

Fluoride Ion Induced Rearrangements of Chloromethyl-Substituted Silanes

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Received March 4, 1985

Fluoride ion solubilized by 18-crown-6 has been reacted in aromatic solvents like toluene, *o*-xylene, and mesitylene with a variety of chloromethyl- and chloroalkyl-substituted silanes. Although both rearrangement and cleavage reactions have been demonstrated, this paper mainly deals with the effect of substituents on the rearrangement. In the case of some substituents like vinyl and aryl ones, secondary reactions occur. These are shown to result from the reaction of RCH_2^- , where R = vinyl and aryl, and primary products like $\text{Me}_2(\text{RCH}_2)\text{SiF}$. Hammett relative reactivity studies are used to probe the details of both the primary and secondary reactions and demonstrate that for the primary reaction pentacoordination followed by rearrangement is controlled by substituents capable of supporting negative charge. To a greater extent this is also true of the secondary reaction substituent effects.

Introduction

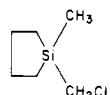
We recently reported that chloromethyl-substituted silanes undergo alkyl and aryl rearrangement induced by fluoride ion solubilized in 18-crown-6.¹ The competitive migration of various groups was studied and controlled by the ability of the migrating group to bear the negative charge which develops in the transition state. A parallel between this work in solution and our earlier² gas-phase studies of trimethyl-substituted silanes reacting with hydroxide ion was noted. In the latter study we established the gas-phase acidities of several weakly acidic alkanes by measuring the competitive cleavage of both alkyl and aryl groups from silicon.

Other recent activity has focused on the degree of negative character associated with groups cleaved from silicon by nucleophiles, particularly when the $\text{p}K_{\text{A}}$ values of the groups undergoing cleavage are less than 37.³ Cleavages in these reactions, induced by both basic and fluoride catalysis, correlate with a variety of substituent and acidity constants.^{3,4} In all cases studied cleavage of the carbon fragment is controlled by its carbanionic character.

Although a number of studies of chloromethyl-substituted silanes undergoing rearrangement under acidic conditions have been reported,⁵ base-induced rearrangements are relatively rare⁶ and seemingly limited to quite specific cases. Furthermore, the rearrangement of a simple alkyl group is still more rare.⁷ Our continued interest in

Table I. Product Ratios for the Reaction of $\text{Me}_2\text{RSiCH}_2\text{Cl}$ and KF

compd, R =	$\text{Me}_2(\text{CH}_2\text{R})\text{SiF}^{\text{a,b}} /$ $\text{MeR}^{\text{c}}\text{EtSiF}$	comments
Et (2)	1.5	clean reaction
c-Pr (3)	0.66 ^c	a number of products form in addition to those reported
<i>i</i> -Pr (4)	0.67	clean reaction
<i>n</i> -Bu (5)	0.87	clean reaction
vinyl (13)	20	secondary products discussed below
phenyl (14)	16	secondary products discussed below



only R migration to 1-fluoro-1-methyl-silacyclohexane

^a Statistically corrected. ^b Ratio determined by gc early in reaction, as soon as two products were observable. ^c This ratio was reported¹ incorrectly due to a calculation error. The proper value does not change the conclusions reported earlier.¹

these systems focuses on both the scope and the mechanistic detail of fluoride ion induced rearrangements, particularly in view of the interesting gas-phase fluoride ion chemistry we have observed with silicon compounds.⁸ What we report herein is some of our further work in this area.

Results

Alkyl-Substituted (Chloromethyl)silanes. We have prepared or obtained several compounds of the type $\text{Me}_2\text{RSiCH}_2\text{Cl}$, where R is Me (1), Et (2), c-Pr (3), *i*-Pr (4), and *n*-Bu (5). In addition, 1-(chloromethyl)-1-methyl-silacyclopentane (6) has been prepared. Each of these compounds has been reacted with anhydrous KF in either toluene, *o*-xylene, or mesitylene with 18-crown-6 present. Our choice of solvent depends on the volatility of the starting materials and products as most of the analyses of these systems have been performed by gas chromatography. Table I summarizes these reactions as well as those where R = vinyl and phenyl. In each we observe reaction resulting in the production of two fluorosilanes obtained by the migration of an R or methyl group to the chloromethyl moiety with loss of chloride. In all of these com-

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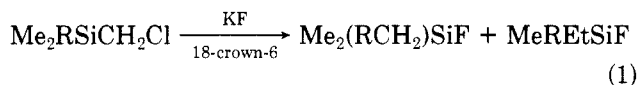
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Table II. Reaction of KF with Me₂RSiCH₂Cl and Me₃SiX

compd	results ^a
Me ₂ RSiCH ₂ Cl	
R = Me ₃ SiCH ₂ (7)	a large number of products; these were not characterized
R = Me ₃ SiO (8)	no reaction with KF; many products with CsF
R = CH ₂ Cl (9)	yields Me ₂ SiF ₂ and CH ₂ =CH ₂
Me ₃ SiX	
X = CH ₂ CH ₂ CH ₂ Cl (10)	no reaction with KF or CsF
X = CHCl ₂ (11)	yields Me ₃ SiF and CH ₂ Cl ₂
X = CHClCH ₃ (12)	no reaction with KF or CsF

^aAll results were determined by GC and GC-MS.

pounds except Me₃SiCH₂Cl there is a competition between two potential migrating groups (eq 1). Our earlier report¹



suggested that the major factor controlling migration was the ability of the migrating group to support the negative charge generated in the transition state. Large differences are not observed among the alkyl groups although the general trend is reasonably correlated with σ_1 constants.

Only the reaction of Me₃SiCH₂Cl (1) and 1-(chloromethyl)-1-methylsilacyclopentane (6) give a single product in high yield. Thus, Me₂EtSiF and 1-fluoro-1-methylsilacyclohexane are obtained, respectively, while the other alkyl reactions, because of the close competition between groups, give two isomeric products which can only be observed under carefully controlled gas chromatographic conditions. In addition, these reactions are generally quite slow often taking a month to complete. The ratios we have used to compare the migratory ability of different R groups have been obtained only in the early stages of these reactions since with R = *c*-Pr, vinyl, and phenyl the reaction gives additional products.

A variety of other conditions have been studied, particularly with Me₃SiCH₂Cl (1); these have included both variations in the fluoride source and solvent choice. Such variations always lead to more complex reaction mixtures. With CsF and 18-crown-6, for example, we observe that these reactions are much more rapid, but that products clearly the result of water involvement become major ones. The only exception is the reaction of Me₃SiCH₂Cl (1) where an 87% yield of Me₂EtSiF is obtained in only 4 days. Reactions in other than aromatic solvents (e.g., THF, pyridine, acetonitrile, DMF, and Me₂SO) have all proved to be quite complex, an observation consistent with work recently reported by Corey and co-workers⁶ on chloromethyl-substituted phenazasilines and phenoxasilins.

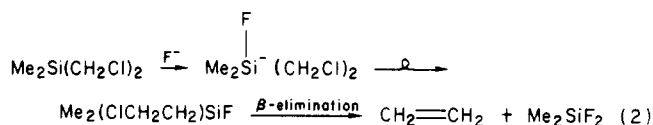
Other Chloroalkyl-Substituted Silanes. To further explore the scope of the reaction of fluoride ion, we reacted several other chloroalkyl-substituted silanes using KF (and in some cases CsF) solubilized by 18-crown-6 in aromatic solvents. These were of two types: (1) Me₂RSiCH₂Cl, where R = Me₃SiCH₂ (7), Me₃SiO (8), and ClCH₂ (9) and (2) Me₃SiX, where X = CH₂CH₂CH₂Cl (10), CHCl₂ (11), and CHClCH₃ (12). Table II gives the results of these experiments for which several comments seem in order. Compounds 12 and 10 with α - and γ -chloro substitution, respectively, do not react under our conditions with either KF or CsF. This first result contrasts with that of Corey and co-workers,⁶ who observed rearrangement in their α -(chloroethyl)phenazasiline compound, while the latter is consistent with their observation that the γ -chloropropyl group does not become involved in reactions of their phenoxasiline systems. Compound 7 gives a very complex

Table III. Reaction of KF and Me₂ArSiCH₂Cl: Product Distribution^a

compd, Ar =	A	B	C	D	E
phenyl (14)	b	6.8	1.0	0.4	
<i>p</i> -tolyl (15)	1.7	3.9	1.0	0.06	
<i>p</i> -fluorophenyl (16)	0.95		1.0	0.15	0.016
<i>p</i> -chlorophenyl (17)	1.4		1.0	0.58	0.065
<i>m</i> -(trifluoromethyl)phenyl (18)	2.5		1.0	1.8	0.59

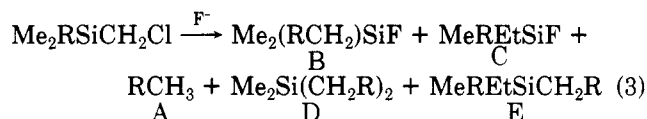
^aLegend: A = ArCH₃; B = Me₂(CH₂Ar)SiF; C = MeArEtSiF; D = Me₂Si(CH₂Ar)₂; E = MeArEtSiCH₂Ar. All of these reactions were carried out in toluene at 55 °C. Sampling was carried out by GC at 23 h. ^bThe product, toluene, and solvent were the same; toluene, however, was detected in other solvents.

reaction in which a number of products have been observed by gas chromatography; these, however, have not been identified because of the complexity of the mixture. Compound 8 also gives such a complex reaction with CsF but is unreactive to KF. In contrast to 7 and 8, compounds 9 and 11 give tractable reactions, 9 giving dimethyldifluorosilane and ethylene in a process we suggest to be similar to that illustrated (eq 2), 11 giving trimethylfluorosilane and methylene chloride by a direct cleavage process.



Vinyl- and Aryl-Substituted (Chloromethyl)silanes.

Vinyl and aryl substituents attached to silicon have a greater propensity to migrate than the alkyl groups already mentioned (Table I). These compounds, Me₂RSiCH₂Cl, where R = vinyl (13), phenyl (14), *p*-tolyl (15), *p*-fluorophenyl (16), *p*-chlorophenyl (17), and *m*-(trifluoromethyl)phenyl (18), all undergo secondary reactions as outlined (eq 3).



In these cases, migration of a vinyl or aryl group places an excellent leaving group, either allyl or benzyl, on silicon and the secondary reactions shown can result. We have not been able to observe each of the products of eq 3 in each reactant; however, as seen in Table III, we can see four of the five products A-E for each of the five aryl cases we have studied. For the R = vinyl case we have demonstrated that products B, C, and D are formed. We believe compound A results from the formation of allyl or benzyl anions which either capture a proton from solvent or react with the primary products B and C to convert them to the secondary products D and E. That A is not seen when R = vinyl is not surprising since we took no steps to trap any products as propene. That various of the possible products were not detected in the R = aryl series is also not surprising in view of the trends suggested in Table III. Here we see that as the substituted benzyl anion becomes more stable, primary products B and C decrease and the amounts of secondary products D and E increase. Similarly, when the substituted benzyl anion is not as stable (Ar = phenyl and *p*-tolyl), the amounts of secondary products are smaller.

We have sought to examine the mechanism of these reactions by combining data from our previous study¹ (Table I) with work on the aryl series 14-18. Thus, we have measured (1) the relative rate of disappearance of 14-18

Table IV. Relative Rate Data for Various Reactions

	Ar				
	A	B	C	D	E
1. disappearance $\text{Me}_2\text{ArSiCH}_2\text{Cl}^b$	0.63	1.0	1.7	2.9	5.7
2. appearance ArCH_3^b	0.055	1.0	0.58	17	31
3. secondary/primary ^c	1.0	<i>d</i>	5.5	10	24

^aLegend: A = *p*-tolyl; B = phenyl; C = *p*-fluorophenyl; D = *p*-chlorophenyl; E = *m*-(trifluoromethyl)phenyl. ^bYield determinations by GC with internal standard. ^cProducts A + D + E/products B + C; data derived from GC peak heights. ^dCould not be determined since reaction was carried out in toluene.

Table V. Substituent Correlations for Various Reactions

1. $\text{Me}_2\text{RSiCH}_2\text{Cl} + \text{F}^-$ (eq 1)	$\rho^* = 1.8$ (0.93) ^{a,b}
2. $\text{Me}_3\text{SiR} + \text{HO}^-$ (eq 4)	$\Delta H_{\text{acid}} = -0.078$ (0.99), ^b $\rho^* = 1.5$ (0.86) ^b
3. disappearance of $\text{Me}_2\text{ArSiCH}_2\text{Cl}^c$	$\rho = 1.6$ (0.99)
4. appearance of ArCH_3	$\rho = 4.5$ (0.94)
5. secondary/primary	$\rho = 2.2$ (0.97)

^aCorrelation coefficient given in parentheses. ^bReference 1. ^c σ constants are *p*-tolyl, -0.15, phenyl, 0.0, *p*-fluorophenyl, 0.06, *p*-chlorophenyl, 0.23, and *m*-(trifluoromethyl)phenyl, 0.47, from: Barlin, G. B.; Perrin, D. D. *Q. Rev., Chem. Soc.* **1966**, *20*, 247.

and (2) the relative rate of appearance of the substituted toluenes, ArCH_3 . In addition, we have measured the relative amount of all five products for each of the five aryl reactions. These substituent data have been treated in standard Hammett fashion as can be seen in Table IV where the relative rate data are collected and Table V where the Hammett correlations are reported. One additional comment is necessary. The data reported in Tables I, III, and IV only serve to point out trends in the reactivity patterns of the compounds. The heterogeneous nature of these reactions makes it critical that conditions like stirring rates be controlled carefully. Although we have tried to do so, it is clear to us that all such factors cannot be fully controlled without going to unusual experimental extremes. We feel that the trends we have seen adequately explain these systems and that the investment in more control measures would not give us a concomitant additional insight into these systems.

Experimental Section

General Remarks. The reactions studied have generally been carried out under atmospheric conditions, although we have demonstrated that the same results are obtained when run in an inert atmosphere of dry nitrogen. Most reactions have been carried out in serum cap vials fitted with a magnetic stirring bar. Gas chromatographic (GC) analysis has been carried out by using a Perkin-Elmer 3020B chromatograph with flame ionization detection. Gas chromatographic yields were determined utilizing the internal standard method; response factors were determined each time yields were determined. Two gas chromatographic column types were used: a $1/8$ in. \times 6 ft 10% OV-1 silicone oil on Chromosorb WHP packed column and a 0.25 mm \times 10 m OV-101 silicone oil wall coated open tubular stainless steel capillary column. GC-MS analysis was carried out on a Finnigan 3200 with a Teknivent data system. NMR analysis was carried out on an IBM NR-80 spectrometer; all shifts are reported relative to Me_4Si . A Perkin-Elmer 237B IR spectrometer was used for IR analysis.

All compounds whose preparations are not reported or referenced were obtained from either Aldrich Chemical Co. or Petrarch Systems. Purities have been checked by gas chromatographic analysis; in general, compounds from these sources have been used without further purification. The yields reported for those compounds prepared for further study are given for only that portion of the material pure enough for subsequent use.

Anhydrous reagent grade KF (MCB Chemicals) has been used in all these studies; it has been stored in an oven at 120 °C, cooled,

and weighed out immediately. The solvents, toluene, *o*-xylene, and mesitylene, were stored over molecular sieves.

Preparation of $\text{Me}_2\text{RSiCH}_2\text{Cl}$ [R = Et (2) and *n*-Bu (5)]. In a typical preparation RMgX (X = Br for Et and Cl for *n*-Bu) was added to a diethyl ether solution of $\text{Me}_2\text{Si}(\text{CH}_2\text{Cl})\text{Cl}$. Saturated aqueous NH_4Cl workup, extraction with diethyl ether and drying, and distillation afforded the known⁹ products in >97% purity in 21.8 and 68.1% yield, respectively.

Preparation of $\text{Me}_2\text{RSiCH}_2\text{Cl}$ [R = *c*-Pr (3)]. In a typical preparation Simmons-Smith addition of methylene iodide to $\text{Me}_2\text{RSiCH}_2\text{Cl}$, where R = vinyl, was carried out in ether. Filtration, aqueous NH_4Cl treatment, ether extraction and drying, and distillation afforded the known product¹⁰ in >96% purity in 16.6% yield.

Preparation of $\text{Me}_2\text{RSiCH}_2\text{Cl}$ [R = *i*-Pr (4)]. Addition of *i*-PrLi in hexane to a solution of $\text{Me}_2\text{Si}(\text{CH}_2\text{Cl})\text{F}$ under Ar afforded the known¹¹ product after aqueous HCl workup, drying, and distillation. Distillation through an annular Teflon-coated spinning band was required and gave an 8.5% yield of material of about 85% purity. This material was used in subsequent studies where the slight impurity did not undergo change.

Preparation of 1-(Chloromethyl)-1-methylsilacyclopentane (6). This compound was prepared from the di-Grignard of 1,4-dibromobutane and $\text{MeSi}(\text{CH}_2\text{Cl})\text{Cl}_2$ in ether. A 60.8% yield of this known¹² compound was obtained in >97% purity.

Reaction of KF and $\text{Me}_3\text{SiCH}_2\text{Cl}$ (1). A mixture of KF (11.6 g, 0.2 mol) and 18-crown-6 (2.5 g, 0.01 mol) in 10 mL of toluene was prepared. $\text{Me}_3\text{SiCH}_2\text{Cl}$ (12.2 g, 0.1 mol) was added; the mixture was magnetically stirred with careful monitoring of the condenser water which was maintained <7 °C. Daily gas chromatographic monitoring showed the buildup of a very short retention time peak over a 2-week period. At the end of week 1 and week 2 a short-path distillation gave a material boiling between 52 and 58 °C, later shown to be Me_2EtSiF (6.5 g, 61.3%). Redistillation through a short Vigreux column gave pure Me_2EtSiF boiling at 41–45 °C (5.1 g, 48.1%). Careful ¹H and ¹³C NMR demonstrated not only the identity of the Me_2EtSiF , but that no $\text{Me}_3\text{SiCH}_2\text{F}$ was present.

Reaction of KF and 1-(Chloromethyl)-1-methylsilacyclopentane (6). The title compound 6 (1.0 g, 0.007 mol), KF (0.78 g, 0.013 mol), and 18-crown-6 (0.178 g, 0.0007 mol) were sealed with 3 mL of mesitylene in a serum cap vial and stirred at 74 °C for 9 h. Periodic GC analysis indicated that a single product formed in a very clean reaction. Short-path distillation gave an initial fraction rich in product with mesitylene as its only other detectable component (about 41% product). This solution was suitable for ¹H and ¹³C NMR analysis which revealed that only 1-fluoro-1-methylsilacyclohexane formed.

Reactions of KF and $\text{Me}_2\text{RSiCH}_2\text{Cl}$ [R = Et (2), *c*-Pr (3), *i*-Pr (4), and *n*-Bu (5)]. In each of these reactions $\text{Me}_2\text{RSiCH}_2\text{Cl}$, KF, and 18-crown-6 (mole ratio = 10:20:1) were sealed in a serum cap vial with the appropriate aromatic solvent. Whether toluene, *o*-xylene, or mesitylene was used was determined by their respective retention times as these reactions were analyzed by GC. Thus, conditions were arranged so that starting materials, products, and solvent gave discrete peaks. Each reaction was studied at the lowest temperature where reasonably fast reaction could be observed. This was generally at about 50 °C; nevertheless, complete reaction generally required between 1 and 2 weeks. We were particularly interested in the ratio of migration of Me and R, so critical GC measurements were taken only in the initial stages of reaction, as soon as both products were discernible. These two products, derived from Me and R migration, respectively, had almost identical retention times, and some care was required for analysis. Generally, we were able to use packed gc columns although these mixtures were also analyzed by capillary

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GC. The migration ratios were determined by comparing the peak heights of the two products; implicit in this analysis is the assumption that the two products of such similar structure have identical GC response factors. Product identification was carried out by GC-MS analysis on a column identical with the one from which ratios were determined. The data obtained in these experiments are summarized in Table I. The critical MS data [m/e (relative intensity)] used for product identification are given as follows: R = Et: MeEtRSiF, 120 (M^+ , 5), 105 ($M - 15$, 5), 91 ($M - 29$, 100); Me₂(RCH₂)SiF, 120 (5), 105 (13), 77 ($M - 43$, 100). R = *c*-Pr: MeEtRSiF, 132 (M^+ , 3), 117 ($M - 15$, 10), 103 ($M - 29$, 100), 91 ($M - 41$, 100); Me₂(RCH₂)SiF, 132 (10), 117 (7), 77 ($M - 55$, 100). R = *i*-Pr: MeEtRSiF, 134 (M^+ , 10), 119 ($M - 15$, 2), 105 ($M - 29$, 4), 91 ($M - 43$, 100); Me₂(RCH₂)SiF, 134 (trace), 119 (23), 77 ($M - 57$, 100). R = *n*-Bu: MeEtRSiF, 148 (M^+ , 5), 133 ($M - 15$, 5), 119 ($M - 29$, 100), 91 ($M - 57$, 100); Me₂(RCH₂)SiF, 148 (2), 133 (12), 77 ($M - 71$, 100).

Reactions of KF and Me₂RSiCH₂Cl [R = Me₂SiCH₂ (7), Me₃SiO (8), and ClCH₂ (9)] and KF and Me₃SiX [X = CH₂CH₂CH₂Cl (10), CHCl₂ (11), and CHClCH₃ (12)]. In a typical experiment the silane, KF, and 18-crown-6 (mole ratio = 10:20:1) were reacted in an appropriate aromatic solvent in a sealed serum cap vial. The reactions were begun at room temperature and analyzed by GC. When no apparent reaction occurred at room temperature, the vials were heated to various temperatures until either reaction ensued or we determined that no reaction was occurring. The results are given in Table II. The reactions labeled as complicated had in excess of five products, none of which was major, and were not further investigated. Those where reaction was seen were investigated by GC-MS. No quantitation was carried out generally because the products were very volatile and because we were only interested in surveying the reactivity of 7-12.

Reaction of KF and Me₂RSiCH₂Cl [R = Vinyl (13)]. Large Scale. Compound 13 (13.5 g, 0.1 mol), KF (11.6 g, 0.2 mol), and 18-crown-6 (2.5 g, 0.009 mol) were reacted at 100 °C in 10 mL of *o*-xylene. After 1 day, two short retention time products were discernible being about double the size of starting silane. After 2 days, they were about 6 times the size of starting silane, but another longer retention time peak was present. This latter peak continued to increase on the next day when the reaction was stopped (no more starting silane). Distillation through a Vigreux column gave 0.5 g of a liquid whose GC indicated it was a mixture of the two short retention time peaks in a ratio of 5:1; this sample was >95% pure. The peaks were very close in retention time and could not be separated by distillation. ¹H and ¹³C NMR of this mixture revealed it to be Me₂(CH₂=CHCH₂)SiF (major) and Me(CH₂=CH)EtSiF (minor). Further distillation yielded a fraction rich in the long retention time peak but contaminated by *o*-xylene. NMR analysis and comparison with an authentic sample identified the high boiling component as Me₂Si(CH₂CH=CH₂)₂. No evidence was obtained for the other possible secondary product Me(CH₂=CH)EtSi(CH₂CH=CH₂).

Reaction of KF and Me₂RSiCH₂Cl [R = Vinyl (13) and Phenyl (14)]. Migration of R vs. Methyl. These experiments were carried out in exactly the same manner as those earlier described for Me₂RSiCH₂Cl, where R is alkyl. The results are collected in Table I. These compounds were more reactive than their alkyl analogues. Measurements of the migration ratio was more difficult because the aryl groups migrate much more readily than methyl. Furthermore, the onset of formation of secondary products makes it essential that all comparisons of migrating ability be carried out before secondary reaction ensues. Thus, we have measured these ratios as soon as primary products could be detected.

Preparation of Me₂ArSiCH₂Cl [Ar = *p*-Tolyl (15), *p*-Fluorophenyl (16), *p*-Chlorophenyl (17), and *m*-(Trifluoromethyl)phenyl (18)]. Known¹⁴ compounds 15-18 were prepared by a standard procedure in which the appropriate ArBr (10% molar excess) was converted to its Grignard in ether under a N₂ atmosphere. Me₂SiCl(CH₂Cl) was slowly added, and the resulting mixture was stirred at reflux for 24 h. Standard workup

with saturated NH₄Cl followed by distillation through a Vigreux column gave the products in yields ranging between 30 and 65% in purities >98%.

Reaction of KF and Me₂ArSiCH₂Cl [Ar = Phenyl (14), *p*-Tolyl (15), *p*-Fluorophenyl (16), *p*-Chlorophenyl (17), and *m*-(Trifluoromethyl)phenyl (18)]. Product Analysis. Compounds 14-18 were each sealed in a serum cap vial with KF, 18-crown-6 (mole ratio = 10:20:1), and the appropriate aromatic solvent, usually mesitylene. These reactions were carried out in a manner similar to that described for compounds 2-5, although the temperature required for reaction was lower, usually 25-35 °C owing to the greater reactivity of the aromatic substitution. Particular attention was given to (1) determining whether all four products, two primary and two secondary, were present and (2) whether the ArCH₃ product could be observed. These observations are detailed in Table III, where we observe that in no reaction are all four products detected. It should be noted that yield determinations were essentially impossible to obtain because of the occurrence of the secondary reactions. Generally the secondary products form as soon as primary products do, although they form at quite different rates. Thus, there is considerable difficulty obtaining yields, and we have chosen to express our data in relative terms as seen in Table III. Structure determination for each of these reactions was carried out by GC-MS. The MS data [m/e (relative intensity)] given illustrate how the various compounds listed in Table III were characterized. Ar = phenyl: Me₂-(CH₂Ar)SiF, 168 (M^+ , 30), 153 ($M - 15$, 10), 77 ($M - Ar$, 100). Ar = *p*-chlorophenyl: MeArEtSiF, 202, 204 (M^+ , (11, 3), 187, 189 ($M - 15$, 3, 1), 173, 175 ($M - 29$, 10, 3); Me₂Si(CH₂Ar)₂, 308, 310, 312 (M^+ , 7, 5, 2), 183, 185 ($M - CH_2Ar$, 100, 60); MeArEtSiCH₂Ar, 308, 310 (M^+ , 1, 1), 279, 281 ($M - 29$, 1, 1), 183, 185 ($M - CH_2Ar$, 43, 15).

Reaction of KF and Me₂ArSiCH₂Cl [Ar = Phenyl (14), *p*-Tolyl (15), *p*-Fluorophenyl (16), *p*-Chlorophenyl (17), and *m*-(Trifluoromethyl)phenyl (18)]. Relative Rates of Disappearance of Starting Silanes. Competitive reactions were carried out in pairs between 15 and each of the other arylsilanes, 14 and 16-18. Reactants were sealed in serum cap vials fitted with magnetic stirbars and reacted at 72 °C. Approximately 0.0025 mol of each silane, 0.0020 mol of KF, and 0.0002 mol of 18-crown-6 in 1.5 mL of mesitylene was used in each experiment. GC analysis using hexadecane as an internal standard was carried out. Relative rates were obtained by standard calculations:¹⁵ *p*-tolyl (15), 0.63; phenyl (14), 1.0; *p*-fluorophenyl (16), 1.7; *p*-chlorophenyl (17), 2.9; *m*-(trifluoromethyl)phenyl (18), 5.7. Suitable competitive conditions (at least at 10-fold excess of silanes over KF) were in force since only a very small amount of KF actually is in solution at any time. The relative rate data are compiled in Table IV; Hammett correlation data are given in Table V.

Reaction of KF and Me₂ArSiCH₂Cl [Ar = Phenyl (14), *p*-Tolyl (15), *p*-Fluorophenyl (16), *p*-Chlorophenyl (17), and *m*-(Trifluoromethyl)phenyl (18)]. Relative Rates of Appearance of ArCH₃. Each silane (0.005 mol), KF (0.010 mol), 18-crown-6 (0.0005 mol), and mesitylene (1.8 ml) was separately reacted at 85 °C. Periodic GC analysis was carried out over 24 h using hexadecane as internal standard. Care was taken to sample frequently enough to have a good measure of when the various ArCH₃ products first appeared. This is on the order of a few minutes for *m*-(trifluoromethyl)phenyl (18) to over an hour for *p*-tolyl (15). To treat the data in a uniform manner, we fit each experimental run to a second-order polynomial and then chose a time early in these reactions when each ArCH₃ product was observable. This was possible at 1.5 h although we would have hoped that the quality of the data would have allowed an earlier time to be used. That the times of appearance of ArCH₃ are so vastly different leads to large uncertainties in these data. Nevertheless, at 1.5 h, we obtained the following relative rates: *p*-tolyl (15), 0.055; phenyl (14), 1.0; *p*-fluorophenyl (16), 0.58; *p*-chlorophenyl (17), 17; *m*-(trifluoromethyl)phenyl (18), 31. The Hammett correlation of these data is given in Table V.

Reaction of KF and Me₂(ArCH₂)SiF (Ar = Phenyl). Me₂(ArCH₂)SiF (1.0 g, 0.0059 mol), where Ar = phenyl, KF (0.68 g, 0.012 mol), and 18-crown-6 (0.15 g, 0.00059 mol) were reacted

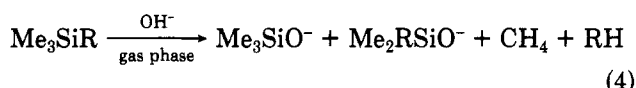
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at 90 °C in 1 mL of toluene. Periodic GC monitoring over several days revealed the decrease of starting material with a concomitant increase in $\text{Me}_2\text{Si}(\text{CH}_2\text{Ar})_2$ (comparison with authentic sample). After 6 days 90% conversion had occurred.

Discussion

In our recent communication¹ we explored substituent effects in the reaction of KF and $\text{Me}_2\text{RSiCH}_2\text{Cl}$ (eq 1). A variety of R groups were studied and the experimental details of that study are presented herein. In choosing R we sought not only to have a broad spectrum of different substituents represented, but also, as closely as possible, to mirror the substituents of our gas-phase study² in which Me and R are competitively cleaved by HO^- (eq 4). In



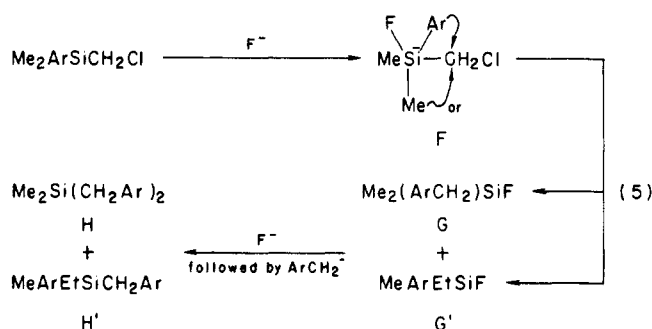
both studies we demonstrated that reaction was controlled by the ability of the migrating group to stabilize its partial negative charge buildup in the transition state. In the case of the KF reaction (eq 1), the log of $\text{Me}_2(\text{CH}_2\text{R})\text{SiF}/\text{MeREtSiF}$ is best correlated with σ_{F} ; in the gas-phase counterpart (eq 4), the log of $\text{Me}_3\text{SiO}^-/\text{Me}_2\text{RSiO}^-$ correlates best with ΔH_{acid} . The solution-phase reactions are considerably more difficult to study, the alkyl-substituted cases reacting very slowly and sometimes yielding complex reaction mixtures (e.g., R = *c*-Pr), the vinyl and aromatic substituted cases yielding secondary reaction products. We have, thus, necessarily determined our migratory ratios early in the reaction before any secondary complications arise. In the rest of this report we will discuss the scope of these reactions, the details of some of the secondary reactions, and the mechanism for the reaction of KF and $\text{Me}_2\text{ArSiCH}_2\text{Cl}$.

The wealth of gas-phase F^- chemistry we have observed⁸ suggested that a solution-phase F^- mimic might be interesting. As a result we chose the KF, 18-crown-6, aromatic solvent reaction conditions. This system has the advantages of being dry (we have seen the involvement of H_2O in our reactions only rarely and at a very low level) and of producing highly reactive F^- . Its disadvantage is that it is a heterogeneous condition and only low concentrations of the reactive F^- are obtained. Thus, the reactions of KF and aliphatic $\text{Me}_2\text{RSiCH}_2\text{Cl}$'s are slow. Only R = Me (1) and 1-(chloromethyl)-1-methylsilacyclopentane (6) give single products in high yield, but neither offers any synthetic advantage over other methods of preparing Me_2EtSiF and 1-fluoro-1-methylsilacyclohexane. As indicated earlier, we generally obtained much more complex reaction mixtures using CsF or solvents other than toluene, *o*-xylene, or mesitylene.

We have explored other substitution patterns in the silane reaction with KF (Table II). We see examples of rearrangement (compound 9) and cleavage (compound 11) as well as very complex reaction where we have not attempted to sort out the products (compound 7) and no reaction (compounds 8, 10, and 12). We have observed no product which would result from F^- substitution of any (chloroalkyl)silane. We, like Corey and co-workers,⁶ do not have a good understanding of the controlling factors for rearrangement, cleavage, and substitution, yet several comments seem in order, at least for the systems we have studied. When a potentially good leaving group is bound to silicon (Cl_2CH^- in 11 and $\text{Me}_3\text{SiCH}_2^-$ in 7), we obtain either cleavage or a complex reaction mixture. When the leaving group is not as good (ClCH_2^- in 9), rearrangement can occur. Other factors like steric hindrance (12) or the difficulty of rearrangement to other than an adjacent

position (10) lead to no reaction. Finally, the case where R = Me_3SiO in $\text{Me}_2\text{RSiCH}_2\text{Cl}$ (8) suggests that the strength of the bond between Si and R, in this case an Si-O bond, may control reactivity. There seems to be a delicate balance here, for with KF there is no reaction, but with CsF a very complex reaction mixture is obtained.

The reaction of KF with a series of $\text{Me}_2\text{ArSiCH}_2\text{Cl}$ compounds allows us to consider the mechanism of the primary and secondary reactions in reasonable detail. Relative rate measurements¹⁵ of $\text{Me}_2\text{ArSiCH}_2\text{Cl}$ disappearance (Table V) give a ρ value of 1.6, suggesting that electron-withdrawing substituents modestly stabilize the transition state for disappearance. The ρ^* value for Me vs. R migration from our previous study¹ is 1.8, suggesting a similar substituent effect for this part of the reaction. In addition we have measured a ρ value for the appearance of ArCH_3 (4.5). This part of the reaction which must be connected with the appearance of secondary reactions has been probed in a second way by plotting the log of the sum of the secondary product yields (including ArCH_3) divided by the sum of the primary product yields vs. σ . Here we obtained a ρ value of 2.2. We believe these data are consistent with the mechanistic scheme presented (eq 5) in

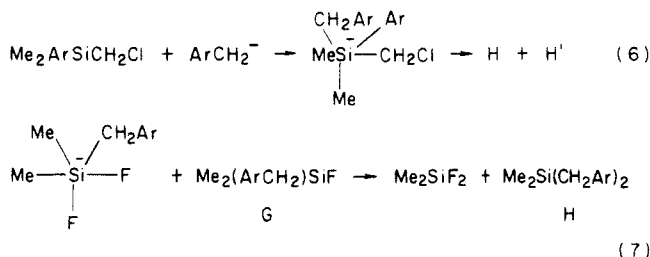


which the rate of disappearance measurements mirror the formation of pentacoordinate intermediate F, in which the ρ^* data measure the propensity of a substituent to migrate to give products G and G', and in which both the rate of appearance of ArCH_3 and the sum of secondary over primary product studies give us a measure of how readily products G and G' convert to the secondary ones H and H'.

The formation of pentacoordinate intermediate F, although not directly observed, finds support, particularly when fluorine is bonded to silicon, in a number of gas-phase studies.¹⁶ Rearrangement of such a pentacoordinate intermediate has not been directly observed in any system of which we are aware; however, our solution- and gas-phase substituent effects (Table V) suggest that a similar charge resides on the group either migrating (solution) or being cleaved (gas phase). The respective ρ values are not large and, consequently, not a great deal of negative charge is localized on these groups. We recognize that it could be argued that F^- attack and rearrangement are simultaneous events and that the data do not definitively settle the question. Although that is true, we, nevertheless, favor the formation of the pentacoordinate intermediate F.

Any qualitative view of the secondary reactions (eq 5) recognizes the remarkable consistency between the distribution of products and the electronic nature of the substituents. Thus, products G and G' predominate when the substituent cannot readily stabilize negative charge, and products H and H' predominate when they can. A more penetrating look reveals that we are unable to pre-

cisely detail the steps leading to secondary reaction. We have two measures of the effect of substituents on secondary product formation: both ρ values are larger than those obtained in the earlier stages of the reaction and suggest that a greater charge develops in the transition state of the secondary reaction ("ArCH₂⁻" like). It could be argued that secondary products form by two other mechanistic schemes (eq 6 and 7). In the first of these,



ArCH₂⁻ (or a "ArCH₂⁻" species) reacts with starting chlorosilane forming a pentacoordinate intermediate from which either Ar or Me migrate giving H and H', respectively. The other reaction scheme is similar to ones we have proposed for gas-phase reactions⁸ where groups are "soft transferred" from pentacoordinate intermediates to neutral silanes. On this point we have obtained direct evidence that Me₂(ArCH₂)SiF, where Ar = phenyl, reacts with F⁻ to give Me₂Si(CH₂Ar)₂ under conditions similar to those of our other reactions. Thus, we feel certain that eq 5 is operating although we cannot exclude the possibility that either or both eq 6 and 7 are occurring simultaneously. It is difficult to know how free the ArCH₂⁻ anion is. Although the ρ values are quite a bit larger when the secondary reaction is probed, the complexity of this part of these reactions makes it impossible to say with certainty

to what extent the carbanion is free. Furthermore, it is difficult to be sure the extent to which water has been excluded from our reactions although we have demonstrated that reactivity is not altered under carefully controlled inert-gas conditions. The nagging doubt remains that water cannot be completely excluded, a doubt fueled by the knowledge that KF is so readily hygroscopic. We believe, however, that in totality the evidence suggests a reasonable amount of carbanionic character in these reactions.

Thus, we feel that the mechanistic scheme set forth in eq 5 adequately describes the series of reactions we have studied. Further mechanistic details as well as studies expanding the scope of such reactions are in progress.

Acknowledgment. We gratefully acknowledge support from the National Science Foundation (Grant CHE-8313826) and Research Corp. We also wish to thank the University of Colorado Health Sciences Center Clinical Mass Spectrometry Resource for extensive use of their GC-MS facility. We also thank Robert Meglen, Center for Environmental Studies, for help with the statistical analysis.

Registry No. 1, 2344-80-1; 2, 3121-77-5; 3, 54690-67-4; 4, 22429-26-1; 5, 3121-75-3; 6, 3944-19-2; 7, 18306-73-5; 8, 17201-83-1; 9, 2917-46-6; 10, 2344-83-4; 11, 5926-38-5; 12, 7787-87-3; 13, 16709-86-7; 14, 1833-51-8; 15, 1833-32-5; 16, 770-90-1; 17, 770-89-8; 18, 779-69-1; MeEt₂SiF, 681-07-2; MeEt(C-Pr)SiF, 97878-78-9; MeEt(*i*-Pr)SiF, 97878-79-0; MeEt(*n*-Bu)SiF, 97878-80-3; Me₂(EtCH₂)SiF, 27977-39-5; Me₂(*c*-PrCH₂)SiF, 97878-81-4; Me₂(*i*-PrCH₂)SiF, 97878-82-5; Me₂(*n*-BuCH₂)SiF, 96164-67-9; Me₂(CH₂Ar)SiF (Ar = phenyl), 1842-25-7; MeArEtSiF (Ar = *p*-chlorophenyl), 14132-22-0; Me₂Si(CH₂Ar)₂ (Ar = *p*-chlorophenyl), 97878-83-6; MeArEtSiCH₂Ar (Ar = *p*-chlorophenyl), 97878-84-7; CsF, 13400-13-0; KF, 7789-23-3; 18-crown-6, 17455-13-9.

Stannylenes: An MNDO Investigation¹

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Received April 17, 1985

Calculations are reported for insertion and cycloaddition reactions of compounds containing divalent tin.

Introduction

While the chemistry of carbon(II) compounds (carbenes) has been extensively studied, references to the organic chemistry of tin(II) compounds (stannylenes) remain sparse.³ While the stable tin(II) halides have been well

characterized and MNDO studies of them reported,⁴ organotin(II) compounds have remained elusive and most of the early claims for their preparation have been refuted.³ In recent years, however, mostly through the efforts of Neumann and his co-workers,⁵⁻¹⁰ clear evidence for the preparation and reactions of stannylenes has emerged. The reactions so far reported include insertion into car-

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