[\text{eq. 8}]{\mathrm{MeAlCl_2}} \underset{\mathbf{8}}{\mathrm{R'{-}SiMe_2{-}CH_2{-}Cl}}$$

$$\xrightarrow[\text{eq. 9}]{\mathrm{KF}} \underset{\mathbf{9}}{\mathrm{F{-}SiMe_2{-}CH_2{-}R'}}$$

RESULTS

Preparation of Triorganylsilylmethyl Chlorides, R–SiMe$_2$–CH$_2$–Cl (**8**)

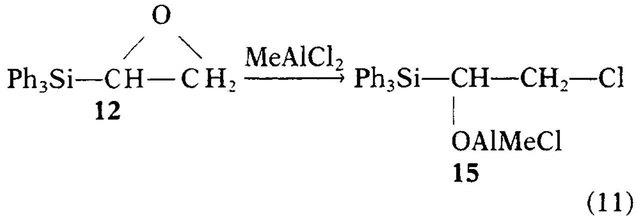
Benzyl(chloromethyl)dimethylsilane (**8a**), chloromethyl(dimethyl)(2-methyl-2-propenyl) silane (**8b**) and chloromethyl(dimethyl)(phenylethynyl)silane (**8c**) were prepared from ClSiMe$_2$CH$_2$Cl and the corresponding RMgX or RLi in 70–90% yield. Similarly, chloromethyl(triphenyl)silane (**11**) was produced from Cl$_3$SiCH$_2$Cl and PhMgBr in over 80% yield. Chloromethyl(dimethyl)phenoxysilane (**8d**) and chloromethyl(diethyl)(*p*-tolyloxy)silane (**8e**) (Me = Et) resulted in 70–90% yields from heating phenol with ClSiMe$_2$CH$_2$Cl and *p*-cresol with ClSiEt$_2$CH$_2$Cl, respectively. Likewise, heating ClSiMe$_2$CH$_2$Cl with N-methylaniline or with KF produced 85% of chloromethyl(dimethyl)(N-methylanilino)silane (**8f**) or 45% of chloromethyl(fluoro)dimethylsilane (**8g**), respectively.

Rearrangement Reactions of R–SiMe$_2$–CH$_2$–Cl Derivatives (**8**)

Nucleophilic relay substitutions of **8** were achieved with KF in refluxing acetonitrile. The resulting rearranged product **9**, F–SiMe$_2$–CH$_2$R′, was alkylated with MeMgBr to yield the hydrolytically stable **10**, Me$_3$Si–CH$_2$–R′ [4].

Electrophilic relay substitution with MeAlCl$_2$ was developed through studies of the rearrangement behavior of Ph$_3$Si–CH$_2$–Cl (**11**) and of epoxyethyl(triphenyl)silane (**12**). As hoped, **11** rearranged smoothly to **13** (Equation 10), but **12** cleaved to give, not the desired rearrangement precursor, Ph$_3$Si–CHCl–CH$_2$OAlMeCl (**14**), but its regioisomer **15** (Equation 11).

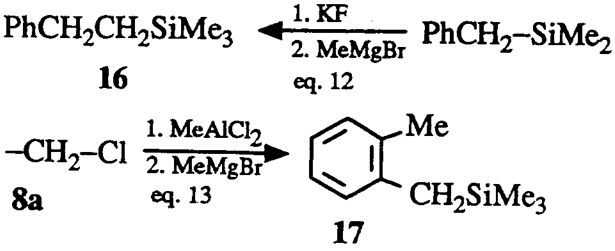
$$\underset{\mathbf{11}}{\mathrm{Ph_3Si{-}CH_2{-}Cl}} \xrightarrow{\mathrm{MeAlCl_2}} \underset{\mathbf{13}}{\mathrm{Cl{-}SiPh_2{-}CH_2{-}Ph}} \qquad (10)$$



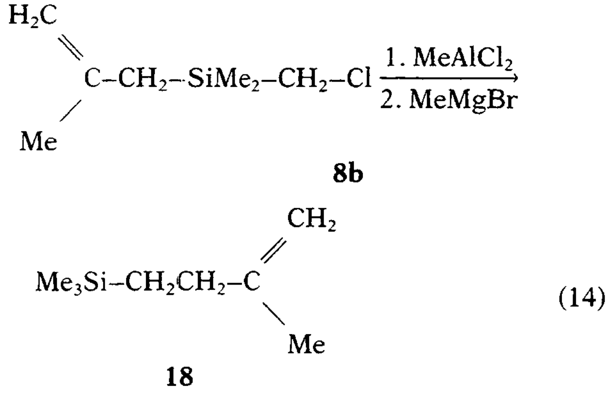
$$\underset{\mathbf{12}}{Ph_3Si{-}CH{-}CH_2}\ (\text{epoxide}) \xrightarrow{MeAlCl_2} \underset{\mathbf{15}}{Ph_3Si{-}CH(OAlMeCl){-}CH_2{-}Cl} \qquad (11)$$

In working up other $MeAlCl_2$-promoted rearrangements, the products $Cl{-}SiMe_2{-}CH_2R'$, were methylated with MeMgBr, just as in the KF-promoted rearrangements.

Benzyl(chloromethyl)dimethylsilane (**8a**). The $MeAlCl_2$- and KF-promoted reactions of **8a** selectively produced two isomeric rearrangement products **16** and **17** in moderate to good yield [7a] (Equations 12 and 13). The identity of **17** was corroborated by comparing its spectral properties with those of an authentic sample and by base-promoted hydrolysis to *o*-xylene.



Chloromethyl(dimethyl)(2-methyl-2-propenyl)silane (**8b**). The reaction with $MeAlCl_2$ (or with KF) formed the same rearrangement product **18** in 45% yield (Equation 14).



Chloromethyl(dimethyl)(phenylethynyl)silane (**8c**). Attempted rearrangement of **8c** with $MeAlCl_2$, under a variety of conditions, led only to brown tars, presumably resulting from cationic polymerizations [7b]. The action of KF on **8c**, however, definitely caused rearrangement, but the resulting propargylic silane (**19**) underwent KF cleavage (Equation 15) to yield the acetylene **20**.

$$\underset{\mathbf{8c}}{Ph{-}C{\equiv}C{-}SiMe_2{-}CH_2{-}Cl} \xrightarrow[2.\ MeMgBr]{1.\ KF} \underset{\mathbf{19}}{[Me_3Si{-}CH_2{-}C{\equiv}C{-}Ph]} \xrightarrow[HS]{KF} \underset{\mathbf{20}}{Me{-}C{\equiv}C{-}Ph} \qquad (15)$$

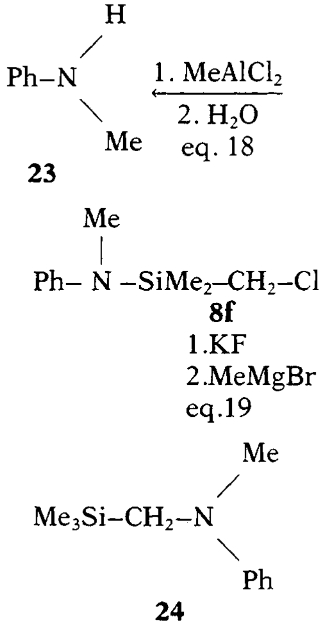
Chloromethyl(dimethyl)phenoxysilane (**8d**). This compound underwent almost complete cleavage to phenol (**21**) with $MeAlCl_2$ but rearranged smoothly with KF in acetonitrile (Equations 16 and 17):

$$\underset{\mathbf{21}}{Ph{-}OH} \xleftarrow[2.\ H_2O]{1.\ MeAlCl_2} \text{eq. 16}$$

$$\underset{\mathbf{8d}}{Ph{-}O{-}SiMe_2{-}CH_2{-}Cl} \xrightarrow[2.\ MeMgBr]{1.\ KF} \text{eq. 17}$$

$$\underset{\mathbf{22}}{Me_3Si{-}CH_2{-}O{-}Ph}$$

Chloromethyl(dimethyl)(N-methylanilino)silane (**8f**). Similarly, **8f** was cleaved without rearrangement by $MeAlCl_2$ to yield N-methylaniline upon hydrolysis, whereas KF gave the expected rearrangement in high conversion (Equations 18 and 19):



Crossover Experiment between Chloromethyl(dimethyl)phenoxysilane (**8d**) *and Chloromethyl(diethyl)(p-tolyloxy)silane* (**8e**) *with Potassium Fluoride.* In preliminary studies, it was shown that **8e** rearranged with KF in acetonitrile to give, after MeMgBr treatment, diethyl(methyl)(*p*-tolyloxymethyl)silane (**25**). Furthermore, heating **8d** and **8e** in refluxing acetonitrile did not lead to exchange of aryloxy groups.

With these results in hand, it is significant that heating **8d** and **8e** with KCN in acetonitrile leads to comparable amounts of all four possible products, **22**, **25**, **26**, and **27** (Scheme 1). From these findings, it can be concluded that the F-anion displaces an aryloxide ion from **8d** and **8e**, which then attacks the methylene carbon intermolecularly. There is thus no evidence of direct, intramolecular aryloxide anion transfer from silicon to carbon (Scheme 1).

Controlled, Direct Nucleophilic Attack on the Methylene Carbon of (1)

By converting Cl–SiMe$_2$–CH$_2$–Cl (**1**) into F–SiMe$_2$–CH$_2$–Cl (**28**), the initial nucleophilic attack by KOPh at silicon was circumvented and direct attack at carbon realized. Intermediate **28** can be produced in a separate step or can be generated by adding KF to a mixture of **1** and phenol (Scheme 2).

Behavior of Chloromethyl(dimethyl)vinylsilane (29) *and Allyl(chloro)dimethylsilane* (30) *with MeAlCl$_2$*

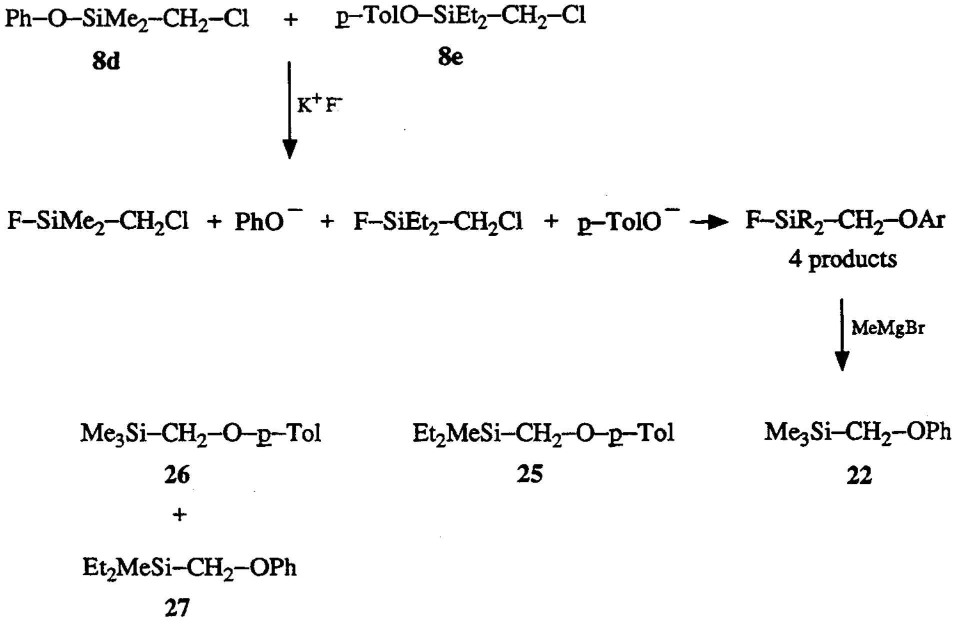
As in previous work [4b], **29** with MeAlCl$_2$ should produce **30**. We find that both compounds produce Me$_2$SiCl$_2$ and polymeric materials. It is likely that aluminum-silicon exchange [8a] yields Me$_2$SiCl$_2$ and vinyl- or allyl-aluminum compounds that undergo polymerization [7b].

DISCUSSION

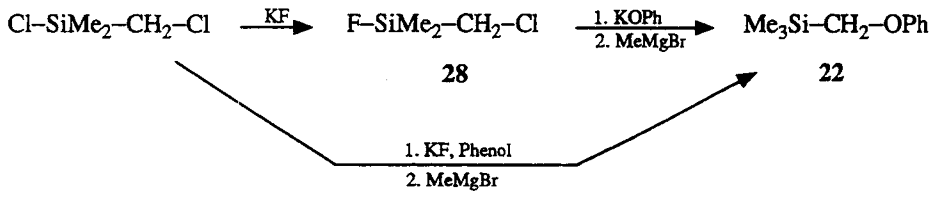
It is clear that a wide variety of groups, encompassing alkyl, vinyl, allyl, 1-alkynyl, aryl, benzyl, aryloxy, and amino, can be induced to rearrange from silicon to carbon in the (chloromethyl)-organylsilane system (**1**), under the agency of Lewis acids, Lewis bases, or both. Furthermore, the mode of group rearrangement can lead to isomeric products when a Lewis acid or Lewis base is employed. The behavior of benzyl(chloromethyl)-dimethylsilane (**8a**) provides a striking example (Equations 12 and 13). It is proposed that **17** is formed by the intramolecular cyclization of complex **31**, whereas **16** results from an intermolecular attack of the PhCH$_2^-$ anion on intermediate **32** (Scheme 3). Support for the intermolecular pathway for the nucleophilic relay substitution, **8a** → **33**, is the finding of crossover products in similar rearrangements of aryloxysilanes **8d** and **8e**. Similarly, support for the intramolecular nature of the electrophilic relay substitution, **8a** → **34**, comes from the specific *ortho*-alkylation of the ring. If an intermolecular pathway were involved, then some *para*-alkylation leading to isomers of **34** would result [8b].

In accord with this interpretation of the mechanism for the rearrangement of **8a**, it is most likely that chloromethyl(dimethyl)(2-methyl-2-propenyl)silane (8b) undergoes allylic migration to yield **18** via a similar cyclic mechanism.

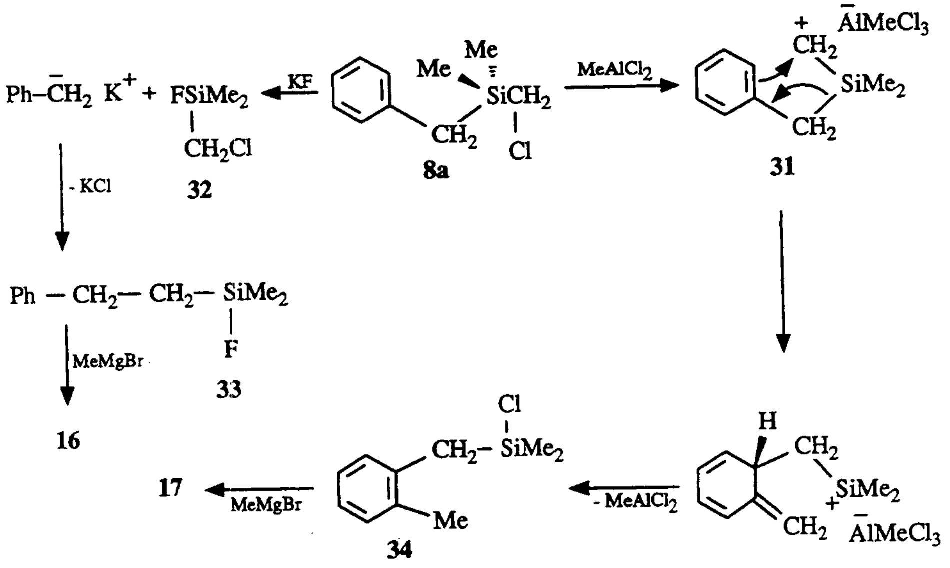
In general, we suggest that all the nucleophilic



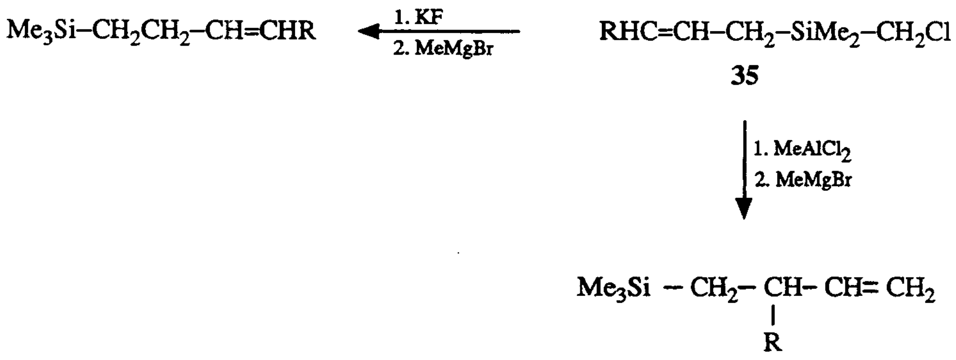
SCHEME 1



SCHEME 2



SCHEME 3



SCHEME 4

relay substitutions reported here occur intermolecularly. The anions involved, benzyl, allylic, 2-phenylethynyl, aryloxy, and arylamino (E^-), therefore, have the possibility of attacking the solvent and being partly destroyed (Equation 20).

$$E^- + CH_3\text{–}C{\equiv}N \rightarrow E\text{–}H + {}^-CH_2\text{–}C{\equiv}N \qquad (20)$$

Such solvent attack may explain the lower yields of rearrangement products in nucleophilic relay substitution.

Aside from the other preparative advantages uncovered by this study, the behavior of the benzylic derivative **8a** shows how unsymmetrical allylic derivatives of **1**, namely, **35**, can be selectively methylenated, simply by employing $MeAlCl_2$ or KF for the rearrangement (Scheme 4).

EXPERIMENTAL

All solvent purification and all preparations or reactions involving organometallic reagents or halosilanes were conducted under an atmosphere of anhydrous, oxygen-free nitrogen or argon in accordance with established procedures [9].

The commercially available trichloro(chloromethyl)silane and chloro(chloromethyl)dimethylsilane, trichloro(vinyl)silane (Petrarch), and methylaluminum dichloride (in hexane, Aldrich) were used as received. Trichloro(vinyl)silane was first converted into triphenyl(vinyl)silane, and this, in turn, epoxidized to produce epoxyethyl(triphenylsilane) [10] by known methods. For the preparation of the various chloromethyl(triorganyl)silanes employed here, chloro(chloromethyl)dimethylsilane was treated with the Grignard reagents formed from benzyl chloride or 3-chloro-2-methylpropene or, in the case of preparing $Ph{-}C{\equiv}C{-}SiMe_2CH_2Cl$, with phenylethynyllithium. To obtain the derivatives $ArO{-}SiR_2CH_2Cl$ and $ArNMe{-}SiR_2CH_2Cl$, the $Cl{-}SiMe_2CH_2Cl$ was treated with ArOH and a tertiary amine or with ArNMeH, respectively. Illustrative preparative procedures are given subsequently, as well as complete ^1H NMR, IR, and MS data for all such derivatives. Only for unusual reaction products were elemental analyses also obtained.

The GC analyses were performed on a Hewlett–Packard instrument, model 5880A; the IR spectra were determined with a Perkin–Elmer grating spectrophotometer, model 1420; the MS spectra were measured by an MS/902 CIS-2 mass spectrometer with a V6 Datasystem 2040 computerized recorder, and the ^1H NMR spectra were measured with a Bruker AM360 spectrometer. Elemental analyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, NY.

Preparation of Chloromethyl(triorganyl)silanes

Chloromethyl(triphenyl)silane (**11**) A Grignard solution was prepared from 39.2 g (0.5 mol) of bromobenzene and 9.1 g (0.38 g atom) of magnesium turnings in 300 mL of anhydrous THF and filtered from the remaining magnesium. To such a solution, cooled and stirred at 0°C, was slowly added a solution of 11.0 g (60 mmol) of Cl_3SiCH_2Cl in 100 mL of dry THF. The reaction mixture was heated at reflux for 24 hours and then hydrolyzed with 200 mL of saturated, aqueous NH_4Cl and 400 mL of ether. The separated organic layer was dried over anhydrous $MgSO_4$ and concentrated by rotary evaporation. The crude product was purified by column chromatography on silica gel and elution effected with a hexane-CH_2Cl_2 mixture (1 : 1, v/v). The colorless product (**11**) provided 10.1 g (81%) upon recrystallization from ethanol, mp 112.5–114°C (Ref. [2], 113–114°C). ^1H NMR ($CDCl_3$): 3.48 (s, 2H), 7.01–7.63 (m, 15H); MS (*m/e*): 308 (M^+), 259 ($M{-}CH_2Cl$), 231 (M–Ph).

Benzyl(chloromethyl)dimethylsilane (**8a**). In a manner similar to the foregoing procedure, the reaction of 0.25 mol of benzylmagnesium chloride with 0.15 mol of $Cl{-}SiMe_2CH_2Cl$ in THF gave, after column chromatography and fractional distillation, a 73% yield of **8a**, bp 241–243°C, at 760 mm Hg. ^1H NMR ($CDCl_3$): 0.09 (s, 6H), 2.21 (s, 2H), 2.72 (s, 2H), 7.01–7.37 (m, 5H); IR (neat): 1610, 1500, 1255, 1180, 840, 695 cm^{-1}; MS (*m/e*): 200 ($^{37}Cl{-}M^+$), 198 ($^{35}Cl{-}M^+$), 183 (M–Me), 149 ($M{-}CH_2Cl$), 107 ($M{-}CH_2Ph$), 91 ($PhCH_2$), 49 (CH_2Cl).

Chloromethyl(dimethyl)(2-methyl-2-propenyl)silane (**8b**). Similarly, the reaction of 0.25 mol of methallylmagnesium chloride with 0.20 mol of $Cl{-}SiMe_2CH_2Cl$ in THF gave, after fractional distillation, 87% of **8b**, bp 160–162°C, at 760 mm Hg. ^1H NMR ($CDCl_3$): 0.15 (s, 6H), 1.67 (s, 2H), 1.73 (s, 3H), 2.80 (s, 2H), 4.58 (broad d, 2H); IR (neat): 1650, 1255, 1170, 875, 845, 745 cm^{-1}; MS (*m/e*): 164 ($^{37}Cl{-}M^+$), 162 ($^{35}Cl{-}M^+$), 113 ($M{-}CH_2Cl$), 107 ($M{-}C_4H_7$), 55 (C_4H_7), 49 (CH_2Cl).

Chloromethyl(dimethyl)(phenylethynyl)silane (**8c**). Similarly, except that $Ph{-}C{\equiv}C{-}Li$ was employed (generated from *n*-butyllithium and phenylacetylene), the reaction of 0.18 mol of $Ph{-}C{\equiv}C{-}Li$ with 0.15 mol of $Cl{-}SiMe_2CH_2Cl$ in diethyl ether gave, after column chromatography and fractional distillation, 87% of **8c**, bp 82–84°C, at 0.25 mm Hg. ^1H NMR ($CDCl_3$): 0.36 (s, 6H), 2.92 (s, 2H), 7.26–7.48 (m, 5H); IR (neat): 2160, 1605, 1495, 1255, 1180, 840, 815, 755, 685 cm^{-1}; MS (*m/e*): 210 ($^{37}Cl{-}M^+$), 208 ($^{35}Cl{-}M^+$), 159 ($M{-}CH_2Cl$), 107 ($M{-}C_2Ph$), 101 (PhC_2), 49 (CH_2Cl).

Chloromethyl(dimethyl)phenoxysilane (**8d**). A mixture of 0.27 mol of phenol and 0.37 mol of $Cl{-}SiMe_2CH_2Cl$ was heated and stirred at reflux for 24 hours under an atmosphere of dry nitrogen (evolved HCl gas was withdrawn through the nitrogen manifold system). Fractional distillation of the resulting mixture yielded 89% of **9d**, bp 228–230°C, at 760 mm Hg. ^1H NMR ($CDCl_3$) 0.36 (s, 6H), 2.88 (s, 2H), 6.84–7.24 (m, 5H); IR (neat): 1605, 1495, 1255, 1170, 1025, 1005, 920, 825, 760, 690 cm^{-1}. MS (*m/e*): 202 ($^{37}Cl{-}M^+$), 200 ($^{35}Cl{-}M^+$), 151 ($M{-}CH_2Cl$), 107 (M–OPh), 93 (PhO), 49 (CH_2Cl).

Chloromethyl(diethyl)(p-tolyloxy)silane (**8e**). This compound was required for the crossover experiment involving **8d** (*qv*). It was prepared in a manner completely analogous to the foregoing, namely, heating $Cl{-}SiEt_2CH_2Cl$ with *p*-cresol, to produce 67% of **8e**, bp 80–82°C, at 0.20 mm Hg. ^1H NMR ($CDCl_3$) 0.88 (q, 4H), 1.04 (t, 6H), 2.27 (s, 3H), 2.95 (s, 2H), 6.76–7.04 (m, 4H); IR (neat): 1620, 1515, 1255, 1170, 1105, 1010, 910, 820, 800, 770, 690 cm^{-1}; MS (*m/e*); 244 ($^{37}Cl{-}M^+$), 242 ($^{37}Cl{-}M^+$), 213 (M–Et), 193 ($M{-}CH_2Cl$), 135 ($M{-}OC_7H_7$), 107 (OC_7H_7).

The requisite Cl–SiEt$_2$CH$_2$Cl was prepared by treating Cl$_3$SiCH$_2$Cl in diethyl ether with two molar equivalents of EtMgBr in ether at 0°C. The ether was then removed under a nitrogen atmosphere and at reduced pressure. The residual mixture was treated directly with *p*-cresol and heated.

Chloromethyl(dimethyl)(N-methylanilinos)silane (**8f**). A mixture of 0.30 mol of freshly distilled N-methylaniline and 0.15 mol of Cl–SiMe$_2$CH$_2$Cl was stirred and heated for 8 hours at 80°C. A precipitation of colorless needles developed during this heating. The cooled suspension was filtered under a dry nitrogen atmosphere, and the resulting filtrate was subjected to fractional distillation. After a forerun of Cl–SiMe$_2$CH$_2$Cl and N-methylaniline, a 75% yield of **8f** was obtained, bp 94–96°C, at 0.20 mm Hg. ^{1}H NMR (CDCl$_3$): 0.34 (s, 6H), 2.90 (s, 3H), 3.05 (s, 2H), 6.43–7.23 (m, 5H); IR (neat): 1605, 1510, 1365, 1255, 1195, 1060, 835, 805, 745, 690 cm^{-1}.

Chloromethyl(fluoro)dimethylsilane (**8g**). Although not a chloromethyl(triorgany)silane, **8g** was prepared in a similar manner. A cooled charge of 0.23 mol of Cl–SiMe$_2$CH$_2$Cl was stirred at 0°C while 0.25 mol of carefully dried and finely powdered KF was *slowly* dusted into the liquid (*Caution*: considerable heat is evolved). After the addition, the reaction mixture was stirred at 25°C for 18 hours. The organic product was taken up in anhydrous diethyl ether and filtered from the suspended solid. Fractional distillation gave 45% of **8g**, bp 84–85°C, at 760 mm Hg (Ref. [11], 84.5°C). By GC analysis, it was at least 99% pure. ^{1}H NMR (CDCl$_3$): 0.37 (d, 6H, J_{H-F} 7.2 Hz), 2.85 (d, 2H, J_{H-F} 3.1 Hz); MS (*m/e*): 128 (^{37}Cl–M$^+$), 126 (^{37}Cl–M$^+$), 111 (M–Me), 107, (M–F), 77 (M–CH$_2$Cl), 47 (SiF).

Reactions with Methylaluminum Dichloride

General Procedure. The reactions with methylaluminum dichloride were carried out in three-necked flasks under a nitrogen atmosphere. Such reaction vessels (100–250 mL) were stirred magnetically and the necks provided with a rubber septum, sometimes an addition funnel, and a reflux condenser. In some cases, a chlorosilane, Cl-SiR$_3$, resulting from rearrangement was treated directly with MeMgBr to produce MeSiR$_3$ and facilitate isolation of a stable derivative [4].

Chloromethyl(triphenylsilane) (**11**). The reaction of 4.4 mmol of **11** with 1.3 mmol of MeAlCl$_2$ in 20 mL of CH$_2$Cl$_2$ was allowed to occur at 25°C over 24 hours. Hydrolysis of the reaction mixture with 40 mL of saturated, aqueous NH$_4$Cl, separation and drying of the organic layer over anhydrous MgSO$_4$, and evaporation of the solvent gave 78% of the crude benzyl(diphenyl)silanol. Even after column chromatography and repeated recrystallizations, no sharp melting point could be obtained. The product is likely contaminated with the disiloxane (Ref. [12], mp 51.5–53°C, 154–155°C). ^{1}H NMR (CDCl$_3$): 2.58 (s, 2H), 6.40–7.50 (m, 16H); IR (neat): 3300 cm^{-1} (broad H-bonded OH); MS (*m/e*): 290 (M$^+$), 213 (M–Ph), 199 (M–CH$_2$Ph).

Benzyl(chloromethyl)dimethylsilane (**8a**). A solution of 40.3 mmol of **8a** and 12.1 mmol of MeAlCl$_2$ in 200 mL of CH$_2$Cl$_2$ was stirred at 25°C for 3 hours. Then 9.6 of dried, powdered NaCl was added (to complex with MeAlCl$_2$), and stirring was continued for 2 hours. The suspension was filtered under nitrogen, and the filtrate was subjected to fractional distillation. A 45% yield of chloro(dimethyl)(*o*-tolylmethyl)silane was collected, bp 227–228°C, at 760 mm Hg. ^{1}H NMR (CDCl$_3$): 0.40 (s, 6H), 2.37 (s, 3H), 2.47 (s, 2H), 6.98–7.30 (m, 4H); MS (*m/e*): 200 (^{37}Cl–M$^+$), 198 (^{35}Cl–M$^+$), 183 (M–Me), 163 (M–Cl), 105 (CH$_2$C$_6$H$_4$CH$_3$), 93 (M–CH$_2$C$_6$H$_4$CH$_3$), 63 (SiCl).

The isolated product (2.4 g, 12 mmol) was dissolved in 60 mL of diethyl ether and treated slowly with 43 mmol of MeMgBr in 15 mL of ether. After stirring for 8 hours at 25°C, the usual hydrolytic workup (cf., *supra*) and column chromatography gave 75% of trimethyl(*o*-tolylmethyl)silane (**17**) as a colorless oil. ^{1}H NMR (CDCl$_3$): 0 (s, 9H), 2.09 (s, 2H), 2.22 (s, 3H), 6.94–7.10 (m, 4H); IR (neat): 1615, 1395, 1260, 850, 775, 745, 720, 690 cm^{-1}. MS (*m/e*): 178 (M$^+$), 163 (M–Me), 105 (CH$_2$C$_6$H$_4$CH$_3$), 73 (Me$_3$Si). A sample of **17** was heated for 24 hours in a solution of KOH in methanol. Hydrolytic workup of the reaction mixture, addition of ether, and GC analysis of the separated and dried organic layer showed that **17** had been consumed and a xylene formed. The xylene was purified by bulb-to-bulb distillation and, by its IR spectrum, was shown to be only *o*-xylene.

Finally, an authentic sample of trimethyl(*o*-tolylmethyl)silane (**17**) was prepared from *o*-methylbenzylmagnesium chloride and chloro(trimethyl)silane in THF and isolated, in the usual manner in 86% yield, bp 212–214°C, at 760 mm Hg. The ^{1}H NMR, IR, and MS spectra of this sample were identical with those of the sample derived from the rearrangement of **8a**.

Chloromethyl(dimethyl)(2-methyl-2-propenyl)silane (**8b**). A similar interaction of 30 mmol of **8b** and 8.7 mmol of MeAlCl$_2$ in 120 mL of hexane was allowed to run for 15 hours at 25°C. Then 60 mL of dry ether and 75 mmol of MeMgBr were introduced, and the resulting mixture was stirred for 24 hours at 25°C. Usual hydrolytic workup and fractional distillation of the crude product gave 45% of trimethyl(3-methyl-3-butenyl)silane (**18**), bp 130–132°C at 760 mm Hg (Ref. [12], 135°C at 750 mm). ^{1}H NMR (CDCl$_3$): 0 (s, 9H), 0.47–2.30 (m, 7H), 4.68 (br, 2H); IR (neat): 1655, 1250, 860, 845, 755, 690 cm^{-1}; MS (*m/e*): 142 (M$^+$), 127 (M–Me), 87 (M–C_4H_7), 73 (Me_3Si), 69 (C_5H_9), 55 (C_4H_7).

Chloromethyl (dimethyl) (phenylethynyl) silane (**8c**). Solutions of 24 mmol of **8c** in hexane were prepared in various concentrations and were admixed slowly with 7 mmol of $MeAlCl_2$, either order of addition being attempted. A sticky, pale brown gum deposited on the wall of the flask. In all cases, however, after a 24 hour reaction period and the addition of an excess of MeMgBr in ether, workup did not provide any rearrangement product or its methylated derivative. Only about 50% of **8c** could be recovered.

Epoxyethyl(triphenylsilane) (**12**). A hexane solution of 13 mmol of $MeAlCl_2$ was added slowly at 0°C to a solution of 9.9 mmol of **12** in 90 mL of CH_2Cl_2. After 2 hours, the mixture was brought to 25°C and stirred for 8 hours. The reaction mixture was worked up with aqueous NH_4Cl solution in the usual way, and the crude product was chromatographed on silica gel (CH_2Cl_2 as eluent) to give 80% of (1-hydroxy-2-chlorethyl)(triphenyl)silane ((**15**), as $AlMe_2$ salt) which melted at 111–111.5°C after recrystallization from hexane (Ref. [13], 110–111°C). ^{1}H NMR ($CDCl_3$): 2.22 (broad 1H), 3.93 (dd, 1H), 4.07 (dd, 1H), 4.27 (dd, 1H), 7.34–7.64 (m, 15H); IR (neat): 3300 cm^{-1} (broad H-bonded OH); MS (*m/e*): 261 (^{37}Cl M–Ph), 259 (^{35}Cl M–Ph). Anal. calcd. for $C_{20}H_{19}ClOSi$: C, 70.88; H, 5.65. Found: C, 70.57; H, 5.73.

Chloromethyl(dimethyl)phenoxysilane (**8d**). A solution of 16 mmol of **8d** and 40 mmol of $MeAlCl_2$ in 100 mL of CH_2Cl_2 was stirred at 25°C for 4 hours. Thereupon, 12.4 g of powdered NaCl was added, and stirring was continued for 8 hours. The suspension was then filtered under dry nitrogen, and the filtrate was treated with 120 mmol of ethereal MeMgBr. After stirring for 8 hours and usual hydrolytic workup, a 94% yield of slightly impure phenol was isolated. No trace of trimethyl(phenoxymethyl)silane (**22**) was observed.

Chloromethyl(dimethyl)vinylsilane (**29**). Treatment of 20 mmol of **29** with 6 mmol of $MeAlCl_2$ in 40 mL of hexanes yielded only brown suspensions. The usual workup with aqueous NH_4Cl led to dark brown sludges and gave no sign of rearrangement products, such as $H_2C{=}CHCH_2SiMe_2OH$. There are indications that the expected product, $H_2C{=}CHCH_2SiMe_2Cl$, would be further cleaved by $MeAlCl_2$ (cf., *infra*).

Allyl(chloro)dimethylsilane (**30**). A solution of 13 mmol of **30** and 13 mmol of $MeAlCl_2$ in a hexane-CH_2Cl_2 mixture turned into a brown suspension when stirred for 24 hours at 25°C. Hydrolysis led to dark, intractable material.

Reactions with Potassium Fluoride

General Procedure. As with the $MeAlCl_2$ reactions, the potassium fluoride reactions required a similar apparatus and were conducted under anhydrous, oxygen-free conditions, that is, under a nitrogen atmosphere and with scrupulously dried KF and acetonitrile. Such precautions are necessary, because F$^-$ attack on Si generates strong bases, such as $PhCH_2^-$ or PhO^-, which could easily be protonated before they rearrange. The lower yields in these rearrangements probably are the result of protonations not by accidental H_2O but by the fairly acidic methyl group of CH_3CN.

Benzyl(chloromethyl)dimethylsilane (**8a**). A mixture of 27 mmol of **8a** and 83 mmol of powdered KF was heated in 60 mL of acetonitrile for 72 hours, cooled and then filtered under nitrogen. The filtrate was freed of solvent in vacuo, and the residual liquid was treated with 60 mL of dry ether and then with 75 mmol of ethereal MeMgBr. After having been allowed to stand at 25°C for 24 hours, the reaction mixture was hydrolytically worked up in the usual way. The resulting crude product was separated on silica-gel column with hexanes to give 29% of pure trimethyl(2-phenylethyl)silane (**16**). ^{1}H NMR ($CDCL_3$): 0 (s, 9H), 0.86 (t, 2H), 2.61 (t, 2H), 7.15–7.28 (m, 5H); IR (neat): 1615, 1505, 1255, 869, 840, 750, 695 cm^{-1}; MS (*m/e*): 178 (M$^+$), 163 (M–Me), 105 ($PhCH_2CH_2$), 91 ($PhCH_2$), 87 (M-CH_2Ph), 73 (Me_3Si).

Chloromethyl(dimethyl)(phenylethynyl)silane (**8c**). Similarly, the reaction of 32 mmol of **8c** and 96 mmol of KF in 60 mL of acetonitrile and subsequent treatment of the acetonitrile-free residue with ethereal MeMgBr gave, upon hydrolytic workup and fractional distillation, a 35% yield of methyl(phenyl)acetylene, (**20**), bp 181–182°C, at 760 mm Hg. It was unambiguously identified by comparing its ^{1}H NMR and IR spectra with those of an authentic sample. Undoubtedly, the volatility of **20** was responsible for significant losses during the reaction procedures.

Chloromethyl(dimethyl)phenoxysilane (**8d**). Similarly, the reaction of 30 mmol of **8d** and 90 mmol of KF in 60 mL of acetonitrile and the usual aftertreatment with ethereal MeMgBr gave, upon column chromatographic separation, 58% of trimethyl(phenoxymethyl)silane (**22**). ^{1}H NMR ($CDCl_3$): 0.16 (s, 9H), 3.56 (2H), 6.89–7.29 (m, 5H); IR (neat): 1610, 1595, 1500, 1435, 1170, 1030, 1015, 850, 750, 705, 685 cm^{-1}; MS (*m/e*): 180 (M$^+$), 165 (M–Me), 107 (CH_2OPh), 73 (Me_3Si).

Chloromethyl(diethyl)(p-tolyloxy)silane (**8e**). Similarly, from 15 mmol of **8e** and 45 mmol of KF in 60 mL of acetonitrile were obtained 59% diethyl(methyl)(p-tolyloxymethyl)silane (**25**). ^{1}H NMR ($CDCl_3$): 0.07 (s, 3H), 0.66 (q, 4H), 0.99 (t, 6H), 2.27 (s, 3H), 3.58 (s, 2H), 6.83–7.06 (m, 4H); IR (neat): 1620, 1595, 1515, 1440, 1280, 1230, 1015, 800 cm^{-1}; MS (*m/e*): 222 (M^+), 207 (M–Me), 193 (M–Et), 121 ($CH_2OC_6H_4CH_3$), 101 ($M-CH_2OC_6H_4CH_3$).

Chloromethyl(dimethyl) (N-methylanilino) silane (**8f**). Similarly, from 40 mmol of **8f** and 120 mmol of KF in 60 mL of acetonitrile were obtained, after the usual workup and fractional distillation, 68% of trimethyl(N-methylanilino)silane (**24**), bp 69–72°C, at 0.20 mm Hg. ^{1}H NMR ($CDCl_3$): 0.09 (s, 9H), 2.75 (s, 2H), 2.81 (s, 3H), 6.25–7.21 (m, 5H); IR (neat): 1605, 1510, 1365, 1250, 1195, 1035, 990, 850, 745, 690 cm^{-1}. MS (*m/e*): 193 (M^+), 178 (M–Me), 120 (CH_2NMePh), 73 (Me_3Si).

One-Pot, Fluoride-Directed Preparation of Trimethyl(phenoxymethyl)silane (**22**). In the absence of fluoride ion, phenol attacks the silicon preferentially in $Cl-SiMe_2CH_2Cl$ to yield $PhO-Si-Me_2CH_2Cl$ (cf., *supra*). In the presence of fluoride ion, as this experiment shows, phenol attacks the methylene carbon. Thus, a solution of 64 mmol of phenol and 63 mmol of $Cl-SiMe_2CH_2Cl$ at 0°C was slowly treated with 190 mmol of powdered KF. Then the reaction mixture was stirred at 125–130°C for 72 hours, cooled to 25°C, and extracted with two 40 mL portions of pentane. The filtered organic extracts were evaporated, and the residue was fractionated to yield 40% of fluoro(dimethyl)(phenoxymethyl)silane, bp 33–34°C, at 0.20 mm Hg. ^{1}H NMR ($CDCl_3$): 0.36 (d, 6H, J_{H-F} 7.2 Hz), 3.62 (d, 2H, J_{H-F} 4.5 Hz), 6.66–7.40 (m, 5H); MS (*m/e*): 184 (M^+), 169 (M–Me), 165 (M–F), 107 (CH_2OPh), 77 (Me_2SiF), 47 (SiF).

Treating this product in the usual manner with ethereal MeMgBr gave a 96% yield of trimethyl(phenoxymethyl)silane (**22**).

Crossover Experiment with a Mixture of Chloromethyl(dimethyl)phenoxysilane (**8d**) *and Chloromethyl(diethyl)(p-tolyloxy)silane* (**8e**). In order first to rule out any thermally promoted exchange between **8d** and **8e**, 14 mmol each of the two compounds were heated in 60 mL of refluxing acetonitrile for 24 hours. The solvent was removed, and the residue was analyzed by mass spectrometry. The mass spectrum showed that the prominent fragments, M^+ and $(M-CH_2Cl)^+$, of the possible exchange products was <1% of the intensity of the M^+ peaks of $PhOSiMe_2-CH_2Cl$ and *p*-$TolOSiEt_2-CH_2Cl$. Therefore, aryloxy group exchange is negligible under these conditions.

A mixture containing 20 mmol each of **8d** and **8e** in 60 mL of acetonitrile was stirred at reflux for 24 hours with 86 mmol of KF. Cooling and filtration of the reaction suspension gave a clear filtrate that was then stripped of solvent in vacuo. The resulting residue was dissolved in 60 mL of dry ether and treated with 90 mmol of ethereal MeMgBr for 24 hours at 25°C. Usual hydrolytic workup gave an organic oil, whose GC analysis revealed four components of approximately equivalent areas having retention times (oven at 80°C) comparable to that of Me_3SiCH_2OPh. The formation of the possible crossover products was established by GC–MS analysis: (1) first peak, trimethyl(phenoxymethyl)silane (**22**): MS (*m/e*): 180 (M^+), 165 (M–Me), 107 (CH_2OPh), 73 (Me_3Si); (2) second peak, trimethyl(*p*-tolyloxymethyl)silane (**26**): MS (*m/e*): 194 (M^+), 179 (M–Me), 121 ($CH_2OC_6H_4CH_3$), 73 (Me_3Si); (3) third peak, diethyl(methyl)(phenoxymethyl)silane (**27**): MS (*m/e*): 208 (M^+), 193 (M–Me), 179 (M–Et), 107 (CH_2OPh), 101 (Et_2MeSi); and (4) fourth peak, diethyl(methyl)(*p*-tolyloxymethyl)silane (**25**): MS (*m/e*): 222 (M), 207 (M–Me), 193 (M–Et), 121 ($CH_2O_6H_4CH_3$), 101 (Et_2MeSi).

Reactions of Chloromethyl(fluoro)dimethylsilane (8g)

Phenol. A solution of 40 mmol of **8g** in 20 mmol of phenol was heated at reflux for 48 hours. The mixture was cooled to room temperature, and the volatiles were removed into a cold trap (−78°C) in vacuo. The volatiles proved to be only **8g**, and the residue was pure phenol.

Potassium phenoxide. Potassium phenoxide was prepared by stirring 40 mg atoms of potassium metal in 100 mL of anhydrous diethyl ether at 25°C with 50 mmol of phenol that was slowly introduced. The white precipitate of KOPh was collected, washed with ether, and dried under nitrogen. It was then combined with 33 mol of **8g** in 60 mL of acetonitrile and heated at reflux for 24 hours. The reaction mixture was cooled and filtered; the filtrate was stripped of solvent in vacuo and treated with 90 mmol of ethereal MeMgBr for 24 hours at 25°C. Usual hydrolytic workup and column chromatography of the crude product on silica gel gave 47% of trimethyl(phenoxymethyl)silane (**22**) (for spectral properties: cf. *supra*).

ACKNOWLEDGMENT

The authors are grateful to the National Science Foundation for support of this research through Grant No. CHE-87-14911.

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[7] (a) As indicated in the Experimental section and suggested in Equation 20, the lower yields of rearrangement products obtained with KF in acetonitrile are most likely a result of the destruction of the migrating anion by attack on the solvent; (b) Cf. J. P. Kennedy and E. Marechal: *Carbocationic Polymerization*, Wiley–Interscience, New York, 1982, where the polymerization of various styrenes by R_nAlX_{3-n} is discussed.

[8] (a) Trimethyl(phenyl)silane reacts with $MeAlCl_2$ to yield Me_3SiCl, MeAlPhCl, and other products; J. J. Eisch, K. Mackenzie, unpublished studies; (b) A somewhat similar rearrangement was observed when benzyl(chloro)chloromethyl(methyl)silane was treated with $AlCl_3$. In this case, both the *ortho*- and *para*-tolyl isomers were reported to have been formed of dichloro(methyl) *o*- and *p*-tolylmethylsilane. The finding of both tolyl isomers in the Russian work leaves open the possibility of their forming through intermolecular alkylation. In our work, we detected no trace of trimethyl(*p*-tolylmethyl)silane (cf. K. A. Petrov, V. A. Chauzov, I. V. Pastukhova, N. V. Pazhitnova, *Zh. Obshch. Khim.*, *48*, 1978, 1377 [*Chem. Abstr.*, *89*, 1978, 109708]).

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