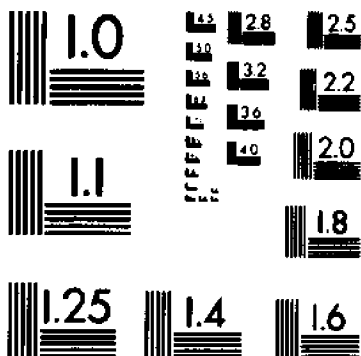
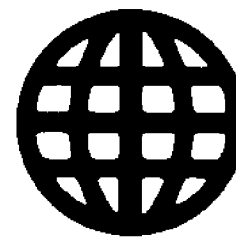


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REARRANGEMENT-DISPLACEMENT OF
ARYL(CHLOROMETHYL)DIPHENYLSILANES WITH NUCLEOPHILES

The Ohio State University

PH.D. 1986

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REARRANGEMENT-DISPLACEMENT OF
ARYL(CHLOROMETHYL)DIPHENYLSILANES WITH NUCLEOPHILES

DISSERTATION

Presented in Partial Fulfillment of the Requirements for
the Degree Doctor of Philosophy in the Graduate
School of the Ohio State University

by

Steve Lawrence Aprahamian, B.S. (with Honors)

* * * * *

The Ohio State University

1986

Reading Committee:

Dr. Steven M. D'Ambrosio

Dr. David J. Hart

Dr. Harold Shechter

Dr. John S. Swenton

Approved by



Adviser

Department of Chemistry

To My Parents:
for allowing me to be everything I've wanted.

To My Wife:
for being everything I've wanted.

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VITA

December 30, 1957 Born - Milwaukee, Wisconsin

1980 B. S. (with Honors), University
of Wisconsin-Madison

1980-1983 Graduate Teaching Associate,
Department of Chemistry,
The Ohio State University,
Columbus, Ohio

1983-Present Graduate Research Associate,
Department of Chemistry,
The Ohio State University,
Columbus, Ohio

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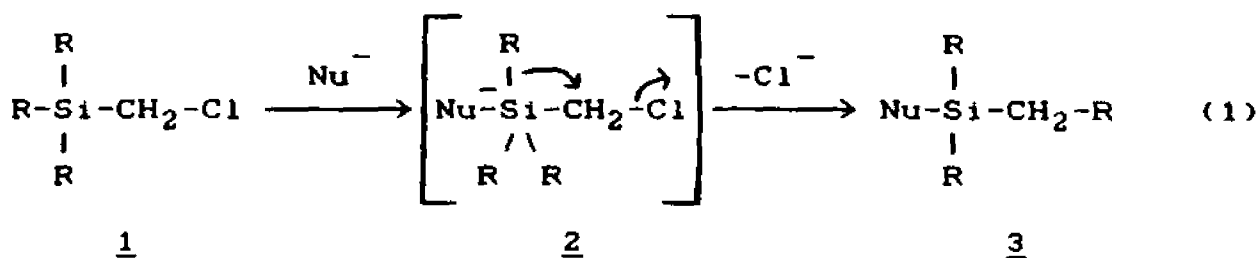
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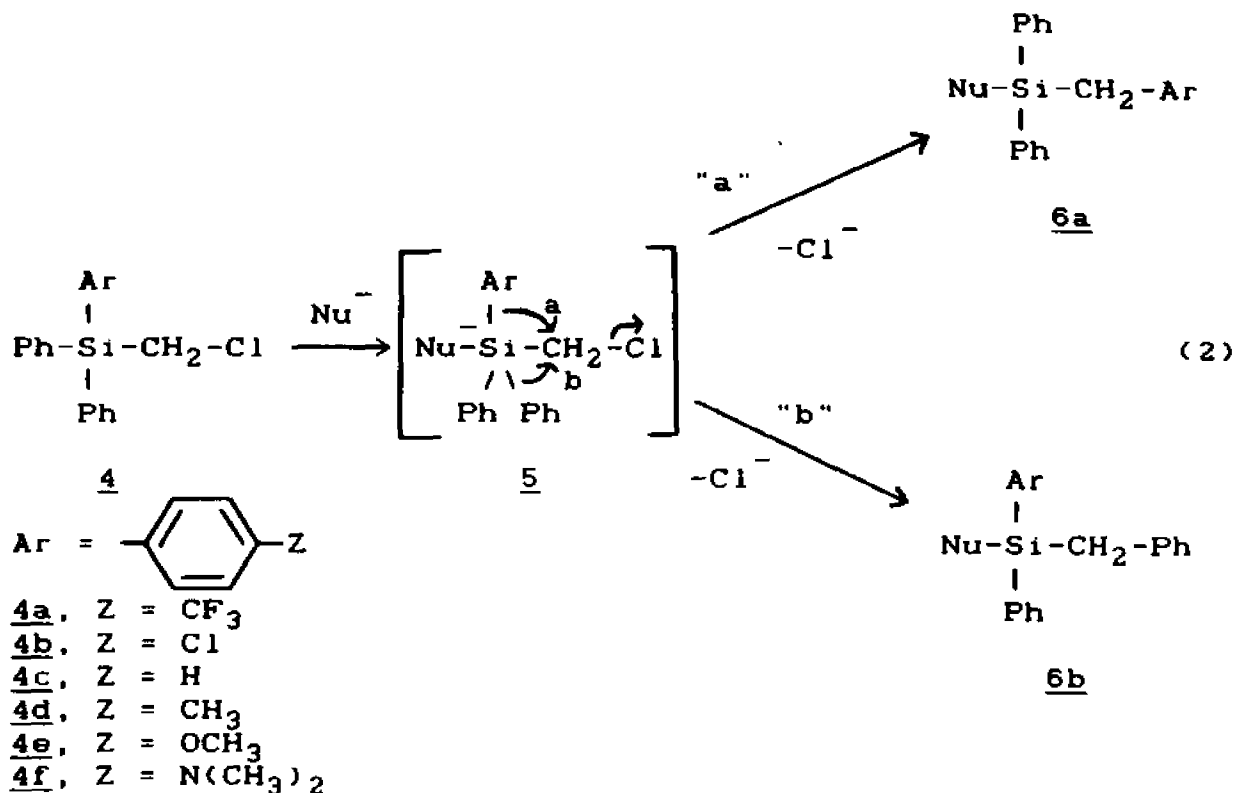
CHAPTER I: STATEMENT OF PROBLEM

The present study involves determination of the migratory aptitudes in rearrangement-displacement of (chloromethyl)trisubstitutedsilanes 1 with nucleophiles at various temperatures (Equation 1). Though previous investiga-



tions,¹ as well as those reported while this work was in progress,^{2,3} indicate that carbanionic features in pentacoordinate silyl processes (Equation 1) control migrations, discrepancies exist in the data and there is speculation that cationic features are important in the rearrangement-displacements.^{4,5}

The purpose of this research, therefore, is to determine the electrical requirements for rearrangement-displacement of pentacoordinate silicon 5 as in Equation 2. The electronic effects were studied by use of aryl(chloromethyl)diphenylsilanes 4, where aryl refers to a



para-substituted-phenyl group. Silanes 6a are formed by aryl migrations and 6b result from phenyl migrations in 5. Migratory aptitudes for various substituted-phenyls could thus be determined by examining the product ratios of 6a to 6b. The rearrangement-displacements were also conducted at different temperatures to study any temperature dependency in the reactions.

CHAPTER II: HISTORICAL

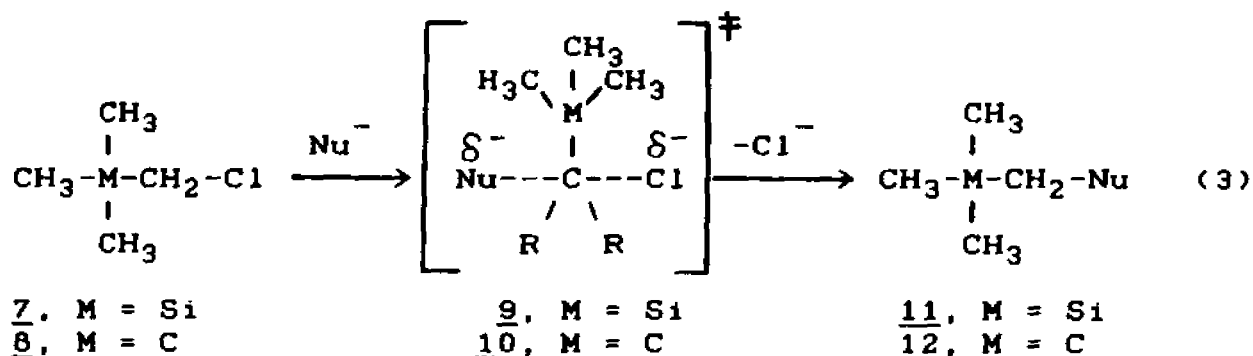
When the first organosilane, tetraethylsilane, was prepared by Friedel and Crafts in 1863,⁶ it was never dreamed that organosilanes would be of any value in organic chemistry. In fact, Kipping, one of the pioneers in the preparation of organosilanes, concluded as late as 1937:

Most if not all of the known types of organic derivatives of silicon have now been considered and it may be seen how few they are in comparison with those which are entirely organic; as moreover the few which are known are very limited in their reactions, the prospect of any immediate and important advance in this section of organic chemistry does not seem to be very hopeful.⁷

In the last two decades, however, the use of silicon in organic chemistry⁸ as well as in other fields⁹ has increased dramatically. The interest in organosilicon compounds has increased so rapidly that since 1973 Annual Surveys of Organosilicon Chemistry have been divided into four topics: *Synthesis and Reactivity*,¹⁰ *Bonding and Structure*,¹¹ *Applications to Organic Synthesis*¹² and *Reaction Mechanisms*.¹³ Since 1980 an Annual Survey of *Silicon: The Silicon-Carbon Bond*¹⁴ has also been published.

More recently, attention has been focused on carbon-functional organosilicon compounds and their abilities to extend the properties and the applications of silicon compounds.¹⁵ Some carbon-functional organosilicon compounds even exhibit biological activity.¹⁶ (Halomethyl)-trisubstitutedsilanes are one such class of carbon-functional organosilicon compounds that has received special attention.¹⁷

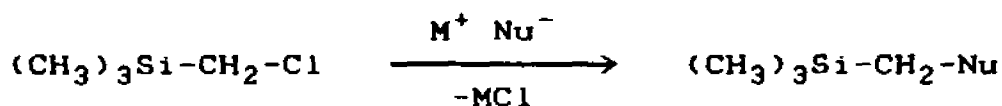
The reactions of nucleophiles with (halomethyl)trisubstitutedsilanes are multi-faceted in that there are many sites for attack. Whitmore and Sommer¹⁸ found that (chloromethyl)trimethylsilane (7) is much more reactive to nucleophiles than its carbon-analog neopentyl chloride (8, Equation 3). This difference is presumed to be due prima-

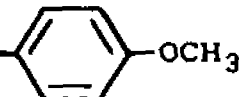
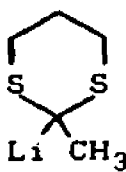



rially to the longer carbon-silicon bond in 7 (1.90 Å¹⁹) as compared to the carbon-carbon bond in 8 (1.54 Å²⁰). The difference in the bond lengths allows a transition state for reaction as in 9 to be less sterically strained than in 10. Oxygen, nitrogen, sulfur and carbon nucleophiles among

others, can displace chloride ion in 7 efficiently to yield carbon substitution products. Table 1 has some examples of such reactions.

Table 1. Reactions of (Chloromethyl)trimethylsilane (7) with Nucleophiles Resulting in Substitution on Carbon.

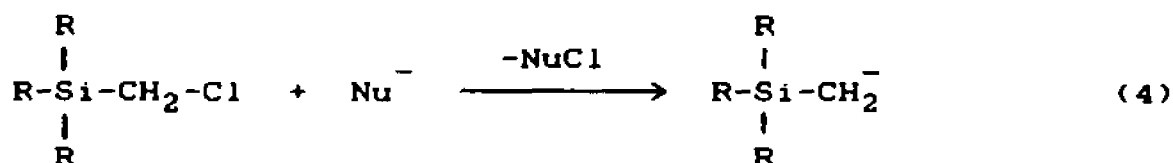


M ⁺ Nu ⁻	Solvent	Yield	Reference
NaOCH ₃	CH ₃ OH	75%	(21)
KO ₂ CCH ₃	CH ₃ CO ₂ H	92	(22)
KSCN	CH ₃ COCH ₃	90	(23)
NaS- 	a	70	(24)
C ₆ H ₁₁ NH ₂	neat	90	(25)
NaN ₃	[(CH ₃) ₂ N] ₃ PO	95	(26)
NaCH(CO ₂ C ₂ H ₅) ₂	C ₂ H ₅ OH	69 ^b	(27)
		a	(28)
NaI	CH ₃ COCH ₃	70	(18)
[NaSeC ₆ H ₅]	CH ₃ OH	90	(29)

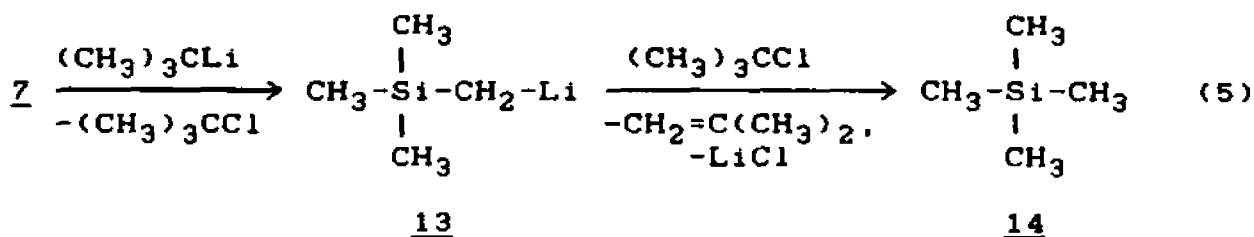
^aNot reported.

^bAfter hydrolysis with KOH and acidification (HCl).

Since strong bases (Nu^-) frequently attack halogen in carbon systems to give metal-halogen exchange, analogous chemistry might be expected for silicon systems (Equation 4). Indeed 7 reacts with *tert*-butyllithium to produce



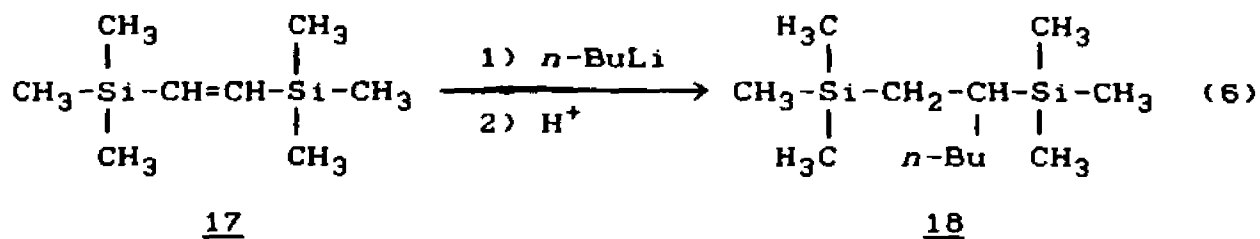
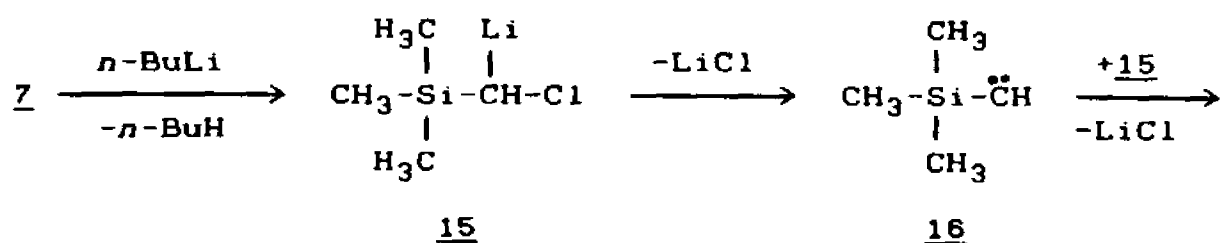
tetramethylsilane (14) and isobutylene (Equation 5).³⁰



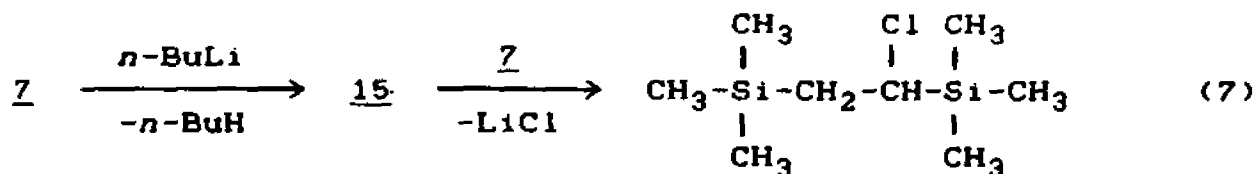
These products apparently result from attack of the alkyl-lithium on (chloromethyl)silane 7 to give *tert*-butyl chloride and trimethylsilylmethyl lithium (13). Lithio-base 13 then eliminates hydrogen chloride from *tert*-butyl chloride to produce isobutylene and silane 14.

A nucleophile may also attack an acidic proton on carbon adjacent to both chlorine and silicon in 7.³⁰⁻³⁴ D'ya-konov and coworkers³¹ report that *n*-butyllithium removes a proton in 7 to yield chloro(trimethylsilyl)methyl lithium

(15) which eliminates lithium chloride to form (trimethylsilyl)carbene (16, Equation 6). Reaction of 15 and 16 with elimination of lithium chloride is presumed to produce 17. Addition of *n*-butyllithium to olefin 17 gives 18 after acidification. Products of intramolecular reaction of 16 were not reported.

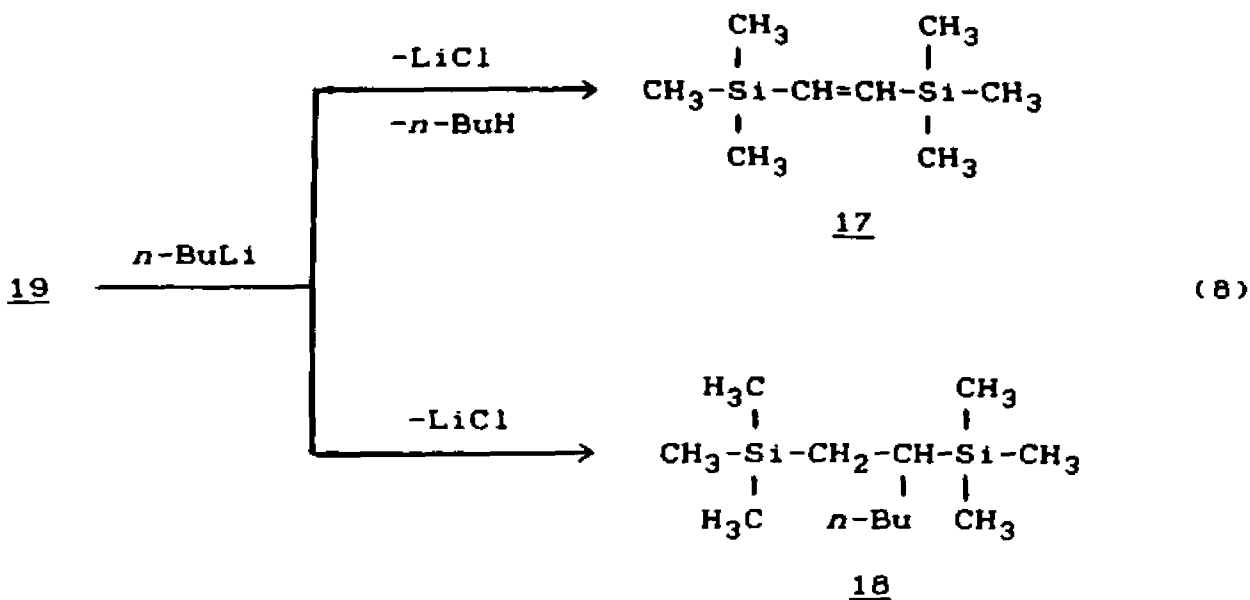


Products 17 and 18 may also have been formed by mechanisms that do not involve carbene 16. Formation of 15 by deprotonation of 7 could be followed by coupling of 15 with 7 to yield disilane 19 (Equation 7). Coupling product

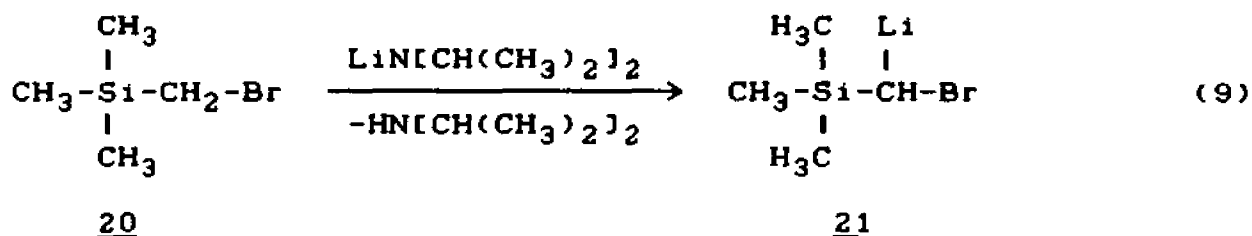


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19 could then react with *n*-butyllithium with elimination of hydrogen chloride to form olefin 17 or be displaced by *n*-butyllithium to yield 18 (Equation 8).



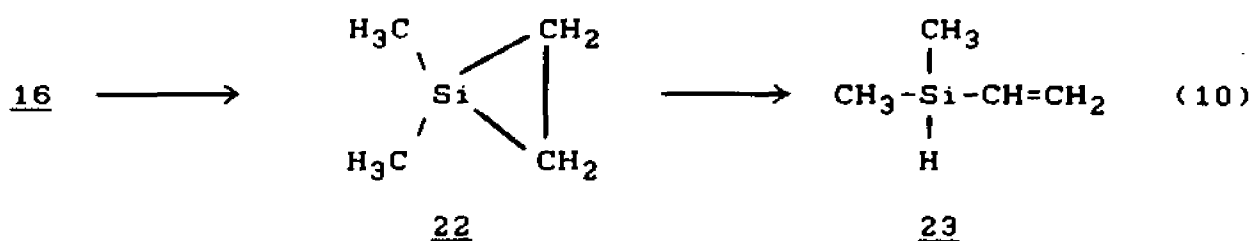
After Kreeger³² reported generation of bromo(trimethylsilyl)methylithium (21) from (bromomethyl)trimethylsilane (20) and lithium diisopropylamide (Equation 9), Magnus



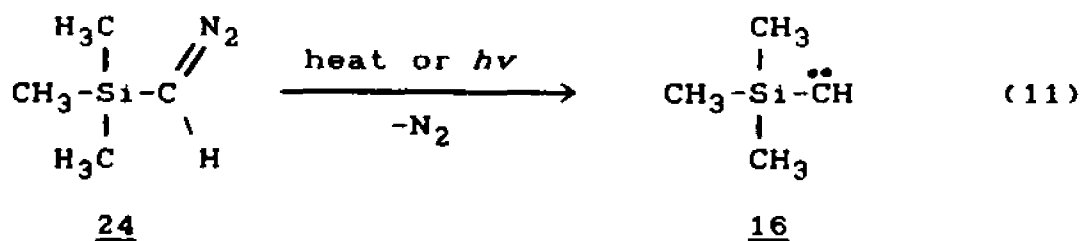
and associates³³ developed preparation of 15 from 7 and *sec*-butyllithium in tetrahydrofuran/tetramethylethylenediamine at -78 °C. *alpha*-Lithio compound 15 was used by Magnus *et al.* to prepare *alpha,beta*-epoxysilanes from

aldehydes and ketones. Under such reaction conditions 15 does not *alpha*-eliminate to give carbene 16.

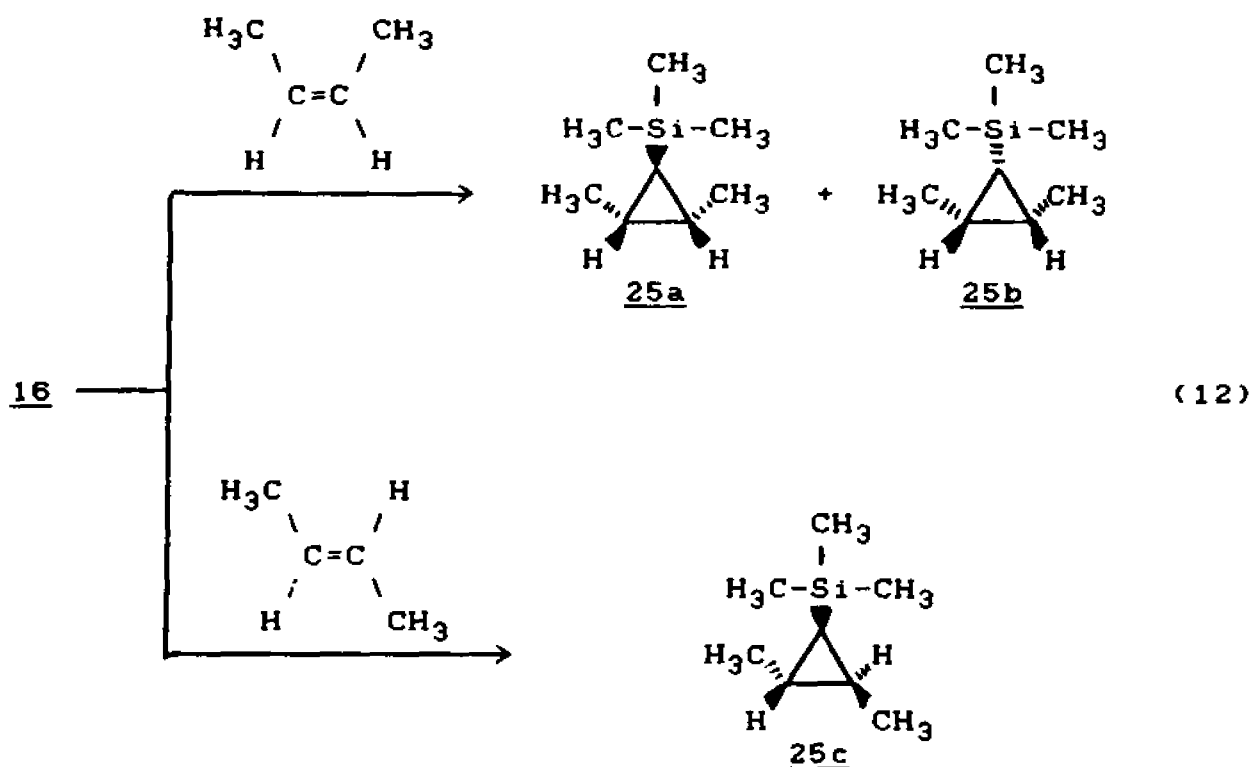
Carbene 16 is reported to be formed in the reactions of (dichloromethyl)trimethylsilane with sodium/potassium in the gas phase at 260-280 °C.³⁵ Intramolecular insertion into a carbon-hydrogen bond of one of the methyl groups in 16 is presumed to give 1,1-dimethyl-1-silacyclopropane (22) which rearranges to dimethylvinylsilane (23, Equation 10).



Reactions of 7 with alkali metals at room temperature are also postulated to involve *alpha*-elimination to give 16 which converts to 22 and its cleavage products.³⁶ The carbene chemistry of 16 has also been investigated via thermolysis^{32,37} and photolysis^{32,37,38} of trimethylsilyldiazomethane (24, Equation 11). Further, nucleophilic

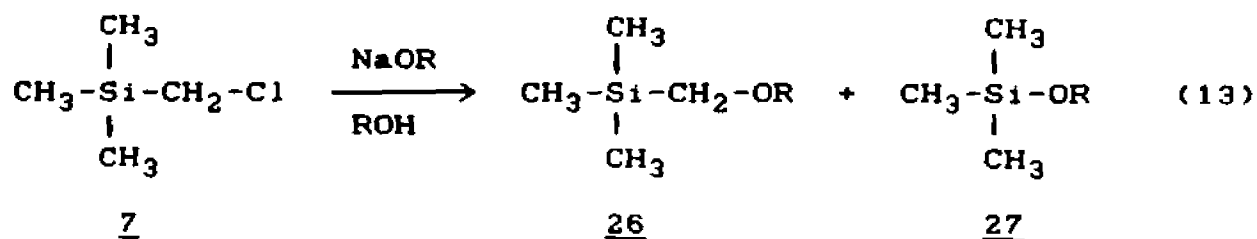


attack on 7 by lithium 2,2,6,6-tetramethylpiperidide (LiTMP) in hexanes involves *alpha*-elimination to 16, which adds stereospecifically to alkenes to give (trimethylsilyl)cyclopropanes 25a-25c (Equation 12).³⁴



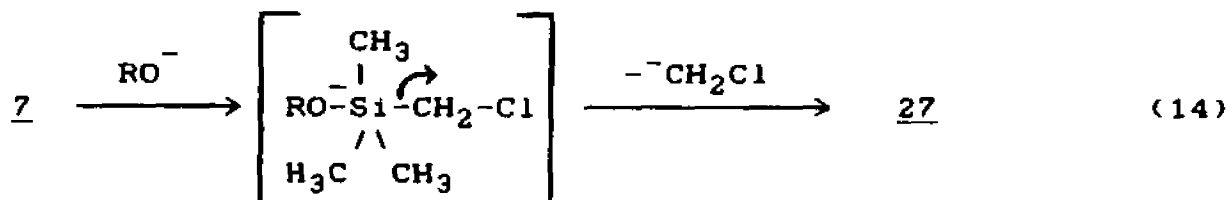
A major difference between 7 and its carbon-analog 8 arises from the electronegativities of silicon and carbon. Carbon has an electronegativity of 2.5³⁹ while silicon's is 1.8.³⁹ Therefore carbon is more electron attracting than silicon and in a carbon-silicon bond, the silicon atom has more positive character. Thus it is not surprising for nucleophiles to attack silicon. In fact reactions of

(chloromethyl)trimethylsilane (7) with alkoxides produce (alkoxymethyl)trimethylsilanes 26 along with alkoxytrimethylsilanes 27 (Equation 13).²¹ Silanes 27 are presumably



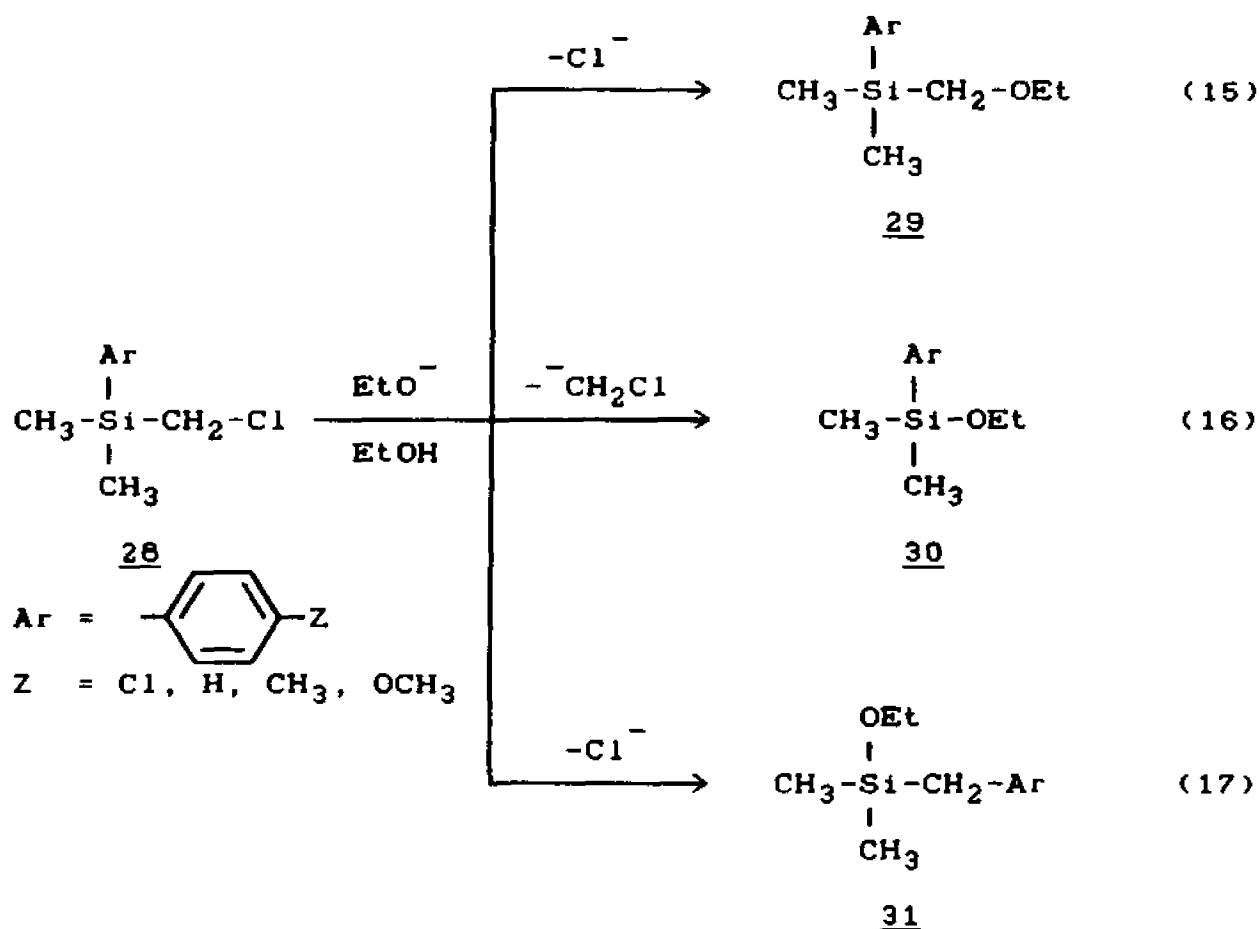
R = CH ₃	75%	0%
CH ₂ CH ₃	70	11
CH ₂ CH ₂ CH ₂ CH ₃	19	31

formed by attack of alkoxides on silicon in 7 with chloromethide ion expulsion (Equation 14). The chloromethide ion is presumed to protonate to methyl chloride. Support for the cleavage process comes from isolation of methyl chloride from reaction of sodium ethoxide with 7 in ethanol.⁴⁰

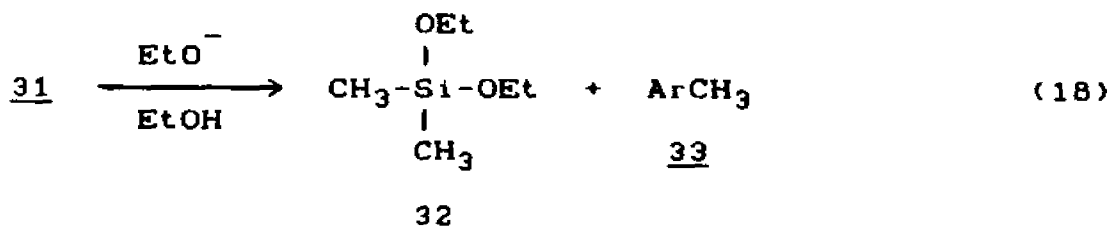


Attack on silicon in (halomethyl)silanes can also lead to interesting rearrangements.⁴¹ It has been found¹ that

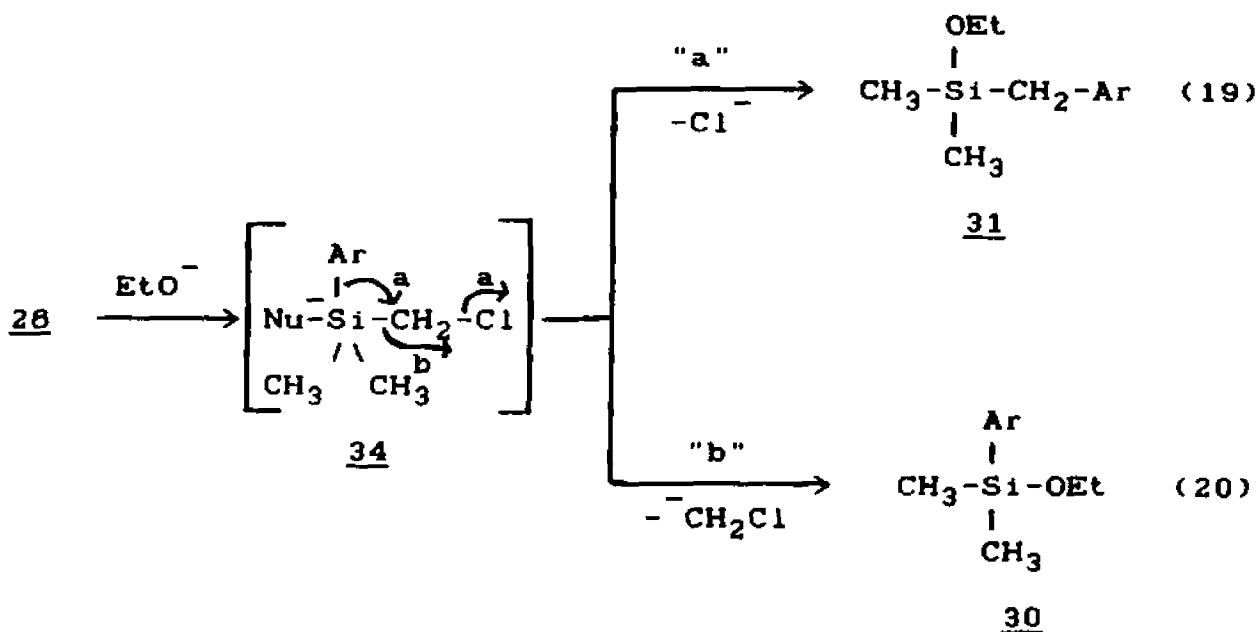
when aryl(chloromethyl)dimethylsilanes 28 react with sodium ethoxide in ethanol several products are obtained. Substitution on carbon produces 29 (Equation 15). Arylethoxydimethylsilanes 30 arise from loss of chloromethide ion (Equation 16). Also produced are (arylmethyl)ethoxydimethylsilanes 31, as formed by migration of the substituted phenyl groups (Equation 17). Further, attack of ethoxide on 31



gives diethoxydimethylsilane (32) and toluene derivatives 33 (Equation 18). It is believed that ethoxide ion attacks



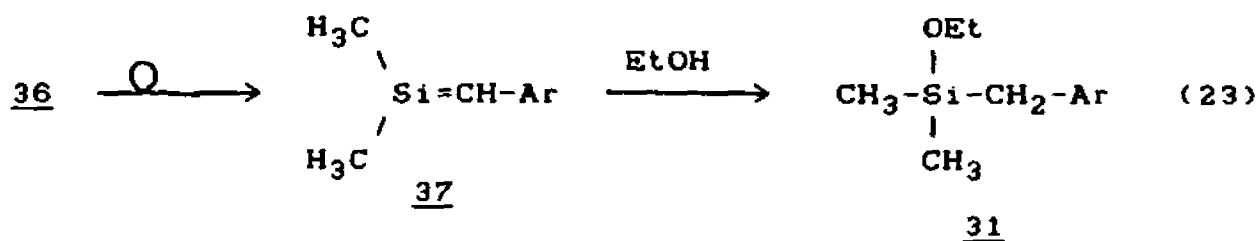
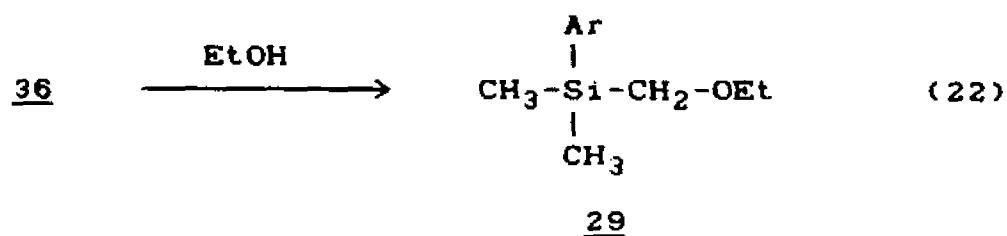
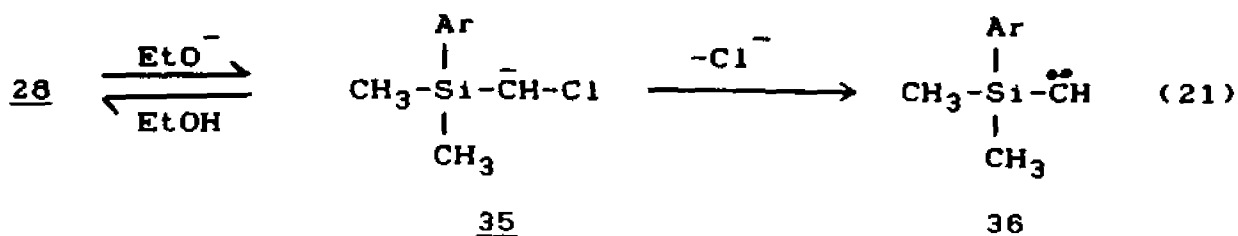
on silicon to form pentacoordinate adduct 34 which either rearranges to give 31 (Equation 19) or loses chloromethide ion to form 30 (Equation 20). The exact nature of 34 is



unknown. Kinetic evidence has been obtained for the rate determining formation of an actual intermediate.⁴² For convenience, 34 and similar structures are generally represented and referred to as intermediates, though they might actually be transition states.

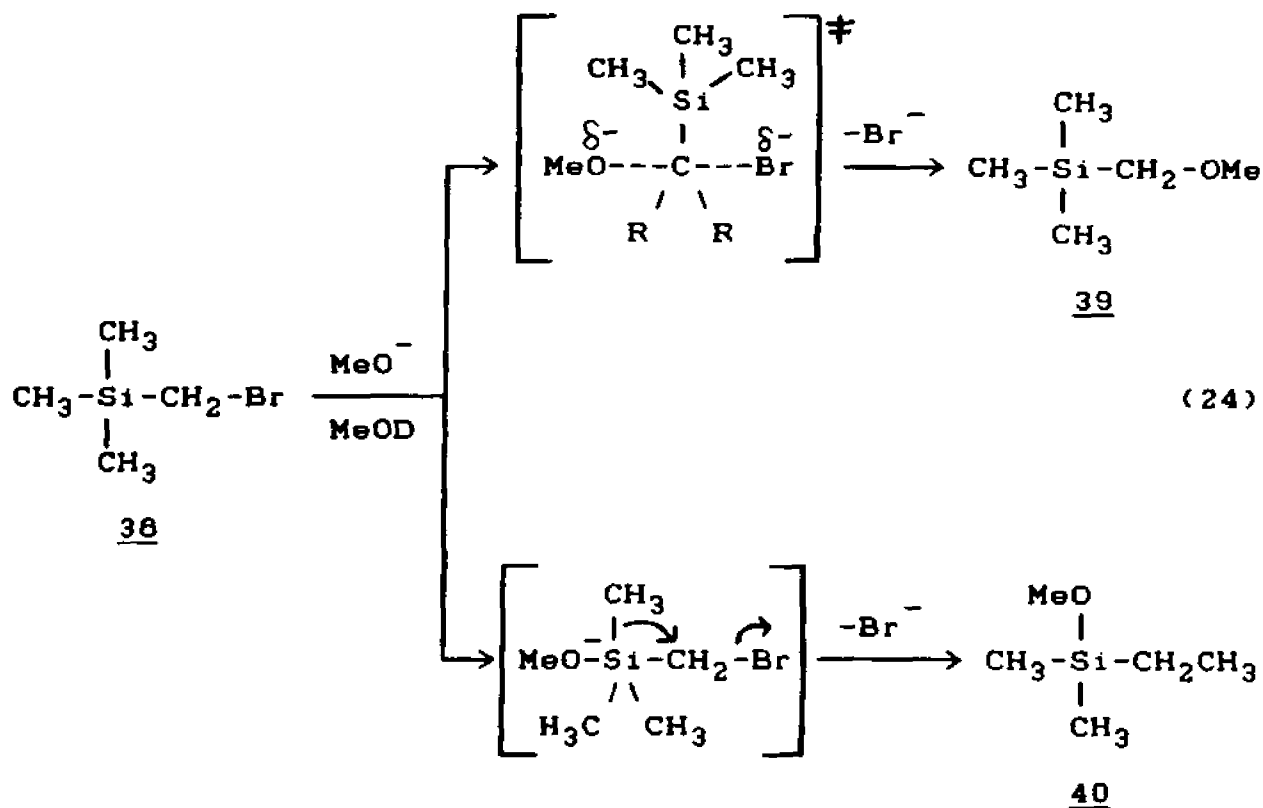
Another possible mechanistic scheme involves formation of aryldimethylsilylcarbenes 36 by *alpha*-elimination

of 28 (Equation 21). Carbene 36 would either be trapped by ethanol to yield 29 (Equation 22) or rearrange to sila-alkene 37 which adds ethanol across its silicon-carbon double bond to give 31 (Equation 23).

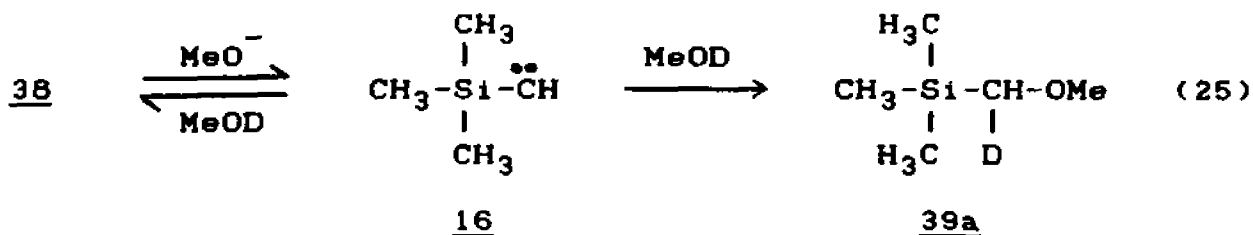


The carbenic mechanism has been examined in reactions of (bromomethyl)trimethylsilane (38) with sodium methoxide in dioxane containing methanol-O-D (~5%).^{30,43} If the alkoxide attacked 38 without forming carbene 16 both the carbon substitution product, (methoxymethyl)trimethylsilane

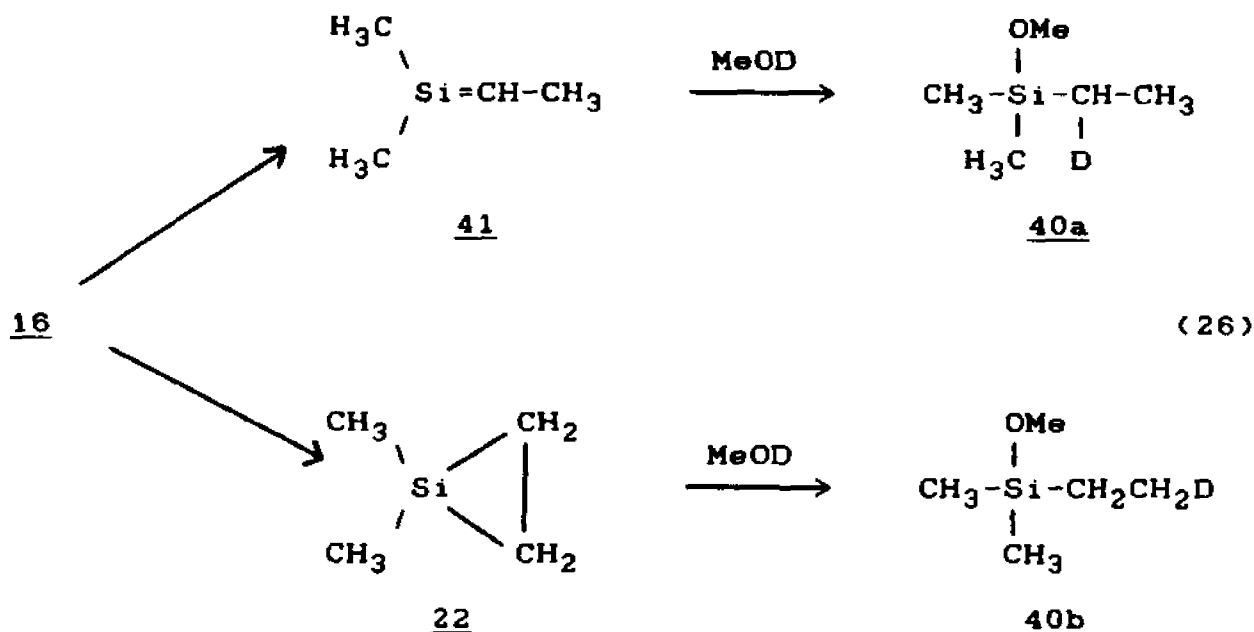
(39) and that derived by attack on silicon with rearrangement-displacement, ethylmethoxydimethylsilane (40, Equation 24), would contain no deuterium. If carbene 16 were formed



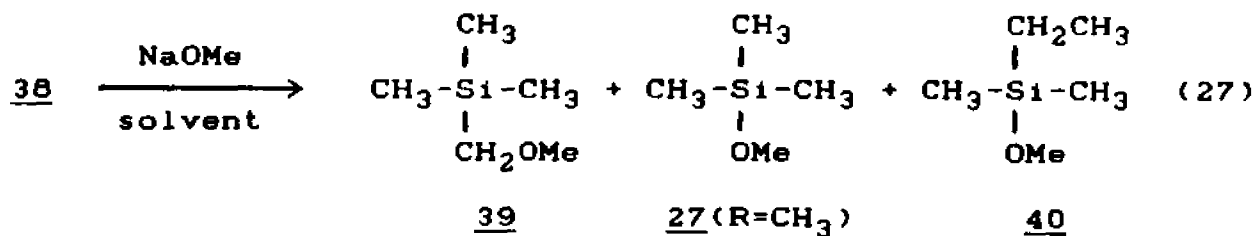
it would be trapped by methanol-O-D to yield deuterated 39 (39a, Equation 25) or else 16 could isomerize to sila-alkene 41 or silacyclopropane 22, either of which would react



with the deuterated solvent to give deuterated 40 (40a and 40b, Equation 26). Indeed, in the above experiment, no deuterium was found in the products or in 38, thus ruling out any process involving 16.

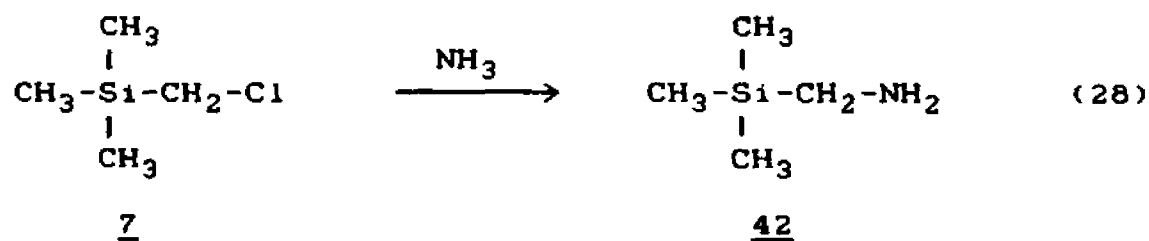


Attack on carbon or silicon in (halomethyl)silanes is dependent on the nucleophile. Reaction of 38 with sodium methoxide in methanol, a protic solvent, yields primarily carbon substitution product 39. When the solvent is aprotic (such as with dioxane or tetrahydrofuran), attack on silicon to give 40 and 27 (R = CH₃) increases (Equation 27).^{30,43} Further the more "naked" the methoxide ion, the greater the attack on silicon.^{2,4,43,44} Thus "hard" nucleophiles attack on silicon whereas "soft" nucleophiles react on carbon.⁴⁵ For example, "softer" liquid ammonia reacts

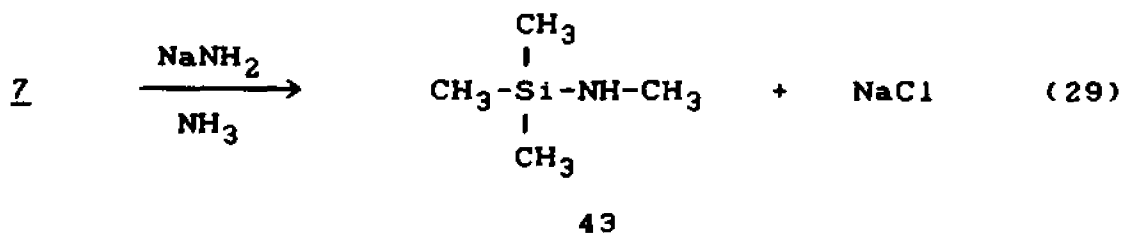


<u>Solvent</u>	<u>39</u>	<u>27 (R=CH₃)</u>	<u>40</u>
MeOH	98%	0.5%	0.0%
50% MeOH/Dioxane	96	1.2	0.3
5% MeOH/Dioxane	24	9	60
Dioxane	1	6	>80

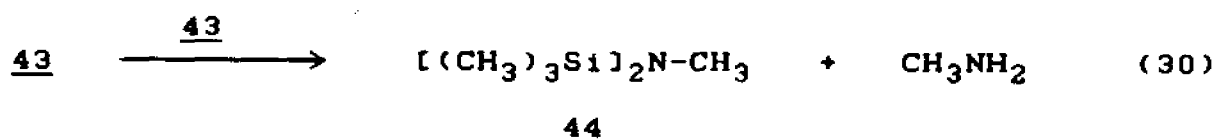
with (chloromethyl)trimethylsilane (7) to form carbon-substitution product 42 (Equation 28) while the "harder" so-



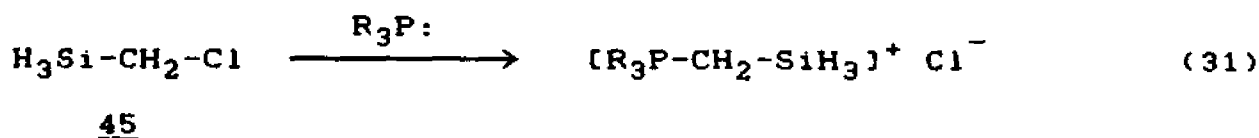
dium amide in liquid ammonia attacks silicon to give methyl(trimethylsilyl)amine (43, Equation 29). Silane 43 then



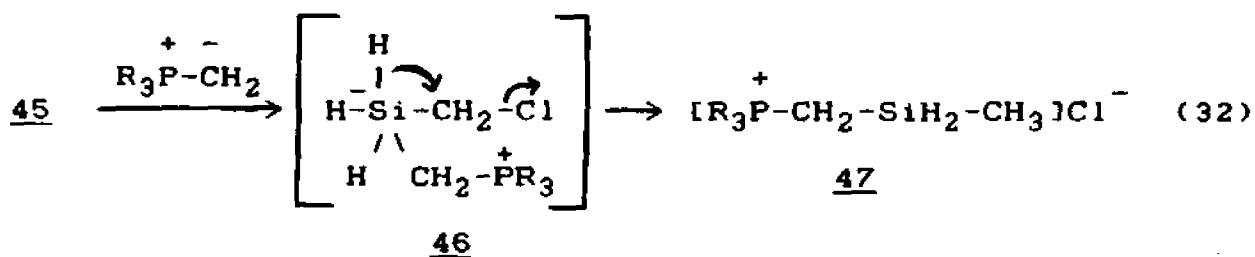
reacts with another molecule of itself to yield methylbis-(trimethylsilyl)amine (44) and methylamine (Equation 30).²⁵



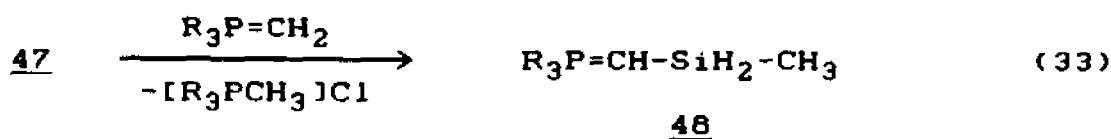
Also, reactions of (chloromethyl)silane (45) with "soft" trialkylphosphines result in attack on carbon (Equation 31), whereas "harder" trialkyl(methylene)phosphoranes



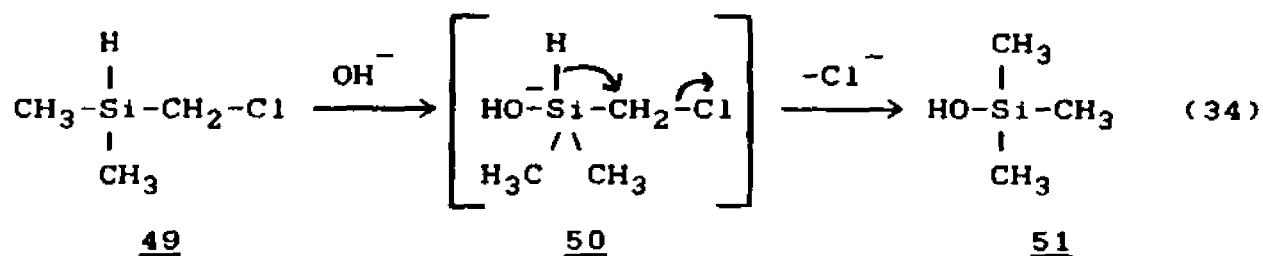
react on silicon to give intermediates 46, which migrate hydride with loss of chloride to form [(methylsilyl)methyl]phosphonium salts 47 (Equation 32). Phosphonium salts



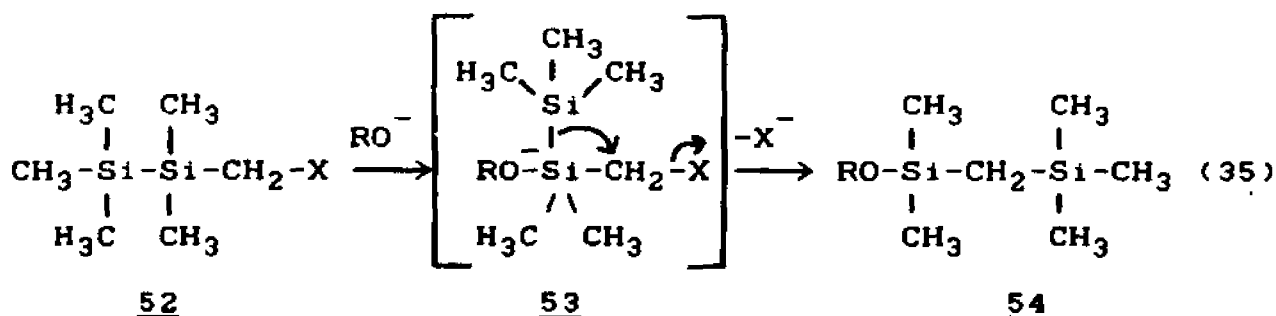
47 are then transformed into [(methylsilyl)methylene]phosphoranes 48 (Equation 33).⁴⁶



Sommer⁴⁷ reported that reaction of (chloromethyl)dimethylsilane (49) with ethanolic potassium hydroxide yields trimethylsilanol (51) via pentacoordinate silicon intermediate 50 (Equation 34).

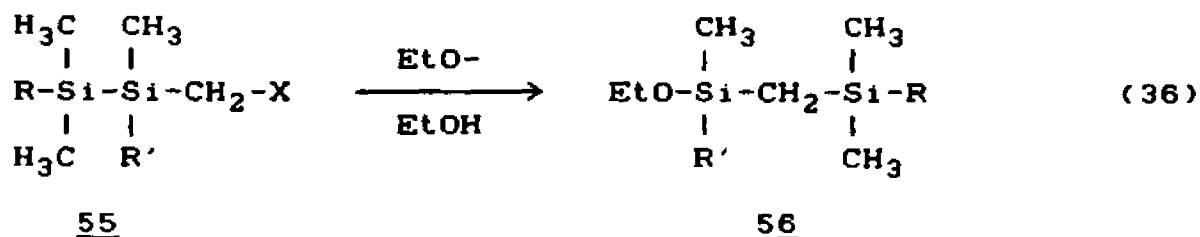


Similarly, reactions of (chloromethyl)pentamethyldisilane (52) with sodium alkoxides in alcohols lead to migration of the trimethylsilyl group to form alkoxydimethyl-[(trimethylsilyl)methyl]silanes 54 (Equation 35).⁴⁸ Silyl



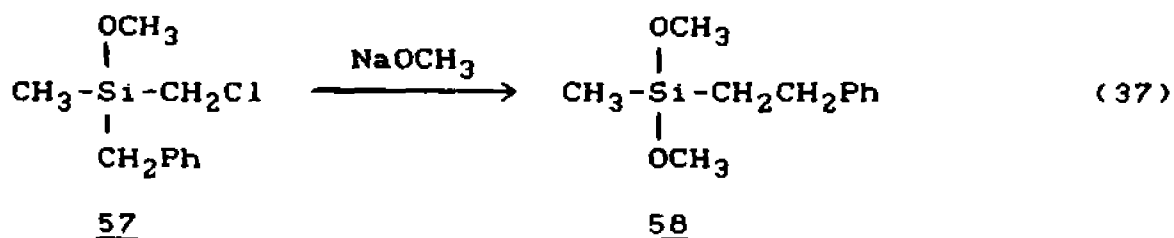
X = Cl; R = CH₃, CH₃CH₂, (CH₃)₂CH, C₆H₅

migration also occurs with (halomethyl)trimethyldiorganodisilanes 55 (Equation 36).⁴⁹ Phenyl or methyl migration was not noted.

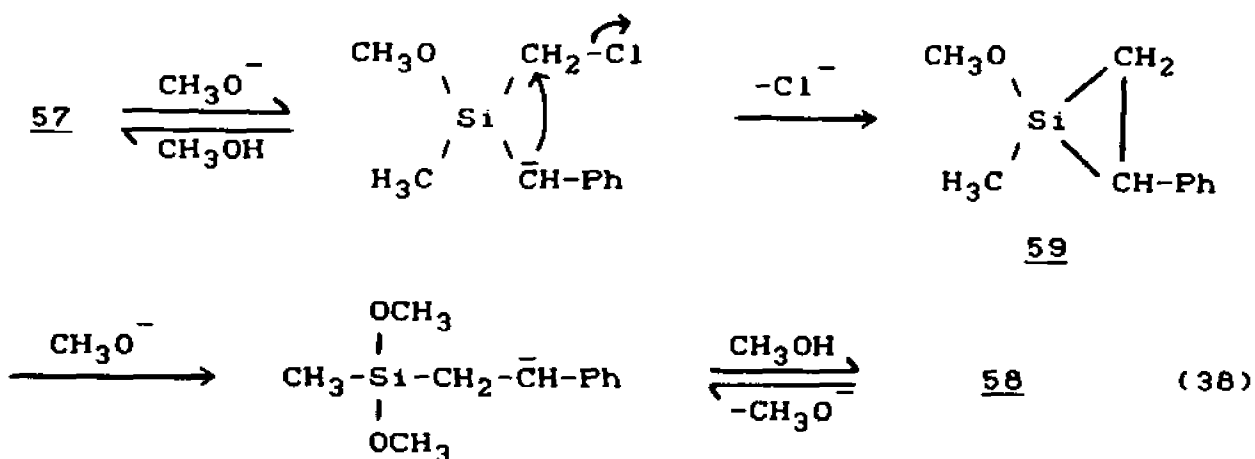


R = CH₃, C₆H₅
 R' = CH₃, C₆H₅
 X = Cl, Br, I

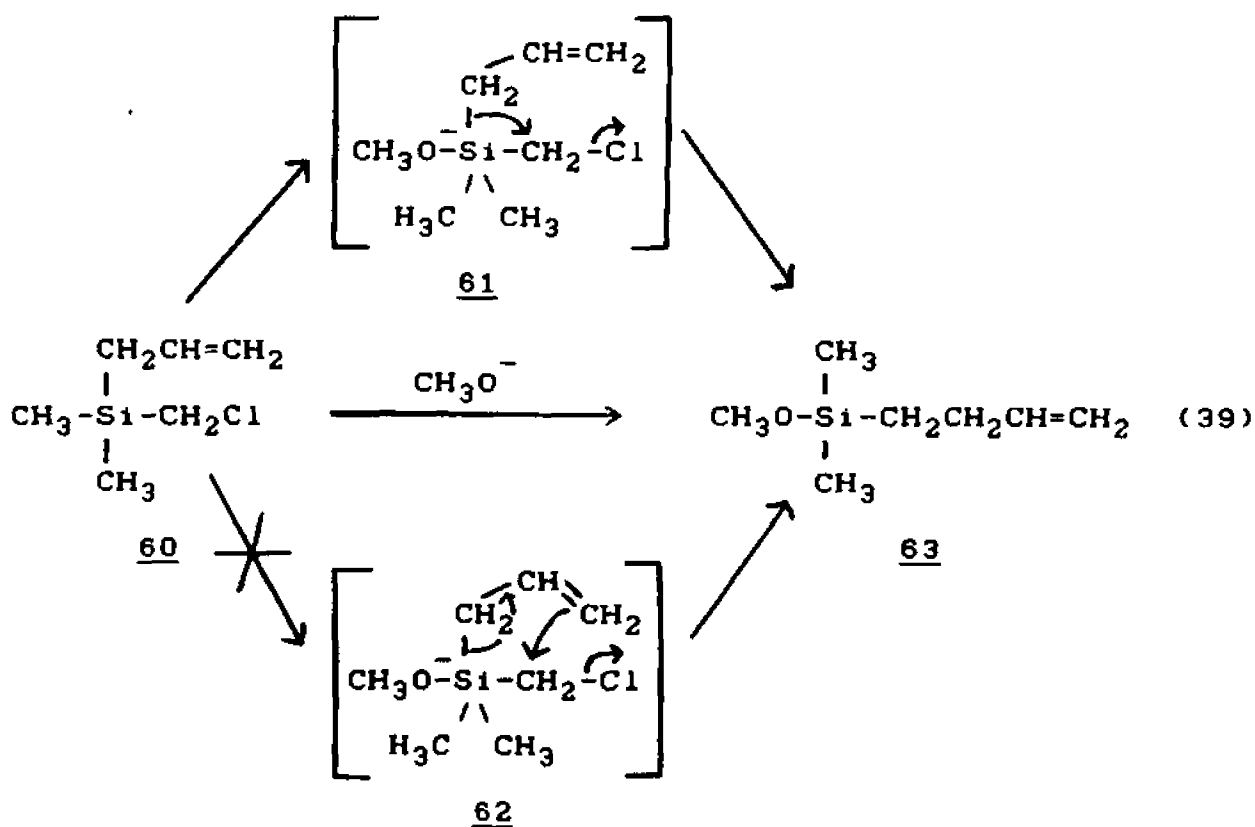
Benzyl migration has been found in the reaction of benzyl(chloromethyl)methoxymethylsilane (57) with sodium methoxide in that dimethoxymethyl(2-phenylethyl)silane (58) is obtained (Equation 37).⁵⁰ The mechanism proposed for



formation of 58 does not involve pentacoordinate silicon. It has been suggested that 58 is formed from silacyclopropane 59 by ring opening and protonation (Equation 38). It is, however, possible that the mechanism does involve rearrangement-displacement.

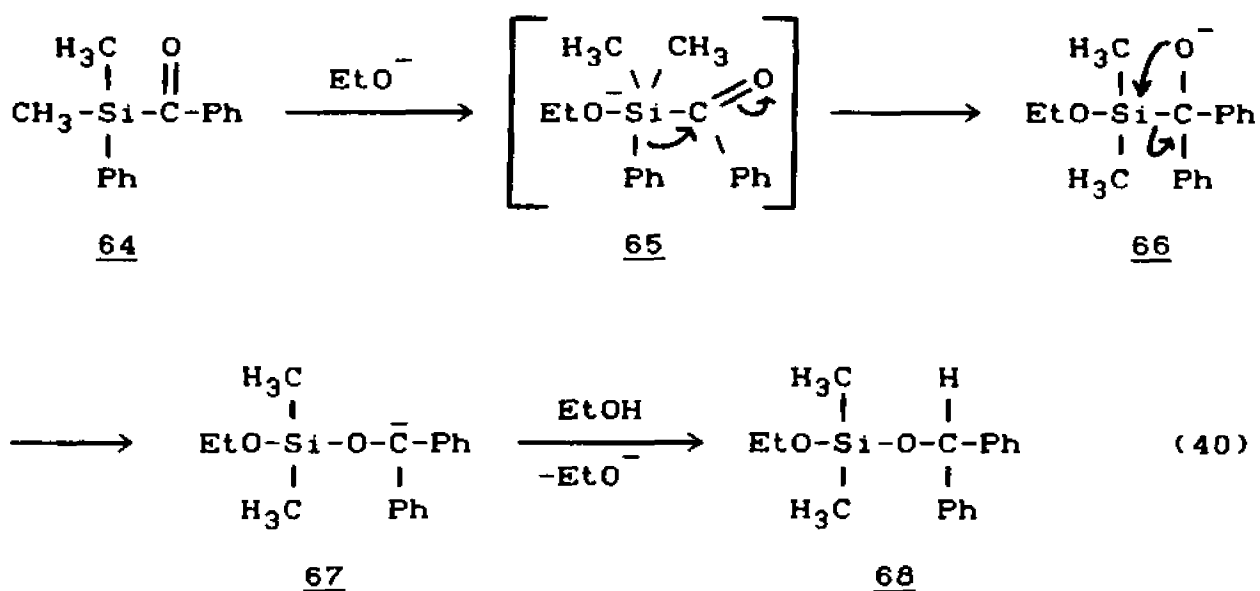


Alkoxide induced migration of hydride in (halomethyl)-silanes has been studied in some detail.^{45,51,52} Migrations of methyl,^{2,4,30,32,43,53} aryl,^{1,4} vinyl and allyl^{2,4} groups also occur by reactions of (halomethyl)silanes with alkoxides. Allyl migration (Equation 39) in

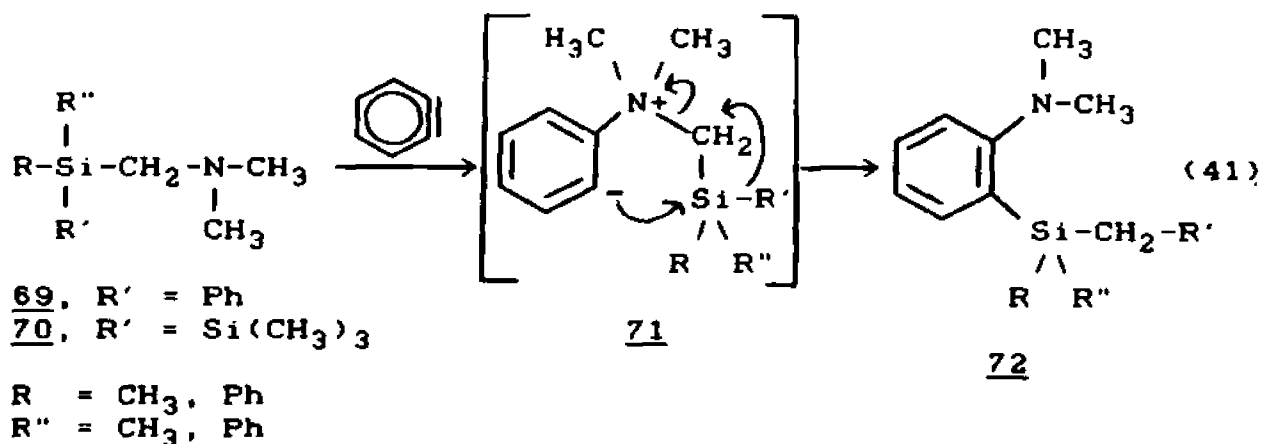


allyl(chloromethyl)dimethylsilane (60) could either occur by 1,2 migration (61) or via a cyclic rearrangement (62) to yield 3-butenylmethoxydimethylsilane (63, Equation 39). Labeling studies proved that migration occurred by 1,2 rearrangement (61).^{2,4}

Nucleophilic rearrangement also occurs in the reaction of benzoyldimethylphenylsilane (64) with sodium ethoxide to yield ethoxydimethyl(diphenylmethoxy)silane (68, Equation 40).⁵⁴ The proposed mechanism is outlined in Equation 40.

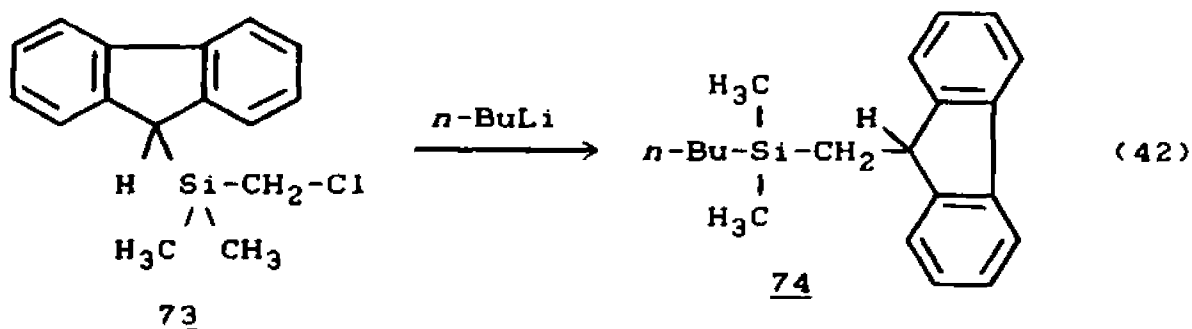


Sato and coworkers⁵⁵ report rearrangements in reactions of [(dimethylamino)methyl]diorganophenylsilanes 69 and [(dimethylamino)methyl](trimethylsilyl)diorganosilanes 70 with benzyne (Equation 41). Addition of an amine to benzyne presumably yields dipolar intermediate 71, which

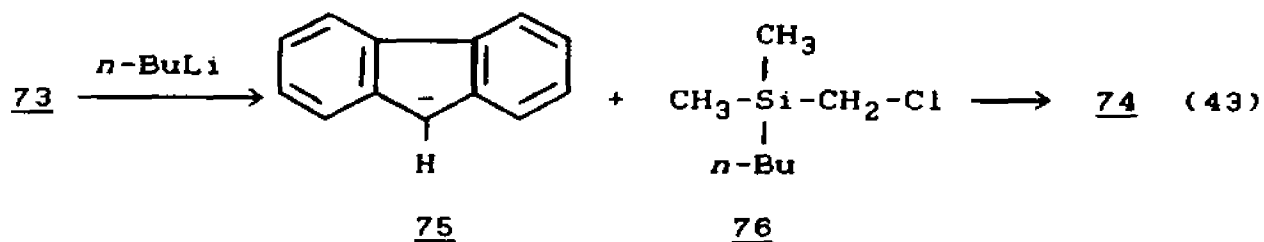


attacks on silicon with migration of R' to yield *ortho*-silyl-N,N-dimethylanilines 72. Migrations of phenyl and trimethylsilyl occur, but methyl migration was not observed.

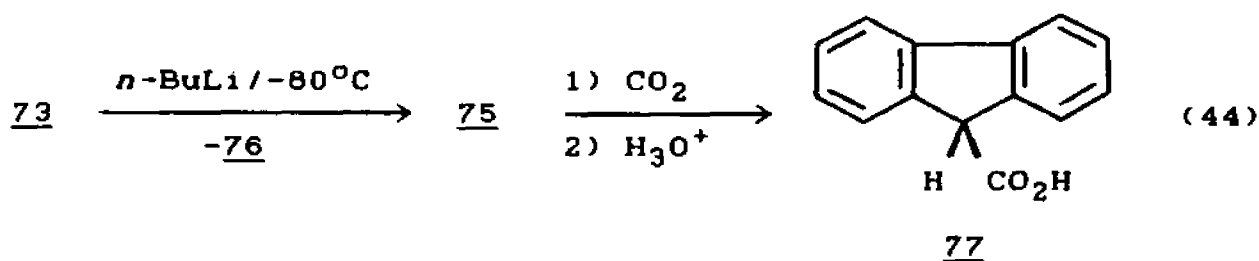
Reaction of (chloromethyl)(9-fluorenyl)dimethylsilane (73) with *n*-butyllithium gives butyl[(9-fluorenyl)methyl]dimethylsilane (74, Equation 42).⁵⁶ This reaction does not



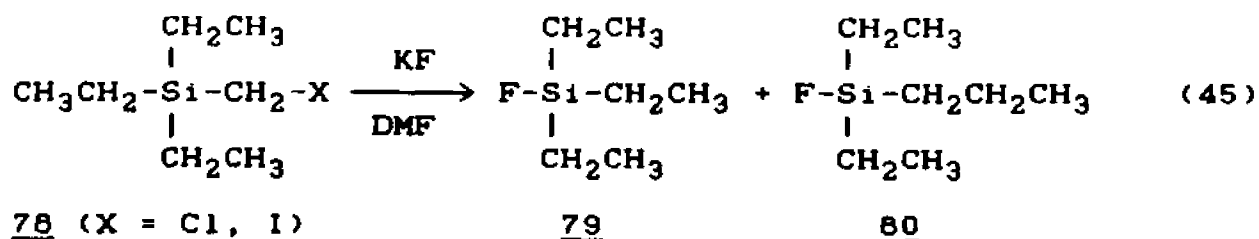
follow the rearrangement-displacement mechanism of previous systems. Displacement of fluorene anion 75 occurs followed by coupling (Equation 43). Evidence for the different mechanism is obtained by trapping 75 with carbon dioxide



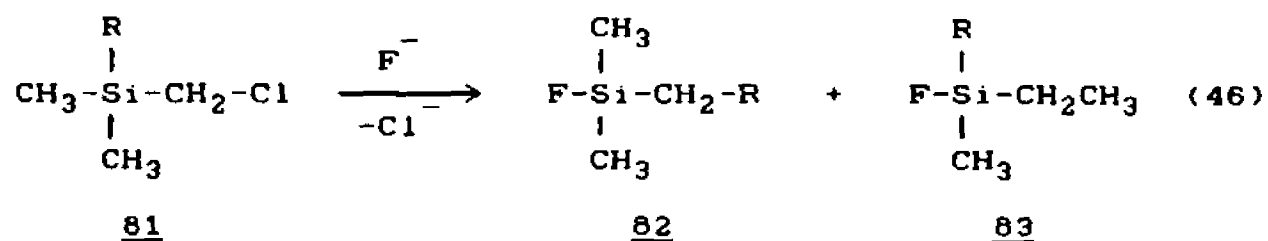
at -80°C to yield 9-fluorene-carboxylic acid (77) after acidification (Equation 44).



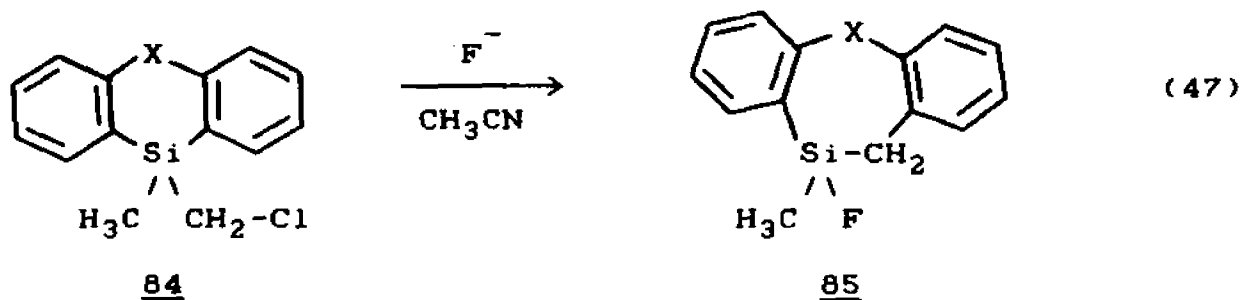
Fluoride ion induces rearrangements of (halomethyl)silanes. Thus (halomethyl)triethylsilanes 78 react with potassium fluoride in dimethylformamide (DMF) to yield the cleavage product, triethylfluorosilane (79) and the rearrangement product, diethylfluoropropylsilane (80, Equation 45).⁵⁷ (Bromomethyl)trimethylsilane (38) behaves similar



to 78 in reactions with potassium fluoride in dimethylformamide or acetonitrile.³⁰ Migrations of vinyl, various alkyl and substituted-phenyl groups have been examined in reactions of (chloromethyl)dimethylorganosilanes 81 with fluoride ion (Equation 46).³



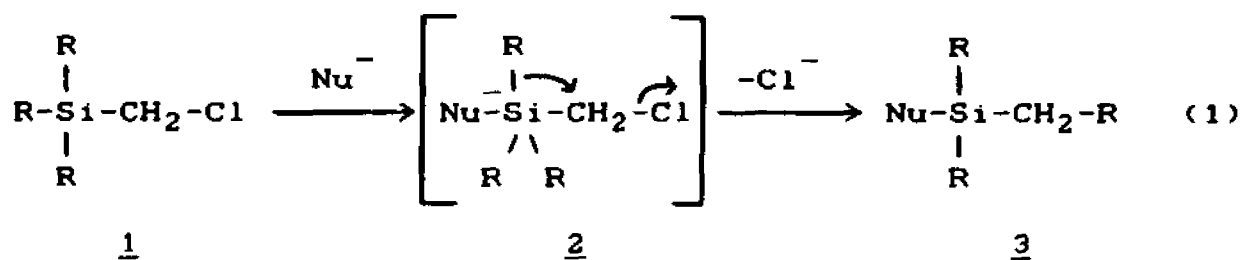
Corey and coworkers^{5,58} have used this rearrangement to advantage in preparing medium-sized rings containing silicon (Equation 47).



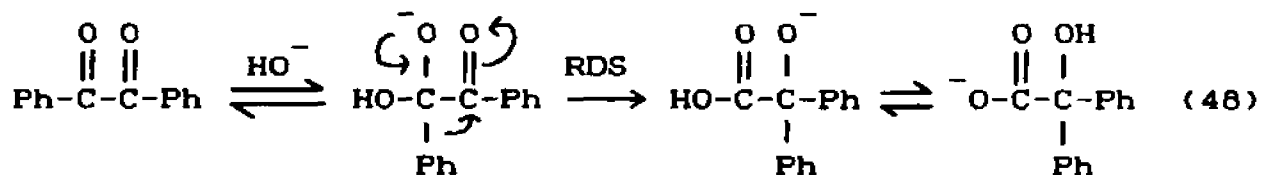
X = CH₂, CH₂CH₂, NCH₃,^a NC₂H₅,^a O, OCH₂, SO₂

^a 2,8-Dibromo Derivative

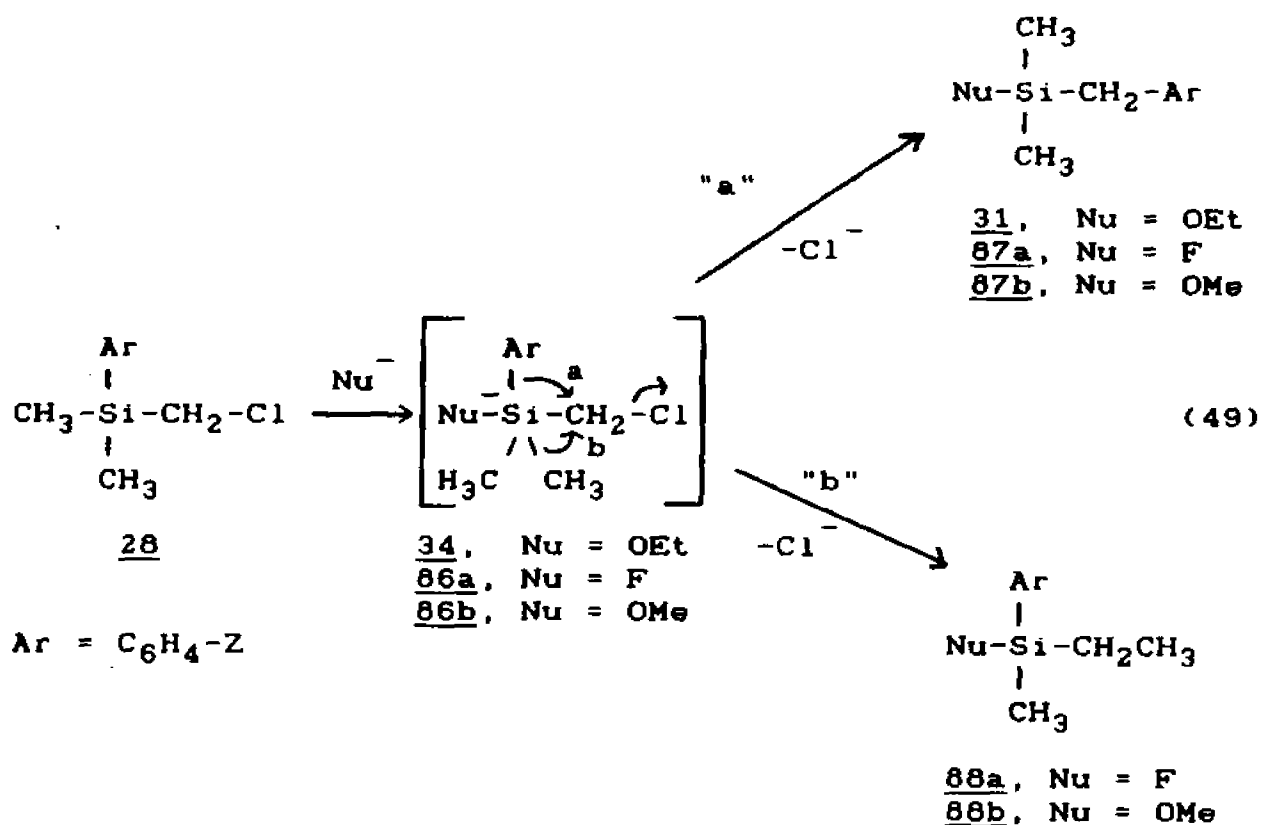
The mechanism proposed for these processes involves initial formation of pentacoordinate silyl intermediates 2 (Equation 1). A substituent then migrates to adjacent



carbon from which chloride is expelled to yield 3. The rearrangement-displacement is analogous to the benzylic acid rearrangement (Equation 48).⁵⁹ The rate-determining-step (RDS) for benzylic acid rearrangement involves



migration of phenyl. Also, substituted-phenyl groups which are more electron-withdrawing migrate better. Thus, it might be expected that more electron-withdrawing substituents on 1 (Equation 1) should also migrate better. Eaborn¹ studied the rearrangement-displacement of aryl(chloromethyl)dimethylsilanes 28 with sodium ethoxide to yield (arylmethyl)ethoxydimethylsilanes 31 (Equation 49) along with



other products. The rates of reaction of starting material leading to rearrangement fall in the order Z = *p*-Cl > H > *p*-CH₃ > *p*-CH₃O. This is what would be expected based on formation of pentacoordinate silyl intermediate 34 as rate determining.

Reactions of 28 with fluoride ion (Equation 49) show a similar trend.^{3b} The rate of disappearance of 28 fall in the order Z = *m*-CF₃ > *p*-Cl > *p*-F > H > *p*-CH₃, suggesting that the ability to stabilize 86a increases the rate of reaction.

The *proportion* of rearrangement of 28 with sodium ethoxide, however, falls in the order $Z = p\text{-Cl} > p\text{-CH}_3 > p\text{-CH}_3\text{O} > \text{H}$,¹ which does not correlate well with the electron-withdrawing capabilities of Z. The aryl/methyl ratios (87b/88b, Equation 49) in the reaction of 28 with sodium methoxide have the same trend: $Z = p\text{-CF}_3 > m\text{-Cl} > p\text{-Cl} > p\text{-CH}_3 > p\text{-OCH}_3 > \text{H}$.⁴ It is noted in both cases that the trend follows electron-withdrawing capabilities except for the unsubstituted-aryl ($Z = \text{H}$) which migrates the worst. It is postulated⁴ that significant carbon-chlorine bond breaking is involved during the rearrangement-displacement (Figure 1). Since the migrating group travels to the developing positive center, stabilization of the positive charge by participation involving the π -system could become dominant. In such cases, phenyls which contain substituents that are more electron-donating will migrate better.

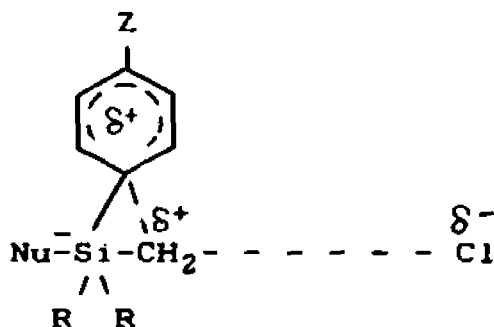
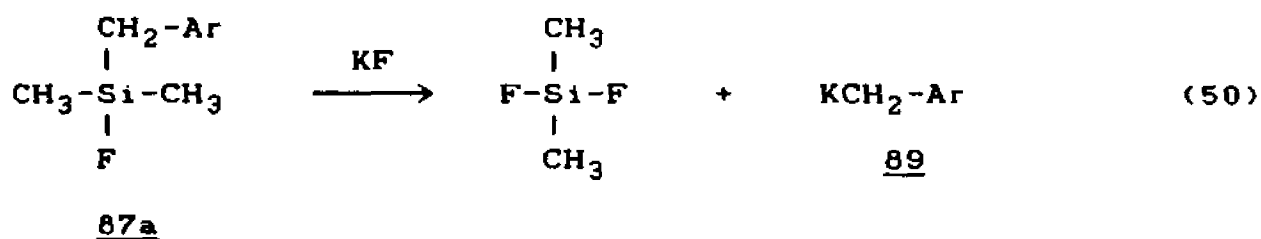
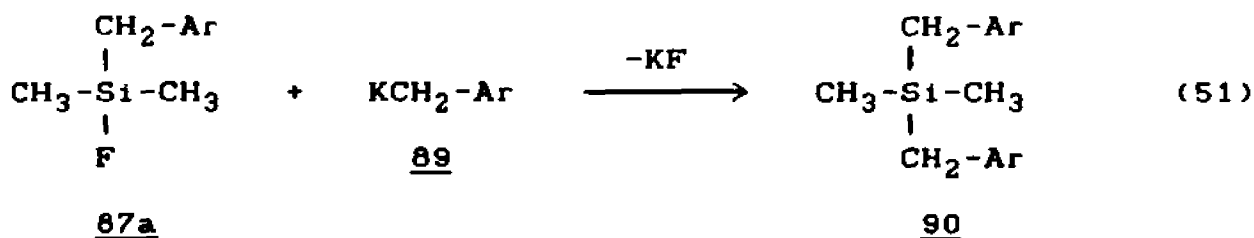


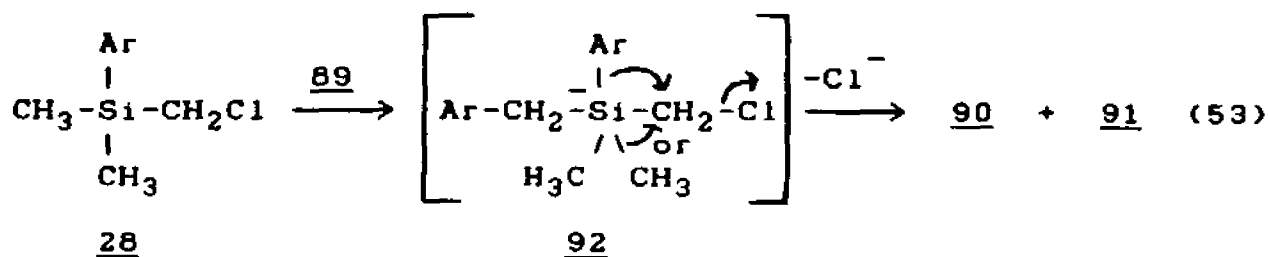
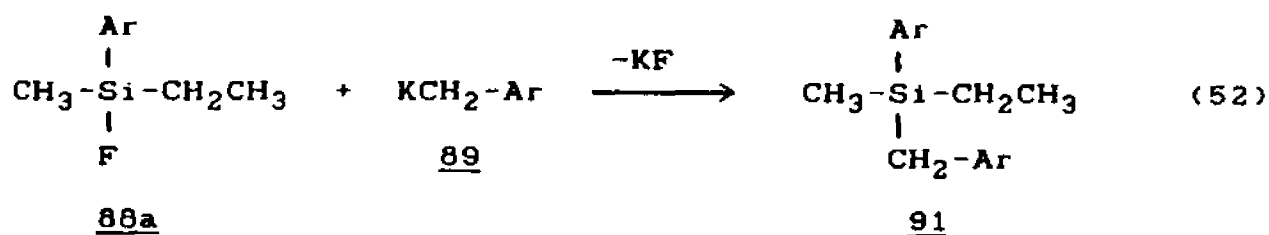
Figure 1. Rearrangement-displacement transition state with significant carbon-chlorine bond breakage.

Attempts to determine the migratory aptitudes (87a/88a) in reactions of 28 with anhydrous potassium fluoride (Equation 49) led to complications.^{3b} The products of displacement with aryl migration, 87a, are cleaved by potassium fluoride to difluorodimethylsilane and potassium salts 89 of substituted-benzyl anions (Equation 50). Metallo



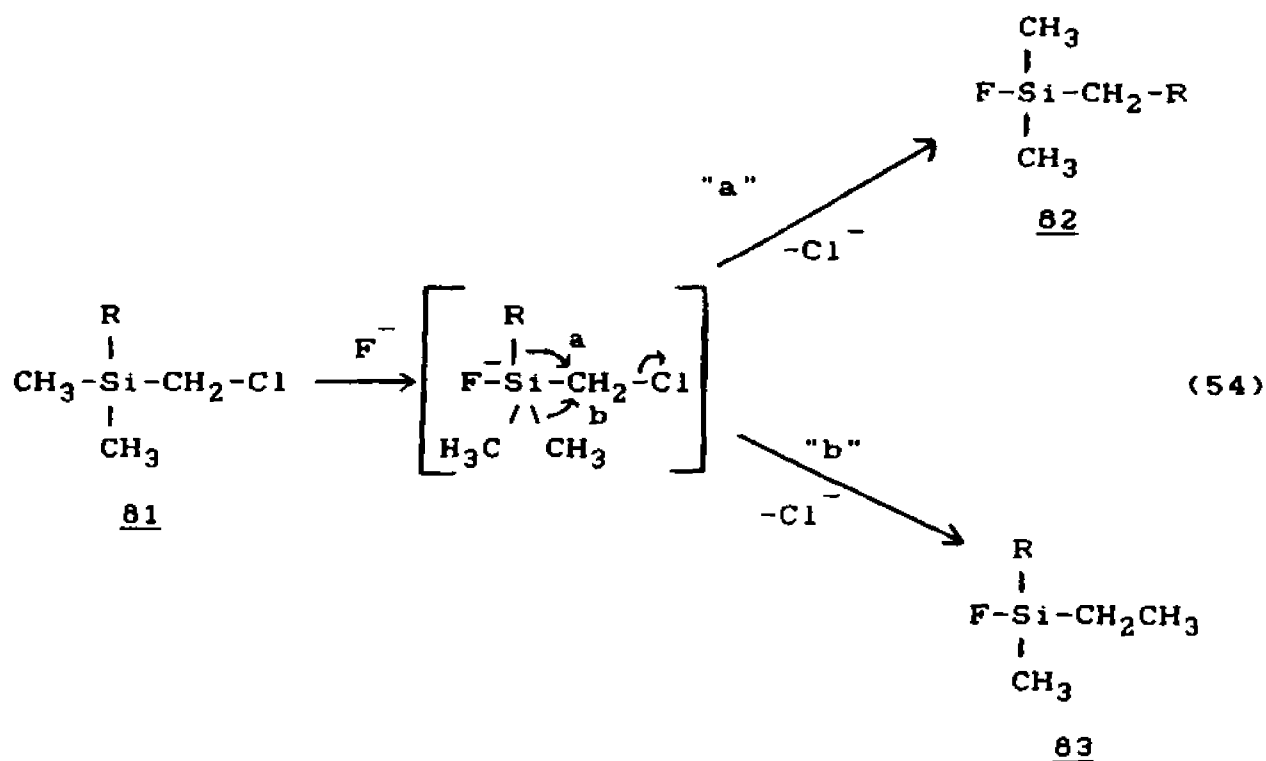
derivatives 89 react further to give products as follows. Displacements of the silicon-fluorine bonds of 87a and 88a by 89 thus yield bis(arylmethyl)dimethylsilanes 90 (Equation 51) and aryl(arylmethyl)ethylmethylsilanes 91 (Equation 52). Metallo derivatives 89 also react with initial (chloromethyl)silanes 28 via pentacoordinate intermediates 92 (Equation 53) to yield 90 and 91.





The data reported^{3b} for reactions of 28 with potassium fluoride as above give migratory aptitudes (Ar/Me) of Z = H > *p*-CH₃ > *m*-CF₃ > *p*-Cl > *p*-F. The correlation coefficient of the regression line calculated⁶⁰ for the logarithm of the migratory aptitudes versus the substituent constants is only 0.21 and thus is very poor.⁶¹ Therefore, the general trend in the data does not support any conclusions based on the electronic effects in the rearrangement-displacements.

Migratory aptitudes from pentacoordinate silicon have also been examined for groups which are non-aryl. Product ratios were determined in reactions of (chloromethyl)dime-thylorganosilanes 81 with fluoride ion (Equation 54).^{3a} Migratory aptitudes leading to 82/83 decrease in the order R = CH₂=CH > C₆H₅ > *c*-C₃H₅ > C₂H₅ > CH₃ > *n*-C₄H₉ > *i*-C₃H₇. The results support the postulate that groups which are



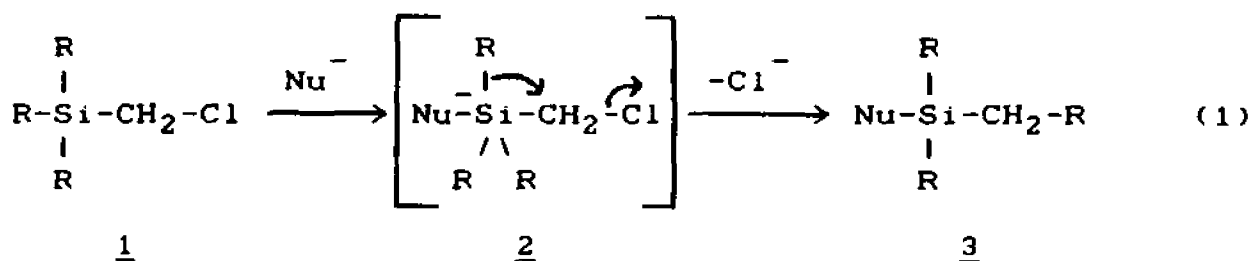
more electron-withdrawing migrate better from pentacoordinate silicon. It is noted, however, that the migratory aptitudes give correlations with very large deviations.⁶²

In the present summary, it has been illustrated that (halomethyl)trisubstituted silanes react with nucleophiles in a variety of ways. The rearrangement-displacement processes involving attack on silicon have been examined to determine the electronic effects. The latter results obtained have been inconclusive, however, and the purpose of this research is to study the electronic effects in rearrangement-displacements in more detail.

CHAPTER III: . RESULTS

INTRODUCTION

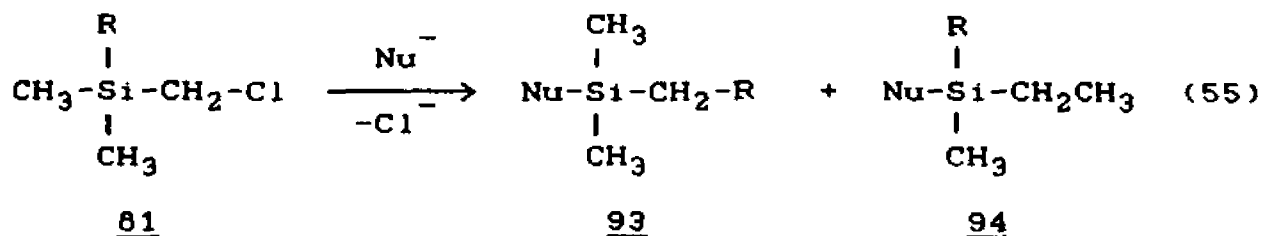
Nucleophilic attack on silicon in (chloromethyl)tri-substitutedsilanes 1 presumably leads to negatively charged pentavalent silyl adducts 2 (Equation 2). It is unclear, however, whether 2 is actually an intermediate or a transition state. In the present dissertation 2 is generally written and discussed as if it were an intermediate. Migration of a substituent from silicon to adjacent carbon with chloride expulsion is one pathway that intermediates such as 2 may take (Equation 1).



Negatively-charged intermediates 2 are presumably stabilized by electron-withdrawing substituents bonded to silicon. Since the substituent migrates with negative charge from silicon to carbon, it might be presumed that the migratory aptitude of a substituent depends on its

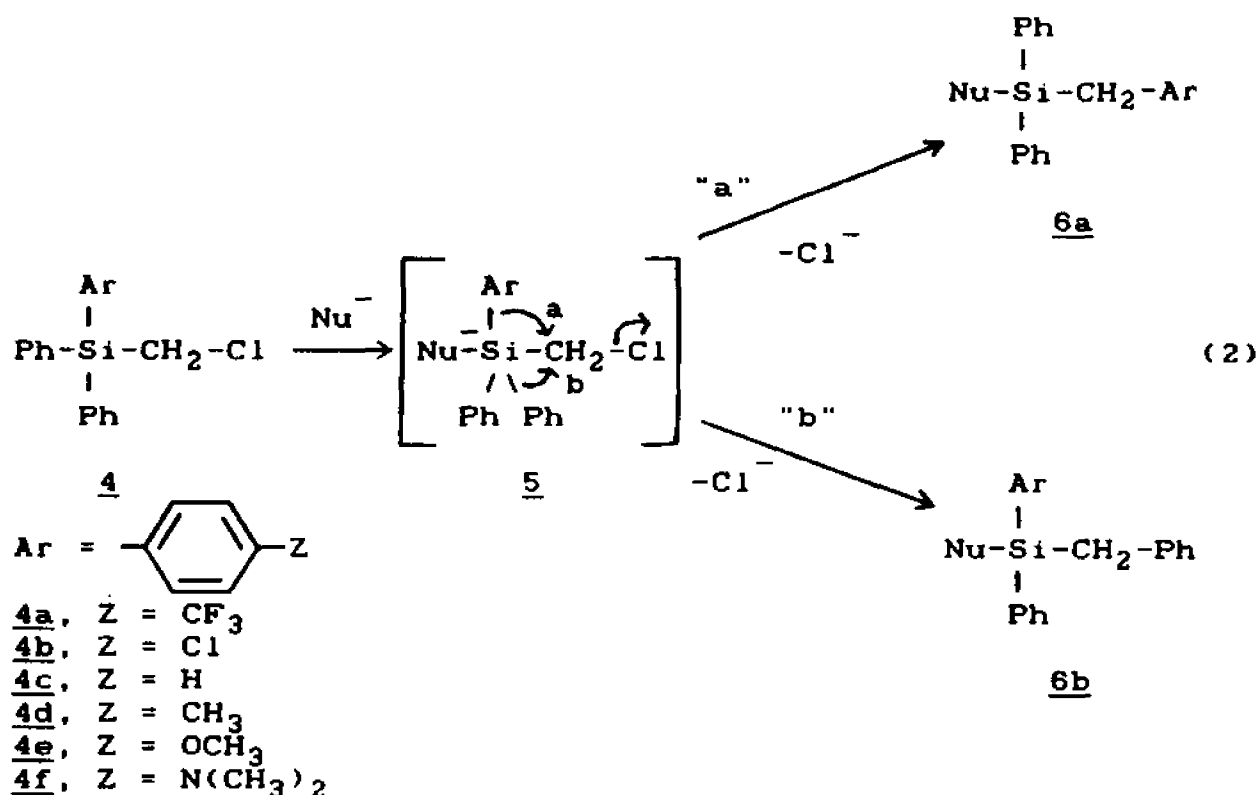
ability to stabilize negative charge. As summarized earlier (see Chapter II: Historical) there is some evidence for carbanionic control in rearrangements from silicon.¹⁻⁴ Results have also been obtained which indicate that positive character at carbon to which the substituent migrates is significant.^{4,5}

Earlier investigators¹⁻⁴ studied migrations in varied (chloromethyl)dimethylorganosilanes 81 (Equation 55). It



R = CH₂=CH-CH₂, CH₂=CH, C₆H₄-Z, various alkyl

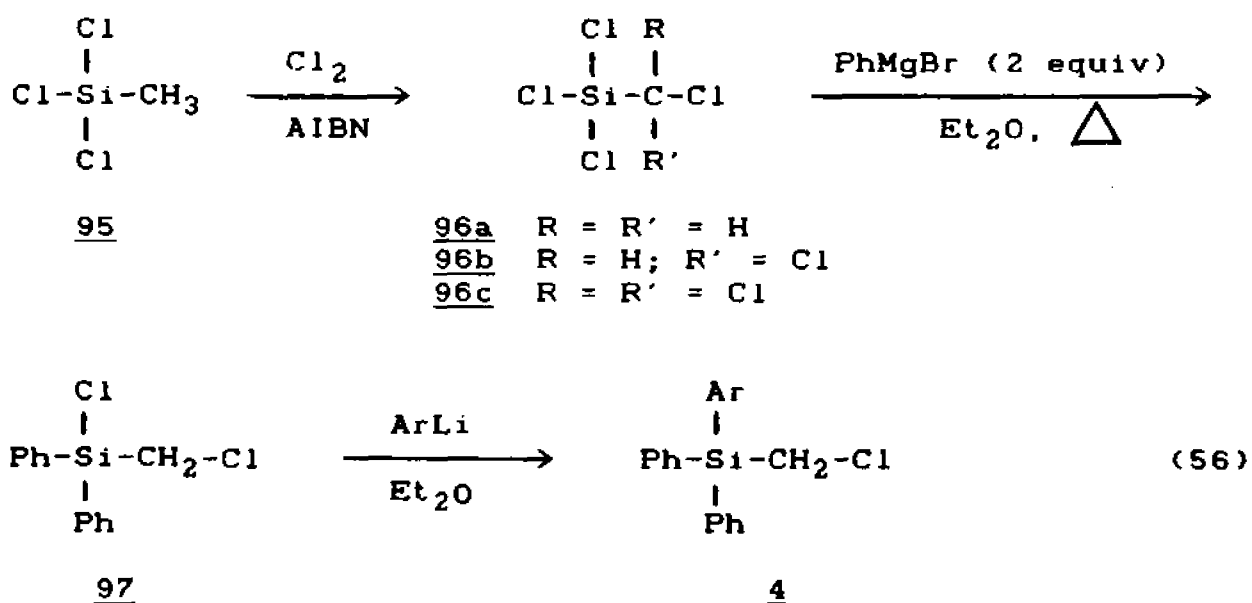
is not known, however, if size differences of the varied organo groups, R, compared to methyl contribute to migratory aptitudes. Thus further investigation of the electronic features of rearrangement-displacement of (halomethyl)silanes is needed. The (halomethyl)silanes presently chosen are aryl(chloromethyl)diphenylsilanes 4 in which aryl is a *para*-substituted-phenyl group (Equation 2). The *para*-substituted-phenyls have the same steric size as phenyl, and the electronics can be modified with various electron-withdrawing (Z = CF₃, Cl) and electron-donating (Z = CH₃,



OCH₃, N(CH₃)₂) groups. The purposes of this research were to effect reactions of 4 on silicon with nucleophiles (F⁻ and CH₃O⁻) and accurate determination of the products of aryl (6a) and phenyl migration (6b, Equation 2). From the relative amounts of 6a to 6b formed from 4 the migratory aptitudes of the varied phenyl groups were to be calculated. With such information it might be possible to assess clearly the electrical effects in rearrangement-displacements of 4.

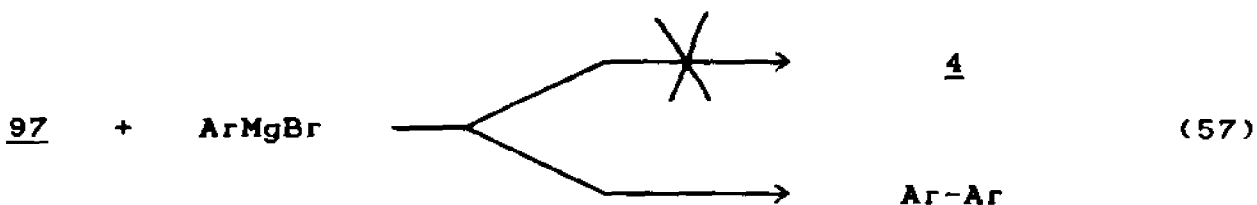
PREPARATION OF ARYL(CHLOROMETHYL)DIPHENYLSILANES 4

Aryl(chloromethyl)diphenylsilanes 4 were needed conveniently and in quantity for the present research. There are many methods for constructing silicon-carbon bonds.⁶³ The most common method is by reaction of silicon halides with Grignard and related organometallic reagents. The ease of replacement of halide on silicon generally decreases with the number of organic groups on silicon. Thus, different Grignard reagents may be used in separate stages of replacement. Since three of the four groups are always the same in silanes 4 it was deemed most efficient to prepare the common trisubstituted product, chloro(chloromethyl)diphenylsilane (97, Equation 56) and then introduce the *para*-substituted-phenyl group in the last step. The method of preparation of 4 is summarized in Equation 56.



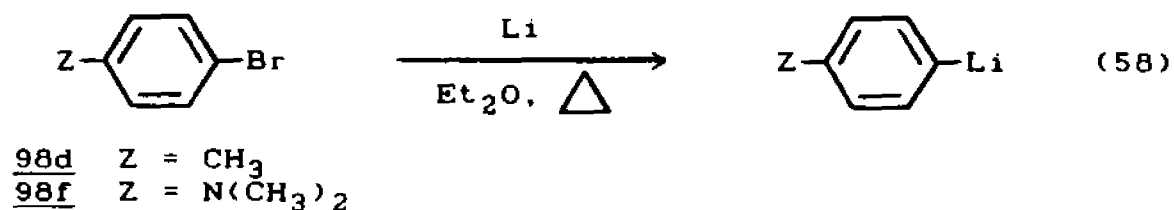
Excess trichloromethylsilane (95) was monochlorinated with chlorine gas as initiated by 2,2'-azobisisobutyronitrile (AIBN) to yield trichloro(chloromethyl)silane (96a).⁶⁴ The reactions were stopped before significant amounts of the dichlorinated 96b and trichlorinated 96c silanes were formed. (Chloromethyl)silane 96a was then reacted with two equivalents of phenylmagnesium bromide to form chloro(chloromethyl)diphenylsilane (97).⁶⁵

It was initially attempted to prepare 4 from 97 and the appropriate Grignard reagent (Equation 57). For whatever reasons, the Grignard did not substitute effectively

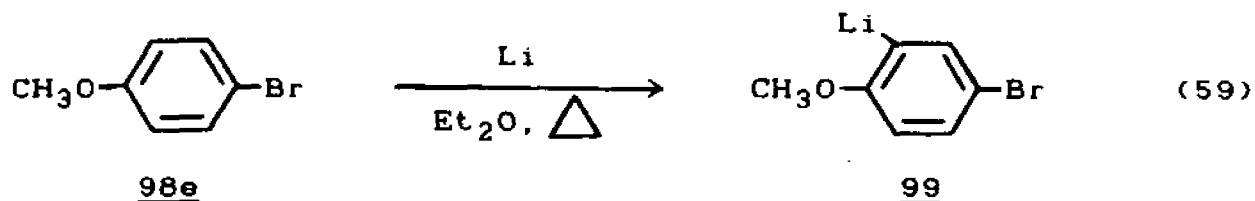


on 97 and only coupling of the Grignard reagent to the biphenyl occurred (Equation 57). Treatment of 97, however, with the appropriately-substituted aryllithium yielded 4. (Chloromethyl)triphenylsilane (4c) was not prepared by reaction of phenyllithium with 97. When phenylmagnesium bromide is reacted with trichloro(chloromethyl)silane (96a) triphenylsilane 4c is formed in addition to diphenylsilane 97. Sufficient quantities of 4c were obtained as a side-product for use in this research.

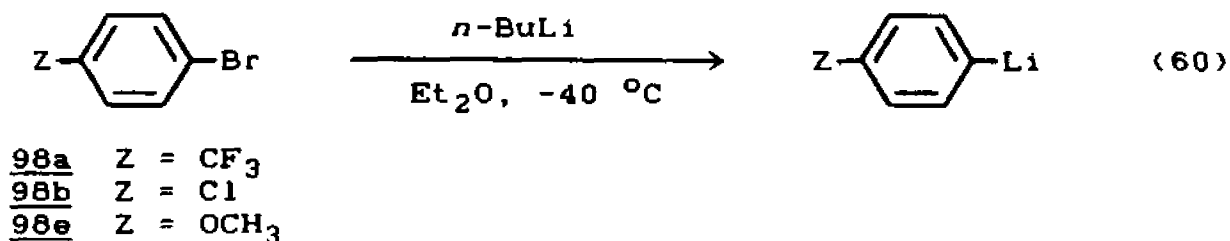
The aryllithiums were prepared by reactions of aryl bromides with lithium or *n*-butyllithium. 4-Bromotoluene (98d) and 4-bromo-*N,N*-dimethylaniline (98f) convert efficiently to their lithium derivatives by reaction with lithium metal (Equation 58). 4-Bromobenzotrifluoride (98a)



did not behave well with lithium, 4-bromochlorobenzene (98b) reacts unselectively at bromine and chlorine⁶⁶ and 4-bromoanisole (98e) undergoes deprotonation *ortho* to its methoxy group to yield 99 (Equation 59) in addition to

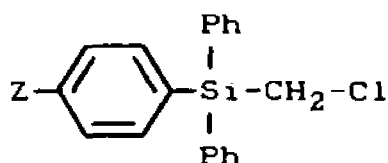


lithium-halogen exchange.⁶⁷ With halides 98a, 98b and 98e lithium-halogen exchange was accomplished satisfactorily with *n*-butyllithium (Equation 60).



Silanes 4 are white crystalline solids and all but (chloromethyl)triphenylsilane (4c) are unreported in the literature. The silanes gave proper analyses and have spectral properties (IR, ^1H NMR, and MS) consistent with the assigned structures. Melting points and yields are given in Table 2.

Table 2. Melting Points and Yields of Aryl(chloromethyl)-diphenylsilanes 4.



Compound Number	Z	mp ($^{\circ}\text{C}$)	Yield ^a (%)
<u>4a</u>	CF_3	98-100	51
<u>4b</u>	Cl	84-85	54
<u>4c</u>	H	113-116 ^b	4 ^c
<u>4d</u>	CH_3	76-79	54
<u>4e</u>	OCH_3	60-62	30
<u>4f</u>	$\text{N}(\text{CH}_3)_2$	106-110	30

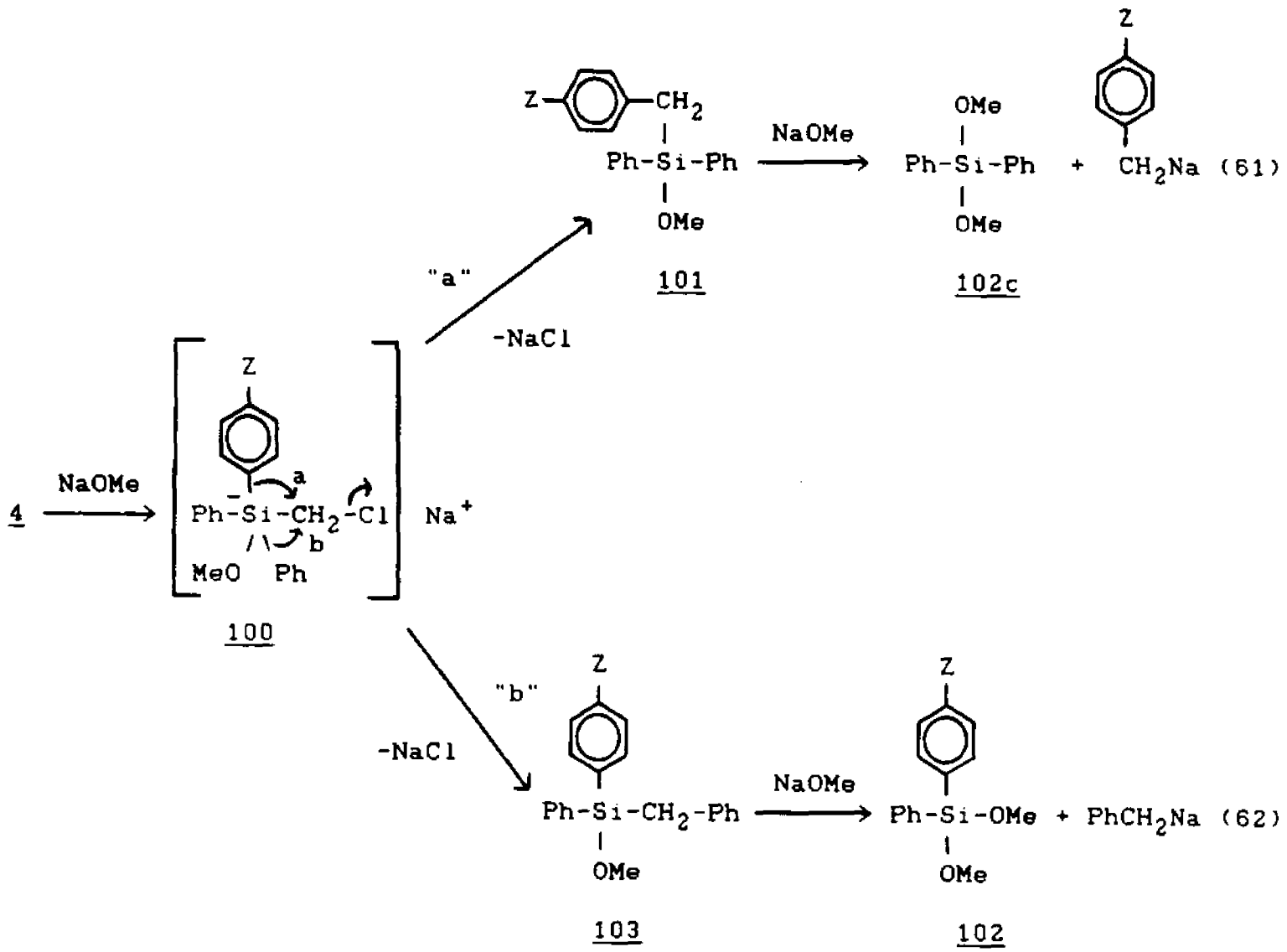
^aBased on reaction of 97 and ArLi , except as noted.

^bLit⁶⁸ 112-115 $^{\circ}\text{C}$.

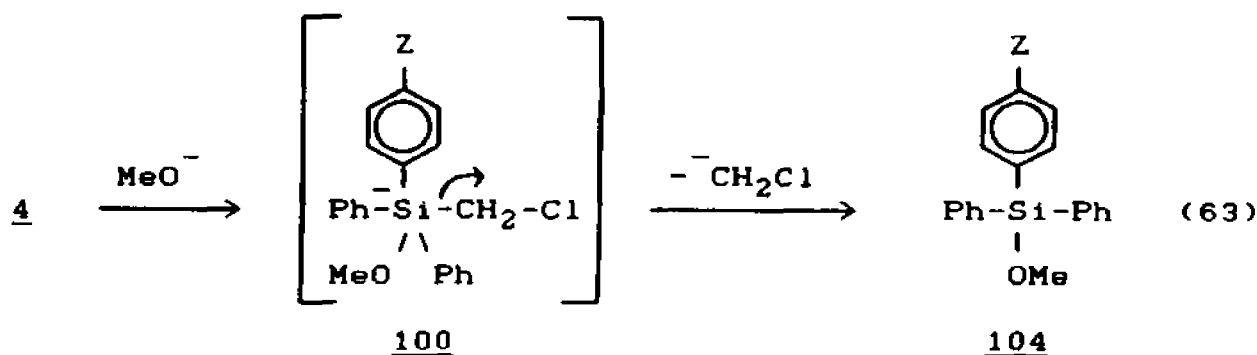
^cObtained as a side-product in preparation of 97.

REACTIONS OF 4 WITH METHOXIDE ION

Studies of migratory aptitudes in reactions of 4 with nucleophiles began with sodium methoxide in 1,4-dioxane, an aprotic solvent. An aprotic solvent was chosen since it had been shown that aprotic solvents favor silicon attack over carbon attack with (halomethyl)silanes.^{2,4,30,43,44} Products were expected to arise via three pathways (Equations 61-63). First, pentacoordinate silyl intermediate 100, as formed from methoxide attack on silicon, could migrate aryl groups (substituted-phenyls) with chloride expulsion to give (arylmethyl)methoxydiphenylsilanes 101. Cleavage of benzyl groups occurs with benzylsilanes and methoxides^{4,69} and thus it was anticipated that 101 would be converted by sodium methoxide to dimethoxydiphenylsilane (102c) and the corresponding substituted benzylsodiums (Equation 61). A second reaction path involves phenyl migration from 100 to form arylmethoxyphenyl(phenylmethyl)silanes 103 which like 101 can be cleaved by sodium methoxide to aryl dimethoxyphenylsilanes 102 and benzylsodium (Equation 62). From the amounts of 101 and 102c and of 103 and 102 the migratory aptitudes should be determinable. A third reaction process is loss of chloromethide ion from 100 to yield arylmethoxydiphenylsilanes 104 (Equation 63). This latter process does not affect any conclusions drawn



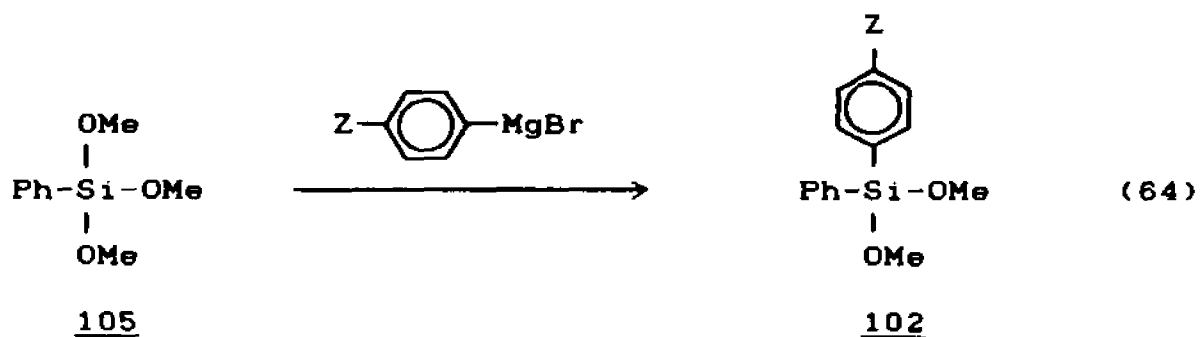
from the migratory aptitudes arising from *rearrangement-displacement*.



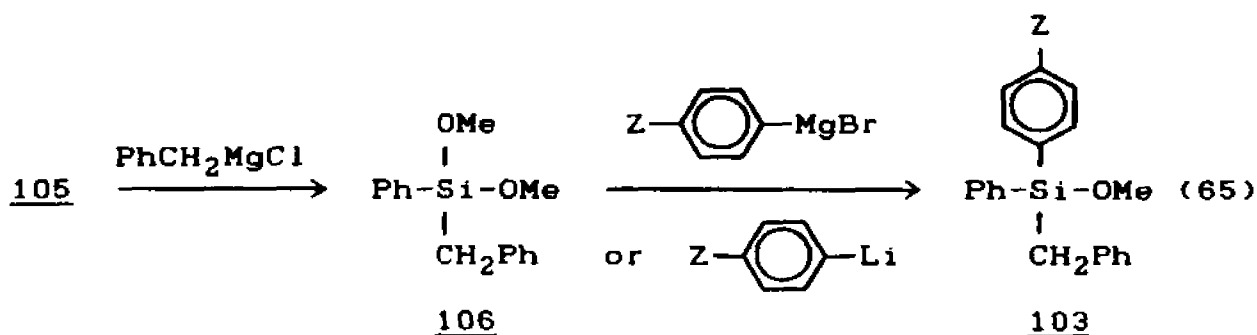
The product ratios and the yields from the above experiments with sodium methoxide were to be determined by gas chromatography using internal standards and response calibration techniques.⁷⁰ There was, therefore, need for the authentic methoxysilanes expected from the above reactions.

Methoxyorganosilanes of the methyl silyl ether type are most commonly prepared by reaction of the appropriate silyl chloride with methanol.⁷¹ However, silyl chlorides can be difficult to work with due to the reactivities of their silicon-chlorine bonds. A synthetic alternative is displacement of silicon-methoxy bonds with Grignard reagents.⁷² The preparations of the authentic methoxyorganosilanes are summarized in Equations 64-67.

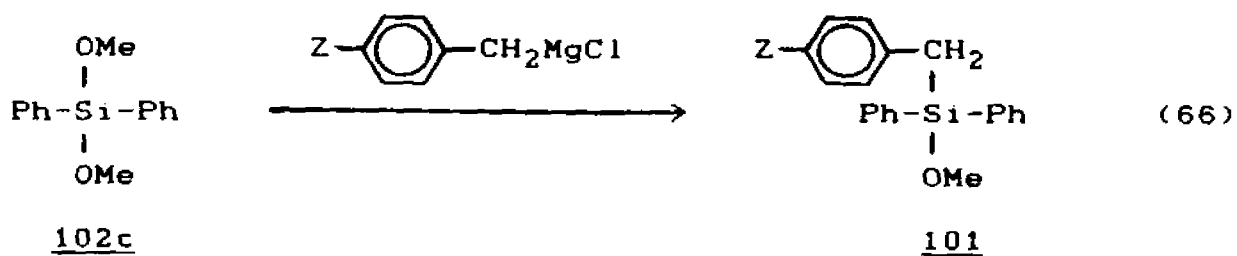
Aryldimethoxyphenylsilanes 102 were prepared from reaction of *para*-substituted-phenylmagnesium bromides with trimethoxyphenylsilane (105, Equation 64). Displacement of 105



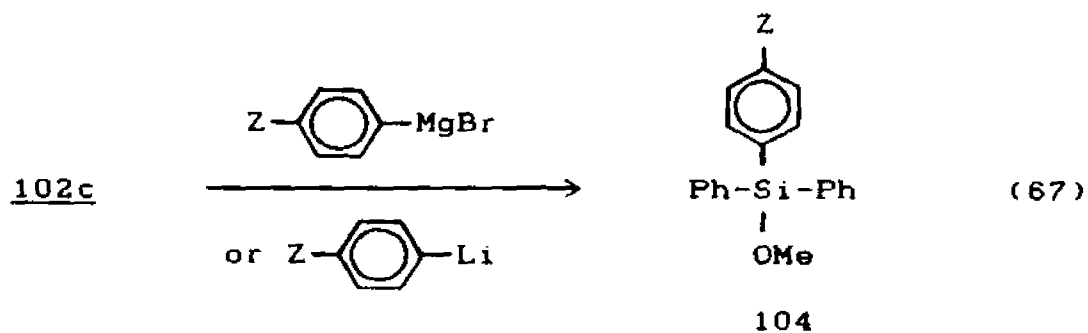
with benzylmagnesium chloride gives dimethoxyphenyl(phenylmethyl)silane (106) which yields arylmethoxyphenyl(phenylmethyl)silanes 103 when reacted with appropriate aryllithiums or arylmagnesium bromides (Equation 65). Treatment of



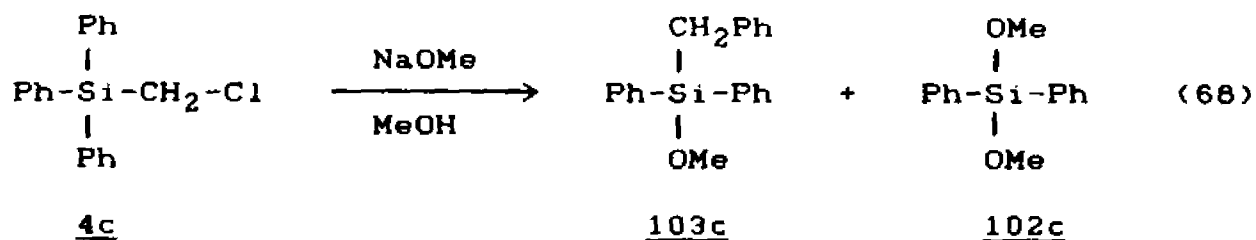
dimethoxydiphenylsilane (102c) with appropriate arylmethylmagnesium chlorides results in (arylmethyl)methoxydiphenylsilanes 101 (Equation 66). Aryldimethoxydiphenylsilanes



104 were obtained from arylmagnesium bromides or aryllithiums and dimethoxydiphenylsilane (102c, Equation 67).

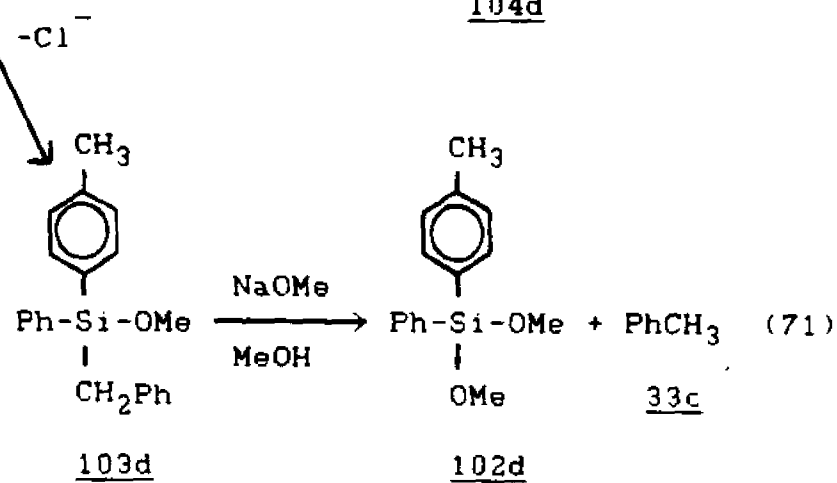
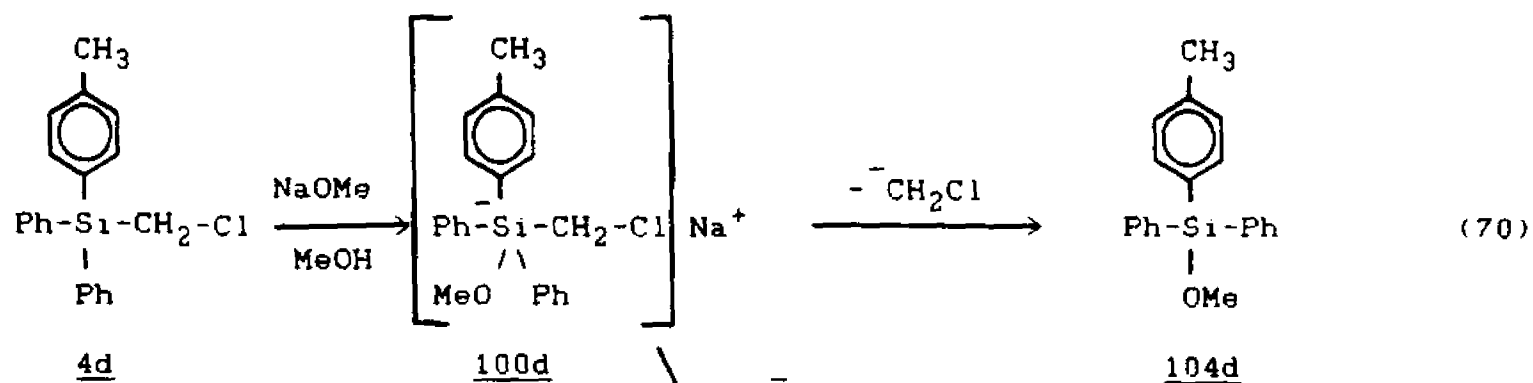
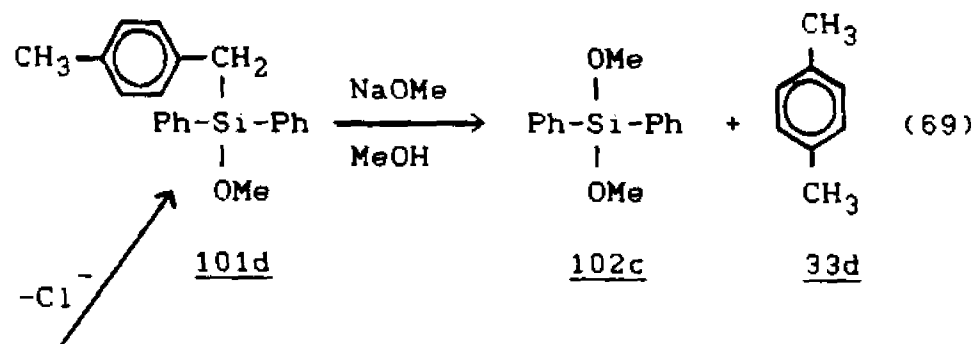


Reactions of sodium methoxide with 4 led to severe complications. Sodium methoxide and (chloromethyl)triphenylsilane (4c) in 1,4-dioxane give unidentified products in low yields which do not contain methoxy groups. Sodium methoxide in methanol, however, reacts with 4c to form mixtures of methoxydiphenyl(phenylmethyl)silane (103c) and dimethoxydiphenylsilane (102c, Equation 68).



Reaction of (chloromethyl)(4-methylphenyl)diphenylsilane (4d) with sodium methoxide in methanol yields products from all three expected pathways (Equations 69-71). The major product, dimethoxydiphenylsilane (102c), presumably results from methoxide attack on methoxy[(4-methylphenyl)methyl]diphenylsilane (101d) initially formed by *para*-tolyl migration and chloride loss (Equation 69). Reaction of methoxide on silicon in 4d with chloromethide loss apparently produces methoxy(4-methylphenyl)diphenylsilane (104d, Equation 70). Phenyl migration and chloride loss from 100d yields methoxy(4-methylphenyl)phenyl(phenylmethyl)silane (103d), cleavage of which by sodium methoxide results in dimethoxy(4-methylphenyl)phenylsilane (102d, Equation 71). Presumably toluenes 33c and 33d are also formed. Isolation of 33c and 33d was not attempted because the GC column temperatures (~250 °C) precluded their separation from solvent.

Benzylsilanes 101d and 103d could not be separated under the GC conditions and, in addition, contained an unidentified compound. Identification of 101d and 103d was made by comparison of their retention times and their ¹H NMRs with those of authentic samples. The additional products: 102c, 102d and 104d, were assigned from retention times and the spectral properties (IR, ¹H NMR and MS) of authentic samples.



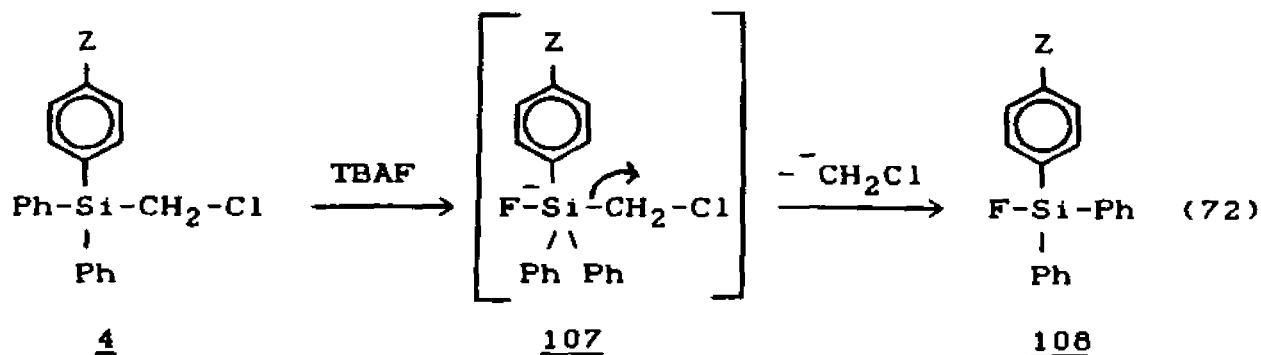
More complications arose in the reaction of sodium methoxide in methanol with (chloromethyl)(4-chlorophenyl)-diphenylsilane (4b). Reaction gives only unidentified products none of which contained methoxy groups. Due to these complications it was impractical to pursue the reactions of 4 with sodium methoxide to determine electronic effects in rearrangement-displacement.

REACTIONS OF 4 WITH FLUORIDE ION AT 25 °C

Since reactions of 4 with sodium methoxide led to severe complications, a more definitive nucleophile was needed. Rearrangement-displacement of (halomethyl)silanes by fluoride ion is known^{3,5,30,57,58} and thus investigation of such reactions of 4 was initiated. Tetrabutylammonium fluoride (TBAF) was the reagent chosen because of the "nakedness" of its fluoride ion and its solubility in tetrahydrofuran (THF). Other common fluorides (*e.g.* potassium or cesium fluoride) are insoluble in organic solvents and thus their reactions with (halomethyl)silanes occur very slowly.

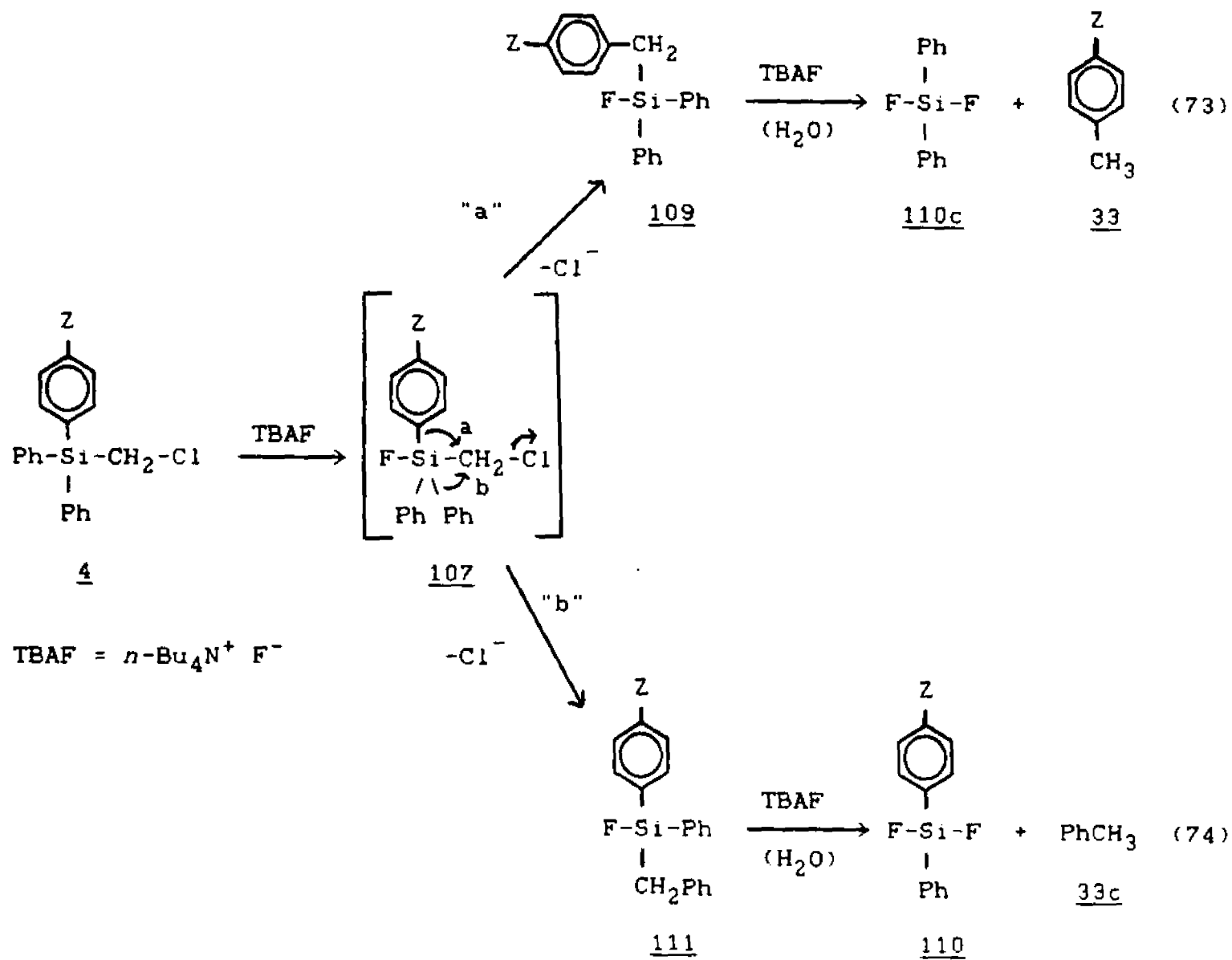
Reactions of 4 with TBAF are expected to result in rearrangement-displacement. Fluoride attack on silicon would presumably form pentacoordinate silyl adducts 107 which can collapse by the pathways outlined in Equations 72-74. Loss of chloromethide from 107 would produce arylfluorodiphenylsilanes 108 (Equation 72). This process does not involve

any migration in 107 and thus will not affect the migratory aptitude.

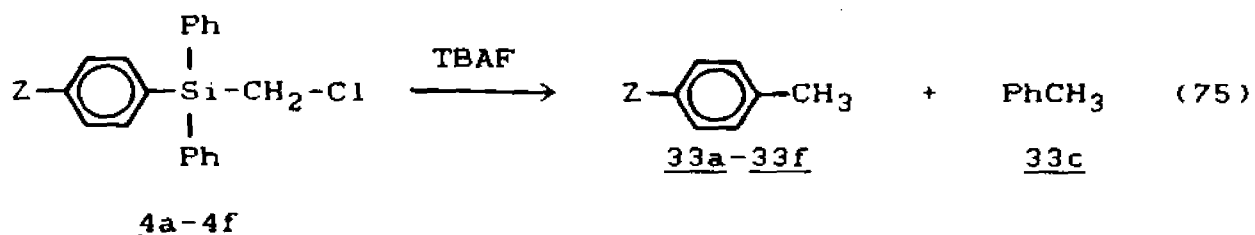


The migratory aptitudes in the rearrangement-displacements were to be determined by measuring the ratios of products from two sequences as follows. Aryl migrations with chloride loss should produce (arylmethyl)fluorodiphenylsilanes 109 which can be cleaved with fluoride ion to yield difluorodiphenylsilane (110c) and substituted-toluenes 33 (Equation 73).⁷³ Similarly, aryldifluorophenylsilanes 110 and toluene (33c) should be produced by cleavage of aryl-fluorophenyl(phenylmethyl)silanes 111 initially formed by phenyl migration with loss of chloride (Equation 74).

Fluoride attack on silicon was subsequently found to produce only products derived from aryl and phenyl migrations (Equations 73 and 74). Arylfluorodiphenylsilanes 108 resulting from collapse of 107 with loss of chloromethide ion (Equation 72) were not formed. Also, with greater than 2 equivalents of TBAF and proper conditions, cleavages of



benzyl anions from 109 and 111 occurred quantitatively for all substituents! Thus, the migratory aptitudes in reactions of 4 with greater than 2 equivalents of TBAF could be obtained directly by comparison of the amounts of substituted-toluenes 33 to toluene (33c, Equation 75). Syntheses of authentic fluorosilanes (109, 110 and 111) were not



a, Z = CF₃
d, Z = CH₃

b, Z = Cl
e, Z = OCH₃

c, Z = H
f, Z = N(CH₃)₂

necessary since the toluenes (33a-33f) were all readily available.

The amounts of toluene and substituted-toluene (Equation 75) were determined using anisole as an internal standard. Gas chromatography peak areas were corrected for detector response. This procedure is accurate to $\pm 5\%$.⁷⁰ This accuracy can be used as an approximation for the minimum random error in the measurements. Migratory aptitudes were calculated by comparing the amounts of 33 and 33c produced in individual experiments. Statistical corrections were made since 4 contains two phenyl groups and only one aryl group. The minimum error in the measurement of the

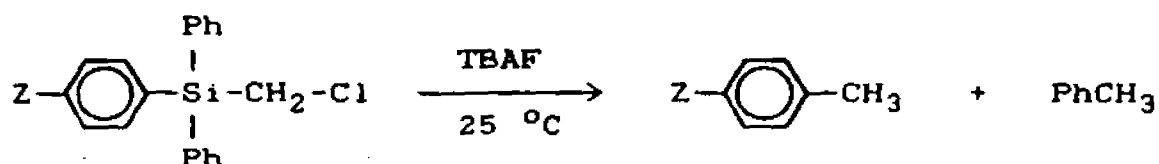
migratory aptitudes can be approximated by the sum of the errors in the measurement of 33 and 33c.^{74,75} Therefore the minimum error is $[(\pm 5\%) + (\pm 5\%) =] \pm 10\%$.

The general conditions for reactions of 4 with TBAF are summarized as follows. Approximately 0.20 mmoles of aryl(chloromethyl)diphenylsilanes 4 were stirred with 2.5 equivalents of tetrabutylammonium fluoride (TBAF) in tetrahydrofuran (THF) at 25 °C. Reaction times of 6-8 hours result in total yields of substituted-toluenes 33 and toluene (33c) of between 93 and 106%. Reactions were conducted for 4-11 times with each silane (4). The migratory aptitudes determined were reproducible for all substituents. Since the relative migratory aptitude of the phenyl group in 4c (Z = H) must be unity, the reaction of 4c was conducted to confirm that its yield was ~100%.

A mean and standard deviation was calculated for the migratory aptitude of each substituted-phenyl group. Standard deviations of the migratory aptitudes for *para*-methoxyphenyl (e, Z = OCH₃) and *para*-(dimethylamino)phenyl (f, Z = N(CH₃)₂) were larger than the minimum error ($\pm 10\%$) because the GC peak areas for the substituted-toluenes were small and broad compared to toluene and the standard. The errors in the migratory aptitudes for these substituted-phenyls were assumed to be the standard deviations of their mean migratory aptitudes. The means for all other substituted-phenyl groups had standard deviations smaller than the

minimum error ($\pm 10\%$) and thus the errors were assumed to be $\pm 10\%$. The average relative error for all the migratory aptitudes is only $\pm 13\%$. Table 3 gives the mean migratory aptitudes and calculated errors for the substituted-phenyl groups at 25 °C.

Table 3. Statistically Corrected Relative Migratory Aptitudes for Substituted-phenyl Groups at 25 °C.



	Z	Corrected	Ar/Ph ^a
<u>a</u>	CF ₃	2.72	± 0.27
<u>b</u>	Cl	1.67	± 0.17
<u>c</u>	H	1.00	± 0.10
<u>d</u>	CH ₃	0.906	± 0.091
<u>e</u>	OCH ₃	0.58	± 0.12
<u>f</u>	N(CH ₃) ₂	0.550	± 0.095

^aMean value obtained \pm the error determined.

It is seen (Table 3) from the small range in values (maximum = 2.72, minimum = 0.55; a factor of ~5) that the migratory aptitudes are not highly substituent dependent.

Such results fit with the ideas that the rate-determining steps for the above reactions involve formation of penta-coordinate silyl intermediates and the subsequent transition states for rearrangement are structurally close to such intermediates. The results do show a trend, however, in that electron-withdrawing groups ($Z = \text{CF}_3, \text{Cl}$) accelerate aryl over phenyl migration whereas electron-donating groups [$Z = \text{CH}_3, \text{OCH}_3, \text{N}(\text{CH}_3)_2$] decrease aryl migration relative to phenyl.

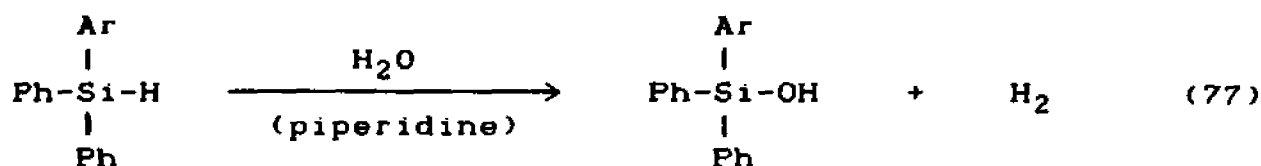
Quantitative evaluation of the above migratory aptitudes was accomplished via the Hammett equation:⁷⁶

$$\log \frac{k}{k_0} = \rho\sigma \quad (76)$$

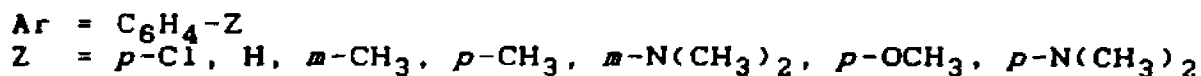
where k denotes a rate (k) or an equilibrium (K) constant for a *meta*- or *para*-substituted aromatic compound and k_0 denotes the rate (k_0) or equilibrium (K_0) constant for the unsubstituted derivative undergoing the same reaction. The first empirical constant, sigma (σ), is a measure of the electron-donating or -withdrawing power of the substituent and is independent of the reaction. The other empirical constant, rho (ρ), is independent of the substituent and is determined by the reaction and the conditions (reagent, solvent, catalyst, temperature, etc.). Rho is a measure of the sensitivity of the kinetic or equilibrium process to a change in the substituent and is defined as unity for the

ionization of benzoic acids. If the logarithms of the relative rates of reactions correlate linearly with sigma values for a series of related substituted-phenyl compounds, a mechanistic consistency is very likely within that series.

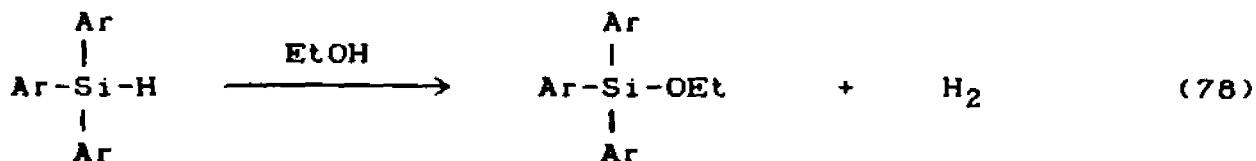
Solvolysis of triarylsilanes by alcohols has been found to give satisfactory linear-free-energy correlations. Gilman and Dunn⁷⁷ found a good correlation of logarithms of the relative rates of reactions of aryldiphenylsilanes 112 with wet piperidine (Equation 77) versus sigma values for



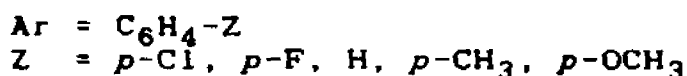
112



the aryl substituents (Z). Schott and Harzdorf⁷⁸ tried to correlate the logarithms of the relative rates of solvolysis of triarylsilanes 113 in 94% ethanol (Equation 78) with



113



sigma substituent values but found a much better correlation with a sigma-silicon (σ_{Si}) parameter which involves less resonance interaction (Equation 79). The different substituent constants were deemed necessary because of the $p_{\pi}-d_{\pi}$ interactions between the aryl group and the silicon atom.

$$\sigma_{Si} = \sigma_I + 0.75\sigma_R \quad (79)$$

It was subsequently found⁷⁹ that the logarithms of the above relative reaction rates could be correlated with Taft's sigma-zero values (σ^0),⁸⁰ values which are used in systems in which there is no conjugation of the substituent and the reaction center. Later Schott⁸¹ showed that the sigma-silicon values were actually sigma-zero values.

In the present study the logarithms of the corrected relative migratory aptitudes were plotted against both sigma and sigma-zero values. Table 4 summarizes the sigma values, sigma-zero values and logarithms of the corrected relative migratory aptitudes including errors. The absolute errors in the logarithmic values equal the relative errors in the values divided by the natural logarithm of 10, since, if $B = \log(A)$, then $dB = (dA/A)/\ln(10)$.⁸²

The data in Table 4 were analyzed by least squares linear regression.⁸⁰ A plot of the logarithms of the migratory aptitudes versus the sigma values (Figure 2) yields

Table 4. Sigma Values, Sigma-zero Values and Logarithms of Corrected Relative Migratory Aptitudes at 25 °C.

	Z	σ^a	σ^{0a}	log (Ar/Ph)
<u>a</u>	CF ₃	0.53	0.53	0.43 ± 0.04
<u>b</u>	Cl	0.24	0.24	0.22 ± 0.04
<u>c</u>	H	0.00	0.00	0.00 ± 0.04
<u>d</u>	CH ₃	-0.14	-0.14	-0.04 ± 0.04
<u>e</u>	OCH ₃	-0.28	-0.12	-0.24 ± 0.09
<u>f</u>	N(CH ₃) ₂	-0.63	-0.32	-0.26 ± 0.08

^aReference 83.

a straight line with slope (p) of 0.64 and an intercept of 0.05. The correlation coefficient (r) for the data is equal to 0.964 which means that the line obtained explains ($r^2 =$) 93% of the variance in the migratory aptitudes and therefore is considered satisfactory.⁶¹ The average standard deviation calculated is ± 0.065 which yields a mean relative error in the migratory aptitudes of ± 14%. The mean relative error determined with linear regression (± 14%) is comparable to that of the mean error in the migratory aptitudes of all groups (± 13%) and less than the ± 15% specified for the Hammett equation.^{75b}

A plot of the logarithm of the migratory aptitudes versus sigma-zero substituent values (Figure 3) yields a

Figure 2. Plot of the logarithms of the corrected relative migratory aptitudes for substituted-phenyl groups at 25 °C versus the sigma values.

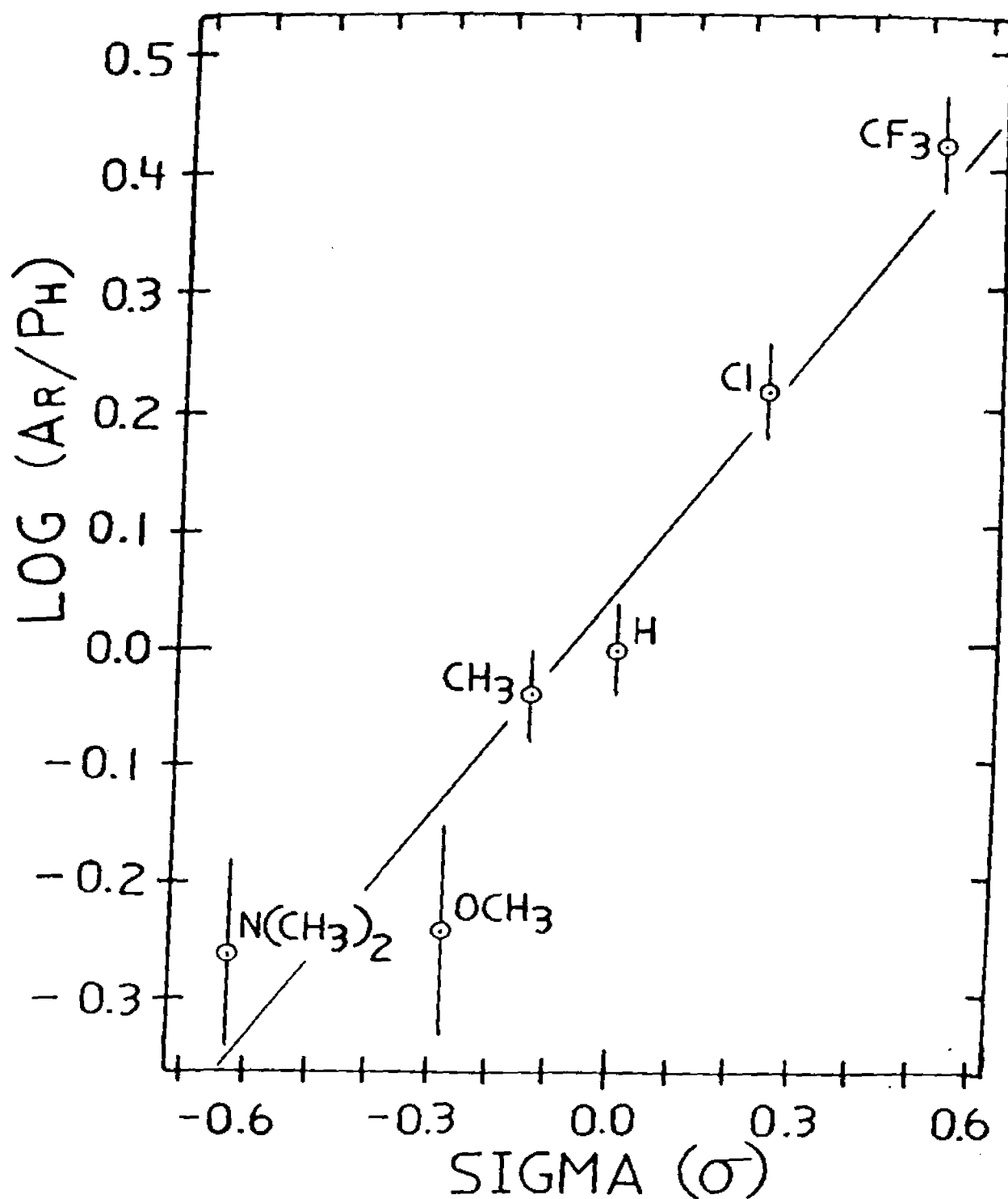
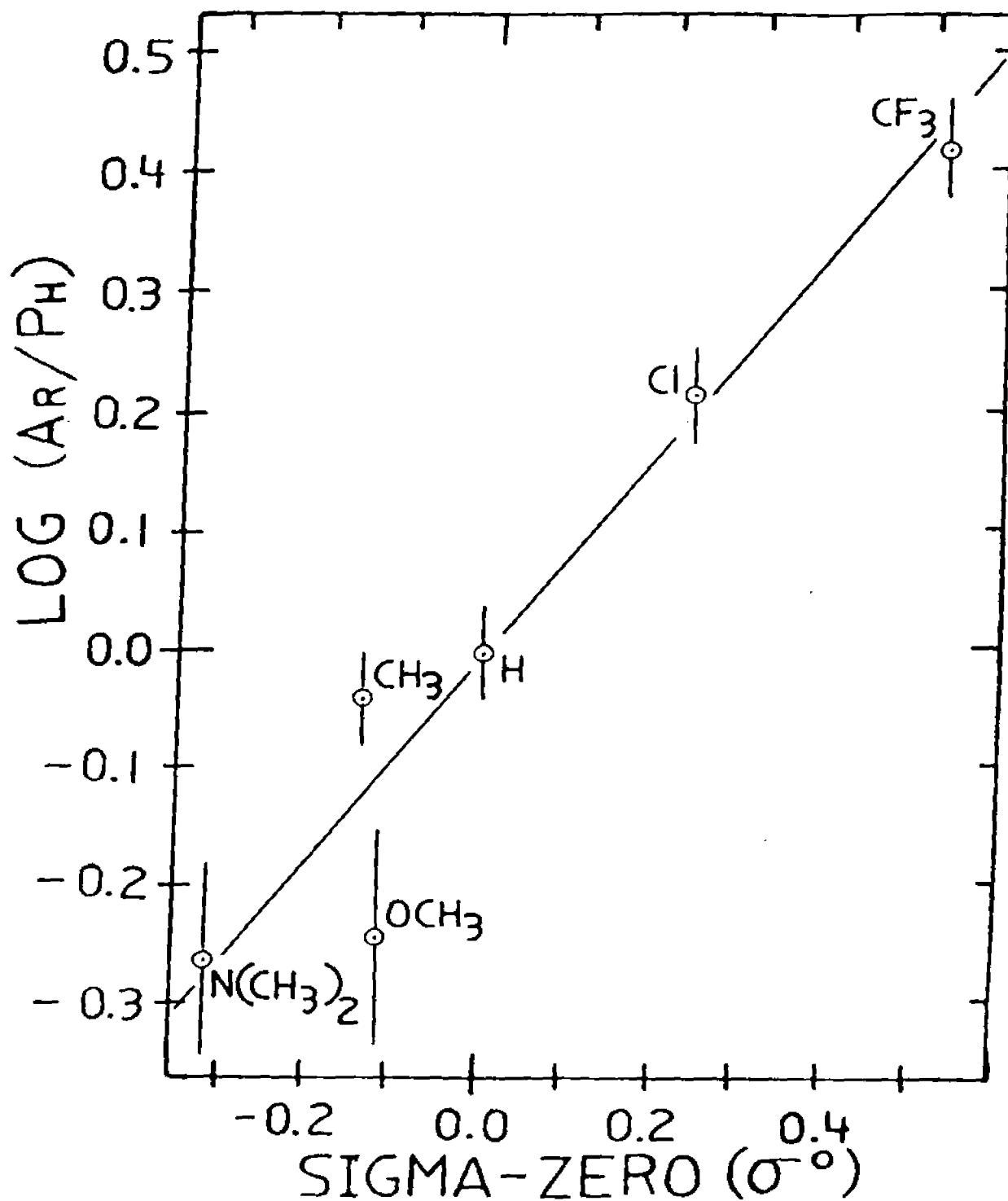


Figure 3. Plot of the logarithms of the corrected relative migratory aptitudes for substituted-phenyl groups at 25 °C versus the sigma-zero values.



straight line with a slope (p) of 0.84 and an intercept of -0.01. There was a satisfactory correlation of 0.964, which explains 93% of the variance of the migratory aptitudes, and an average standard deviation of ± 0.065 , giving an average relative error in the migratory aptitudes of $\pm 14\%$. The correlation coefficients and standard deviations are identical for both regression with sigma and sigma-zero.

REACTIONS OF 4 WITH FLUORIDE ION AT LOWER TEMPERATURES

Because the range of migratory aptitudes for the rearrangements at 25 °C (Table 3) was small, it was desired to try and increase the range. It was postulated that if the temperature of the reactions were lowered the range in these values could be increased since, in general, lower reaction temperatures make reactions more selective. Thus the migratory aptitudes for the electron-withdrawing groups would increase and those for the donating groups would decrease. This would effectively increase the range of values.

Reactions were thus conducted at both 0 °C and -20 °C in a manner analogous to the 25 °C reactions. Like the 25 °C reactions, all products resulted from a rearrangement-displacement pathway and subsequent cleavage of

benzylsilanes to give toluenes. Table 5 contains the statistically corrected migratory aptitudes at 0 °C and their logarithms.

Table 5. Statistically Corrected Relative Migratory Aptitudes for Substituted-phenyl Groups at 0 °C and the Logarithms of the Values.



	Z	Corrected	Ar/Ph	log (Ar/Ph)
<u>a</u>	CF ₃	3.00 ±	0.30	0.48 ± 0.04
<u>b</u>	Cl	2.01 ±	0.21	0.30 ± 0.05
<u>c</u>	H	1.00 ±	0.10	0.00 ± 0.04
<u>d</u>	CH ₃	0.981 ±	0.098	-0.01 ± 0.04
<u>e</u>	OCH ₃	0.974 ±	0.097	-0.01 ± 0.04
<u>f</u>	N(CH ₃) ₂	1.13 ±	0.17	0.05 ± 0.07

Comparison of the migratory aptitudes for reactions at 0 °C (Table 5) to those at 25 °C (Table 3) shows as predicted an increase for electron-withdrawing groups (Z = CF₃, Cl), though the increases are probably statistically insignificant. The electron-donating groups, on the other hand,

do not behave as if the reactions are getting more selective but are acting like they are becoming *non-selective*!

Figures 4 and 5 show plots of logarithms of migratory aptitudes at 0 °C versus sigma and sigma-zero values, respectively. Regression analysis of all points for the 0 °C versus sigma plot (solid line in Figure 4) yields a slope of 0.41 and an intercept of 0.15. The average deviation is ± 0.11 , which yields a relative error of $\pm 25\%$. The $\pm 25\%$ is significantly larger than the average error calculated (± 0.047 or $\pm 11\%$ relative error) and the correlation of 0.805 can best be termed poor.⁶¹ Since the correlation coefficient implies that the line calculated can only account for 65% of the variance in the points, other factors must be affecting the migratory aptitude than just substituent effects. It is noted from the graph in Figure 4 that for the points with sigma less than zero (electron-donating groups) there is a change in slope and the data might fit better with two intersecting lines (dotted lines in Figure 4). Linear regression of the points with sigma values greater or equal to zero leads to a line with slope of 0.90 and intercept of 0.03 with a good correlation of 0.981 (96% of variance is explained by the line) and average deviation of ± 0.039 ($\pm 8\%$ relative error in migratory aptitudes). The slope of the line for points with sigma values less than or equal to zero, was calculated to be -0.09 with an intercept of -0.02. Average deviation was ± 0.014 ($\pm 3\%$ of relative

Figure 4. Plot of the logarithms of the corrected relative migratory aptitudes for substituted-phenyl groups at 0 °C versus the sigma values.

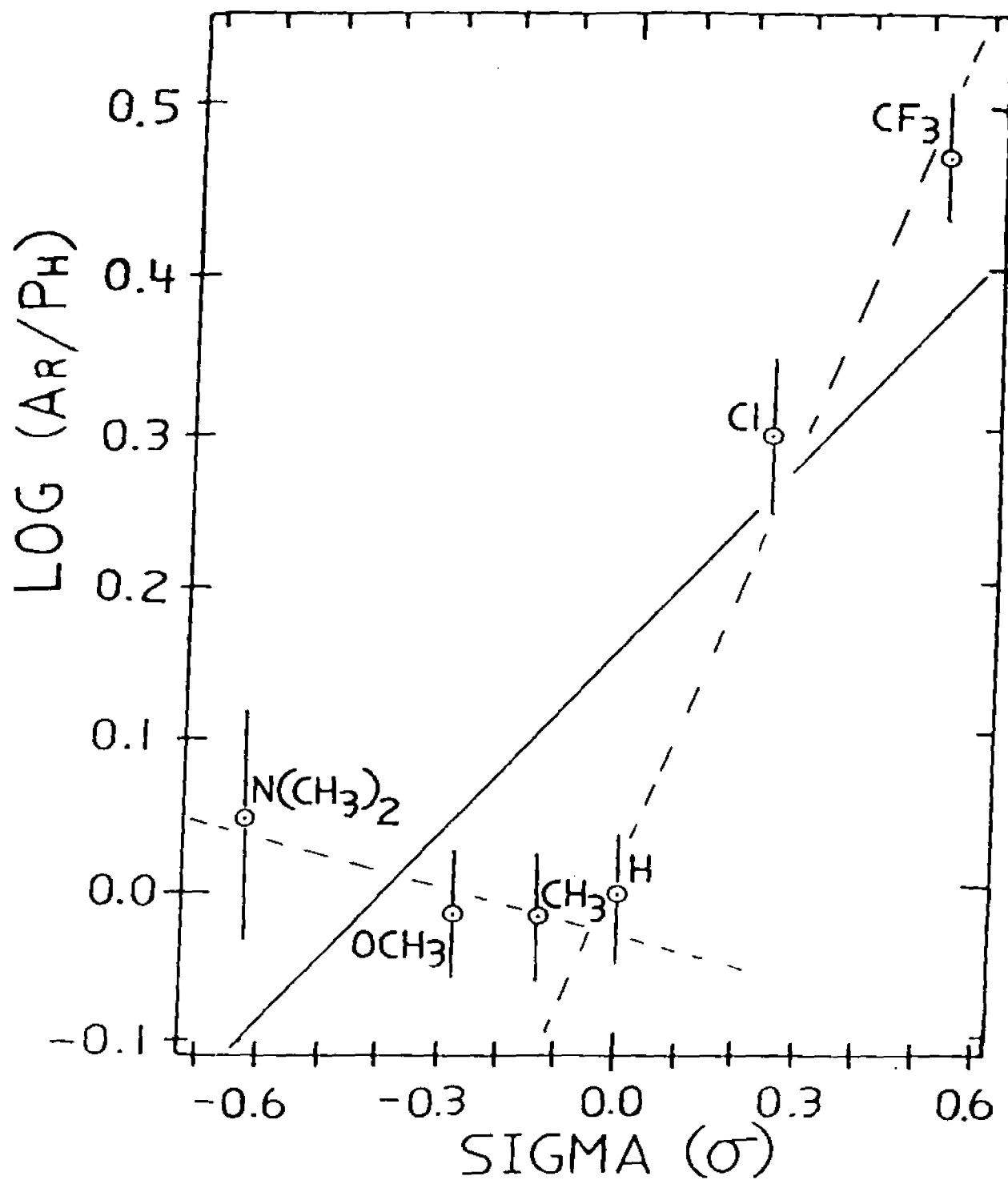
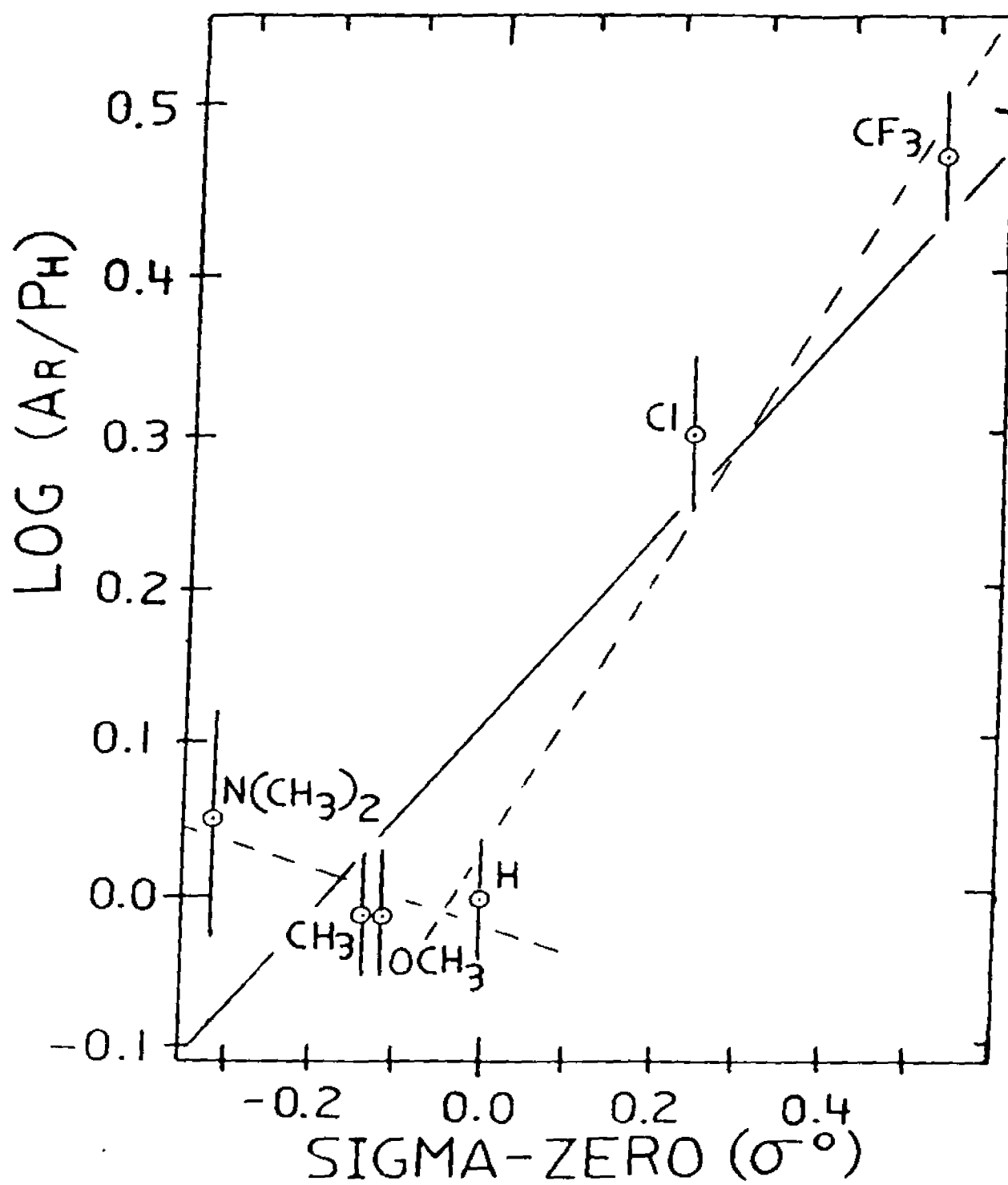


Figure 5. Plot of the logarithms of the corrected relative migratory aptitudes for substituted-phenyl groups at 0 °C versus the sigma-zero values.

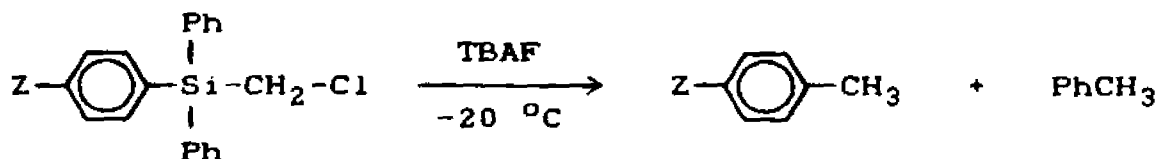


error in migratory aptitude), but the correlation coefficient was only 0.834 (only 70% of the variance is explainable by the line). The poor correlation is due to the very small slope (within the errors the slope could actually be 0.0) implying that the migratory aptitudes for electron-donating phenyls are not very substituent dependent.

Changing to sigma-zero values alters the plot only slightly (Figure 5). The regression line using all the points (solid line in Figure 5) yields a slope of 0.61 and an intercept of 0.12 with only a fair correlation of 0.908 (82% of the variance in the data are explained) and an average deviation of ± 0.079 ($\pm 18\%$ relative error). Analyzing the data with separate lines for electron-donating and electron-withdrawing phenyls yields for electron-donating groups virtually the same line as obtained with sigma values (since for these points the sigma and sigma-zero values are equivalent). The donating groups give a slope of -0.17 and an intercept of -0.02 with an average deviation of ± 0.014 ($\pm 3\%$) and like that with sigma values a poor correlation of 0.795 (only 63% of the variance is explained) due to the small slope.

Table 6 contains migration aptitudes at -20°C along with their respective logarithmic values. Comparison with the values at 0°C (Table 5) reveals very little change. Figures 6 and 7 are plots of the logarithms of migratory

Table 6. Statistically Corrected Relative Migratory Aptitudes for Substituted-phenyl Groups at -20°C and the Logarithms of the Values.

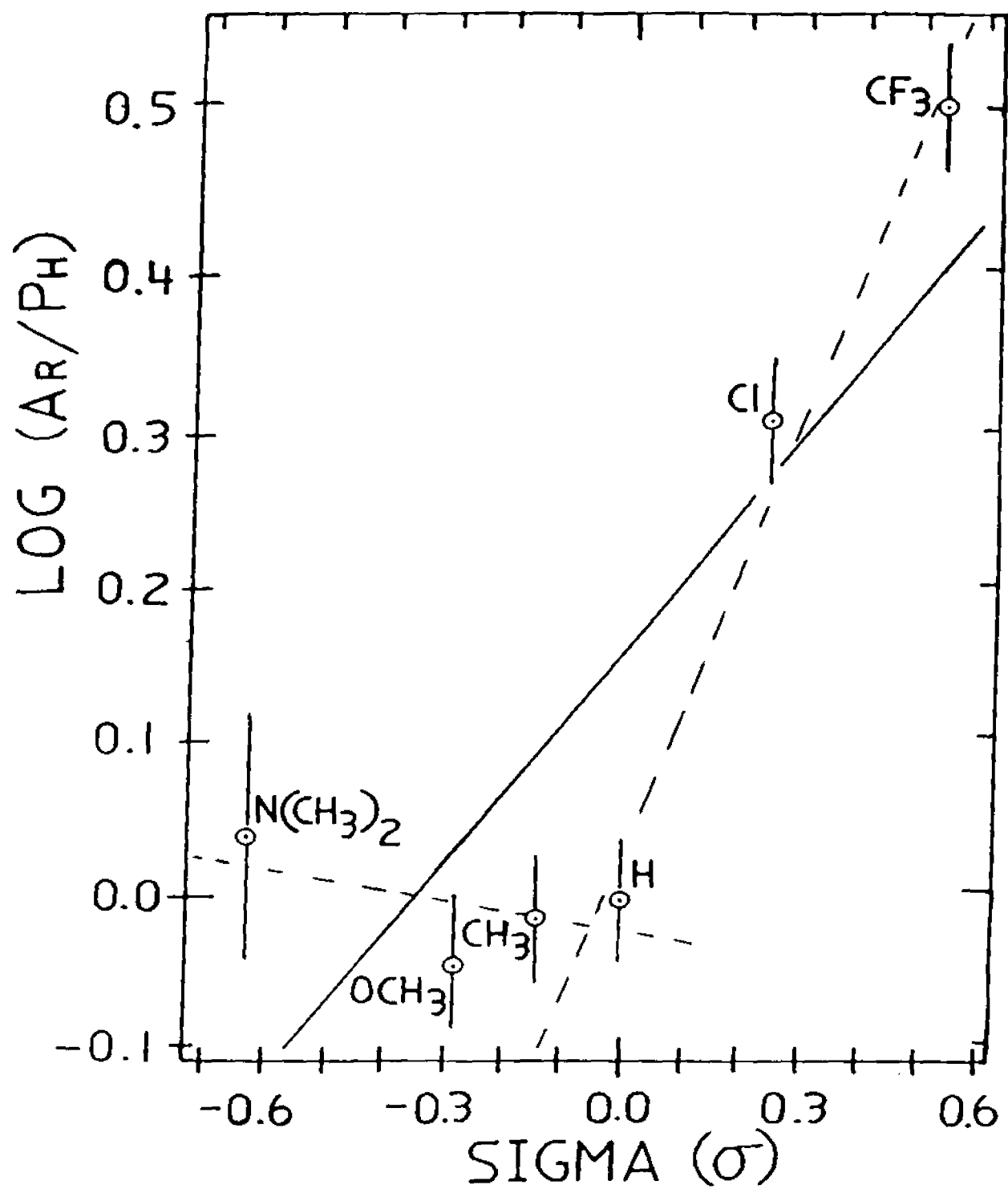


	Z	Corrected	Ar/Ph	log (Ar/Ph)
<u>a</u>	CF ₃	3.20	\pm 0.32	0.51 \pm 0.04
<u>b</u>	Cl	2.02	\pm 0.20	0.31 \pm 0.04
<u>c</u>	H	1.00	\pm 0.10	0.00 \pm 0.04
<u>d</u>	CH ₃	0.974	\pm 0.097	-0.01 \pm 0.04
<u>e</u>	OCH ₃	0.906	\pm 0.091	-0.04 \pm 0.04
<u>f</u>	N(CH ₃) ₂	1.09	\pm 0.19	0.04 \pm 0.08

aptitudes at -20°C versus sigma and sigma-zero, respectively. Like the 0°C reactions, the graphs are bent, and quantitatively there is very little difference at the two temperatures.

Regression analysis using all the points at -20°C plotted against sigma values (Figure 6) yields a calculated line of slope 0.45 and intercept of 0.16. Average deviation is \pm 0.118 (\pm 27% average relative error in the migratory aptitudes) and the correlation coefficient is a poor 0.817 (only 67% of the variance is explainable by the line).

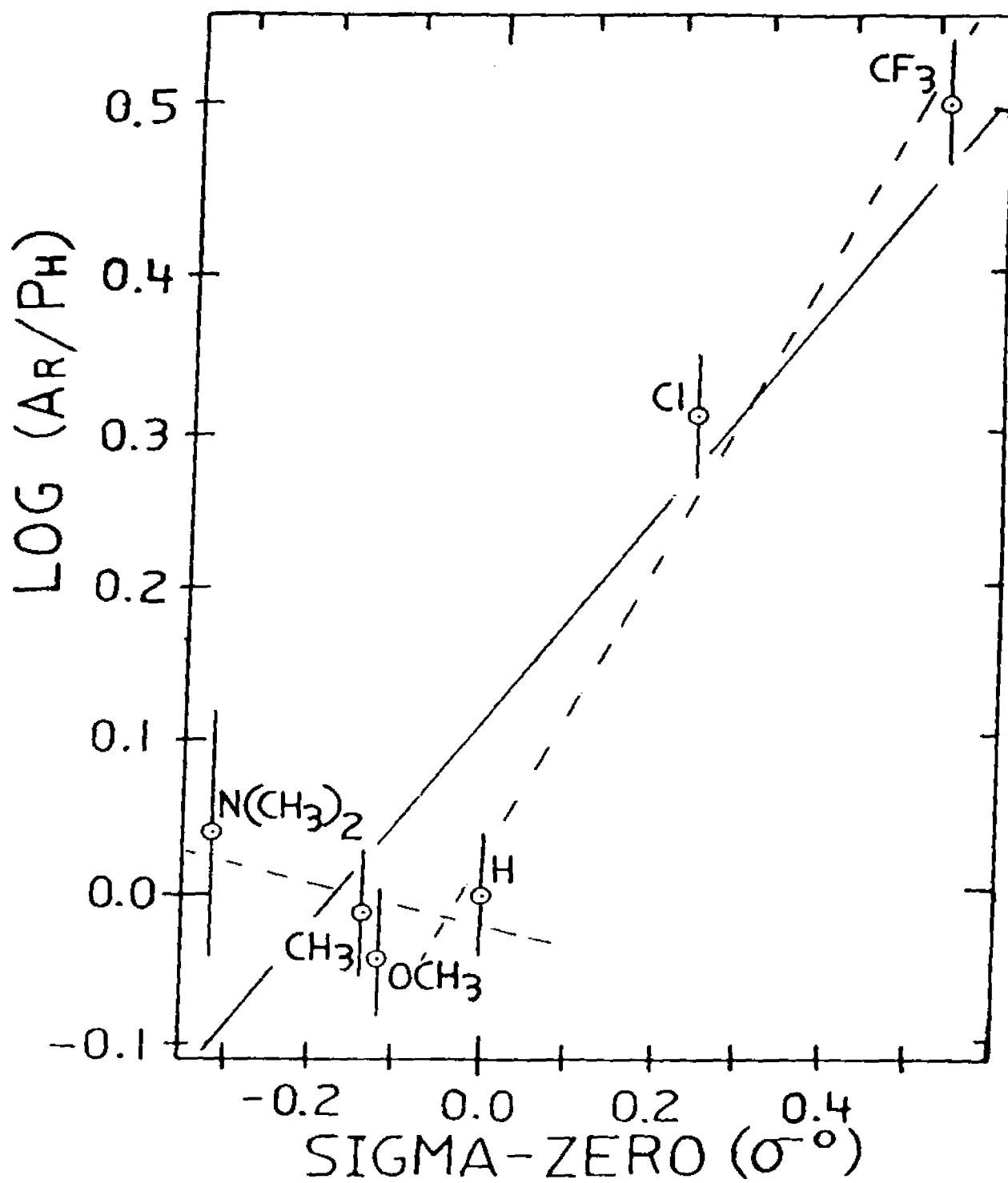
Figure 6. Plot of the logarithms of the corrected relative migratory aptitudes for substituted-phenyl groups at -20°C versus the sigma values.



Two lines can be drawn from the data using electron-donators or electron-withdrawers for each respective line (dashed lines in Figure 6). That for electron-withdrawing phenyls versus the sigma values a least squares slope is calculated to be 0.95 with an intercept of 0.03. The average deviation is ± 0.037 ($\pm 8\%$ relative error in the migratory aptitudes) and there is a satisfactory correlation of 0.984 (97% of the variance is explained). The logarithms of the migratory aptitudes for electron-donating phenyls plotted versus sigma yield a slope of -0.07 and intercept of -0.02 with a very poor correlation (due to the non-selectivity for migrations) of 0.568 (only 32% of the variance is explained by the line) and an average deviation of ± 0.024 ($\pm 5\%$ relative error).

The plot of the logarithms of the migratory aptitudes at -20°C versus sigma-zero values is given in Figure 7. Least squares regression analysis for all the data points in Figure 7 results in a line with a slope of 0.67 and an intercept of 0.11. The correlation is fair, 0.912, explaining only 83% of the variance in the data and the average deviation is ± 0.084 yielding a relative error in the migratory aptitudes of $\pm 19\%$. The fair correlation and large error point to other factors and two lines can again be drawn through the points (the dashed lines in Figure 7). The line using the electron-withdrawing groups gives an

Figure 7. Plot of the logarithms of the corrected relative migratory aptitudes for substituted-phenyl groups at -20°C versus the sigma-zero values.



analysis exactly like that for the sigma values. The plot of the logarithms of the migratory aptitudes of the electron-donating groups versus the sigma-zero values has a slope of -0.15 with an intercept -0.02 and only a poor correlation of 0.615 (explaining only 38% of the variance) with a relative error of only $\pm 5\%$ and an average deviation of ± 0.02 .

In the present study there seems to make little difference whether the logarithms of the corrected migratory aptitudes are plotted versus the sigma or the sigma-zero values. Low temperature effects do seem to be changing the migratory aptitudes causing deviations in the Hammett plots. In the next chapter explanations for these changes will be presented and discussed in more detail.

CHAPTER IV: DISCUSSION

OVERALL MECHANISTIC FEATURES

The data for the reactions of fluoride ion with 4 (see Chapter III: Results) lead to various speculations as to the structures of the transition states for rearrangement-displacements. Table 7 shows the rho values obtained for the reactions at various temperatures using the migratory aptitudes of all substituted-phenyls.

Table 7. Rho Values Calculated for Reactions at Various Temperatures Using Regression with all Points.

$$\log (Ar/Ph) = \rho\sigma$$

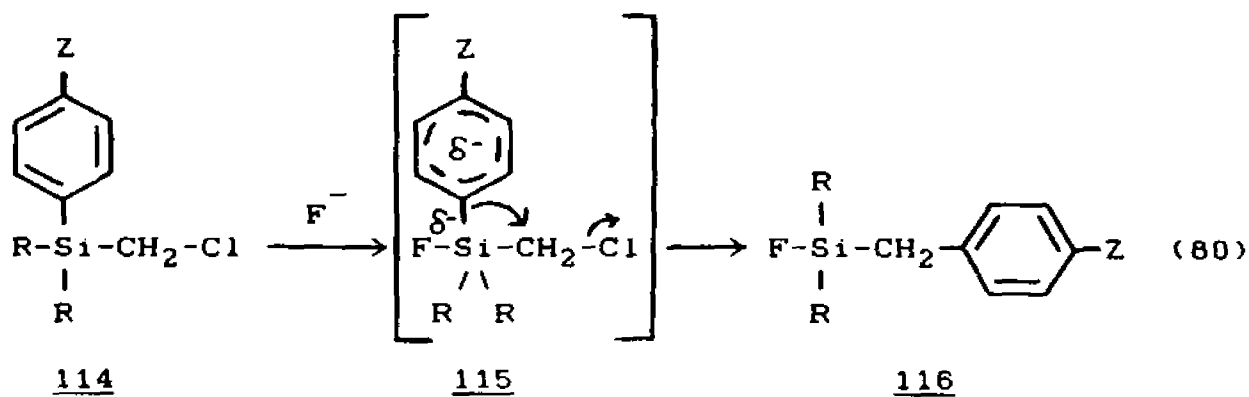
Reaction Temp (°C)	Sigma Type Used	Rho Value(ρ)	Correlation Coefficient	Relative % Error in Ar/Ph
25	σ	0.64	0.964	± 14
	σ°	0.84	0.964	± 14
0	σ	0.41	0.805	± 25
	σ°	0.61	0.908	± 18
-20	σ	0.45	0.817	± 27
	σ°	0.67	0.912	± 19

It can be seen in Table 7 that for all temperatures the rho values using sigma constants are lower than with sigma-zero constants. These results are due to the fact that the range in sigma values is larger than the sigma-zero values. It is not clear from the data which correlations are more significant, however, since they are equivalent at 25 °C and poor with sigma and only fair with sigma-zero values and with the errors in the calculated line neither of which are that reliable at 0 and -20 °C.

For reactions at different temperatures with substituent constants of the same type, the rho values increase, as expected, at -20 °C compared to 0 °C.⁷⁶ However, upon decreasing the reaction temperatures from 25 °C to the lower temperatures the rho values decrease. Because of the large errors in the correlations it becomes evident that quantitative interpretations should be made conservatively.

What is most important, however, is that the rho values for rearrangement-displacement are all greater than zero. This means that the reaction is facilitated by reducing the electron density at the reaction center, but since the rho values are less than unity, the effects of substituent are not very large. These results fit well with previous findings¹⁻⁴ in which it has been concluded that carbanionic stabilization is important in the rearrangement. Thus, when fluoride ion attacks on the chloromethylsilane

114 a pentacoordinate silane intermediate such as 115 is presumably formed (Equation 80). The phenyl group attached



to silicon which can best stabilize negative charge on silicon and also stabilize the negative charge that is carried in rearrangement migrates better. Therefore, the more electron-withdrawing a phenyl group is, the better it migrates and the more electron-donating a phenyl group is, the poorer it migrates.

The poor to fair linear free-energy correlations at the lower temperatures raise extremely interesting questions. From the graphs of the logarithms of the migratory aptitudes versus sigma or sigma-zero values for the lower temperatures (Figures 4-7), it can be seen that the plots are not highly linear. When the substituent constants are less than zero the line seems to change slope. It is therefore possible that Hammett plots of the results should

not be linear. The poor correlations would then arise from assigning linear relationships when none exist.

It has been found previously that Hammett relationships are not all linear.^{76,84-86} Deviations arise from experimental errors, impurities in the compounds, side reactions, etc. Though experimental error cannot be totally ruled out in the present research, the deviations throughout are consistent and the reactions are reproducible. The Hammett deviations from linearity arise at the lower temperatures, and thus impurities are not the cause. Since the reactions go to completion and mass balances are excellent, side reactions are not the cause.

Deviations in attempted linear free-energy correlations are frequently improved by changing to substituent constants which take into account varying polar and/or resonance effects. For example, as discussed in Chapter III, a change from sigma to sigma-zero constants can sometimes change a correlation. Such a change can not be made in the present work since the deviations do not occur for the data at 25 °C, but only at the lower temperatures. If different substituent constants would make the reactions at the lower temperatures give a linear free-energy correlation, then the results at 25 °C should deviate significantly. It is therefore very likely that there are other factors which become important at lower temperatures.

TWO COMPETING MECHANISMS

The dashed lines in Figures 4-7 represent fitting the data into two lines instead of a single line for all points. The rho values for each of the sets of data are given in Table 8. If the data do fit "best" into two lines of this sort, each of the lines would represent a Hammett plot for a competing mechanism in the reaction.

Table 8. Rho Values Calculated for Rearrangement-displacement at Lower Temperatures Assuming Two Competing Mechanisms.

$$\begin{aligned} \log (\text{Ar/Ph}) &= \rho_W \sigma & (\sigma \geq 0) \\ \log (\text{Ar/Ph}) &= \rho_D \sigma & (\sigma \leq 0) \end{aligned}$$

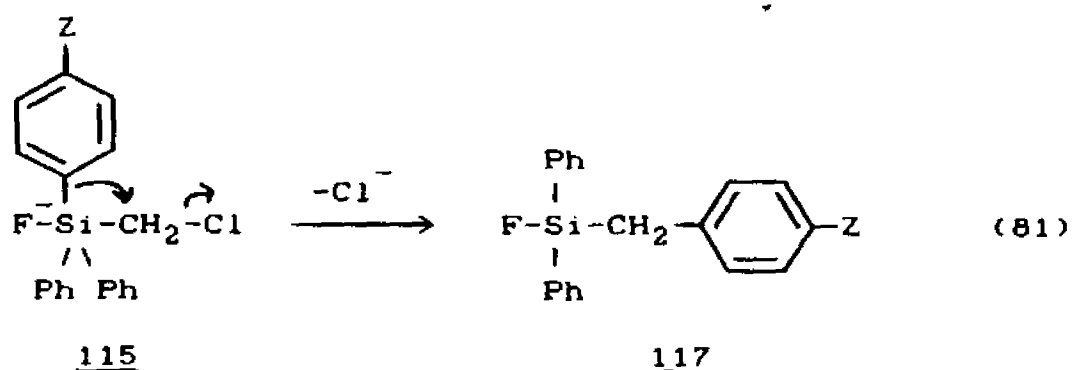
Reaction Temp ($^{\circ}\text{C}$)	Sigma-Rho Type Used	Rho Value	Correlation Coefficient	Relative % Error in Ar/Ph
0	$\rho_W \sigma$	0.90	0.981	± 8
	$\rho_W \sigma^{\circ}$	0.90	0.981	± 8
	$\rho_D \sigma$	-0.09	0.834	± 3
	$\rho_D \sigma^{\circ}$	-0.17	0.795	± 3
-20	$\rho_W \sigma$	0.95	0.984	± 8
	$\rho_W \sigma^{\circ}$	0.95	0.984	± 8
	$\rho_D \sigma$	-0.07	0.568	± 5
	$\rho_D \sigma^{\circ}$	-0.15	0.615	± 5

The rho values for rearrangements (Table 8) of phenyl groups containing electron-withdrawing substituents (ρ_W) are seen to be greater than zero and very close to unity. Further, on lowering the reaction temperatures from 0 to -20°C the rho value increases as would be expected. Also, on comparing the rho values with that for the line containing all the points for rearrangement-displacement at 25°C (Table 7), it again is observed that the values for rho increase at the lower temperatures.

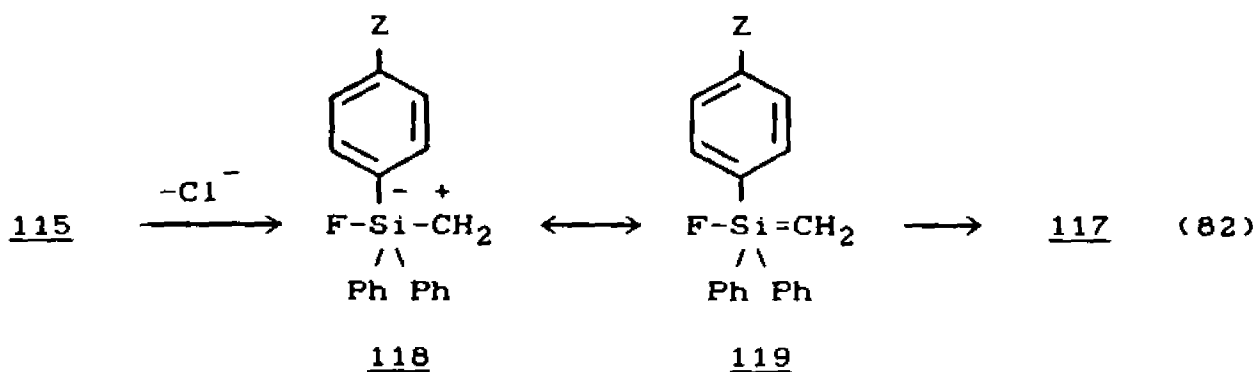
For rearrangements of phenyl groups containing electron-donor substituents (ρ_D), the rho values (Table 8) are all less than but very near zero. Such an analysis for these rearrangements might indicate that the transition states leading to migration become increasingly electron-deficient and thus electron-donor phenyl groups actually migrate very slightly better than does phenyl. It is emphasized, however, that from the slight slope of the line and the errors, the rearrangements of phenyl groups containing the electron-donor substituents could be totally non-selective.

From the above correlations it might be argued that there are at least two mechanisms for rearrangement-displacement from pentacoordinate silicon. One of the possibilities to consider is that phenyls substituted by electron-withdrawing substituents stabilize negative charge on pentacoordinate silicon and then migrate (S_N2 like) with

their sigma electrons to adjacent carbon displacing chloride ion (Equation 81). This is the same mechanism that

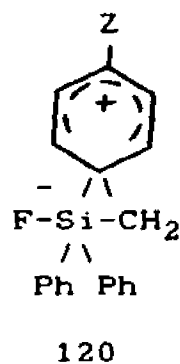


has been proposed earlier based on rho values determined for all points. A second mechanistic possibility is that electron-donor groups on phenyl destabilize the negative charge on pentacoordinate silicon and thus there is S_N1 like loss of chloride leading to ylid 118 (Equation 82).



Ylid 118 might be expected to make use of *d*-orbitals in silicon and thus have considerable character expressed as 119. Collapse of the pentacoordinate silicanion would thus

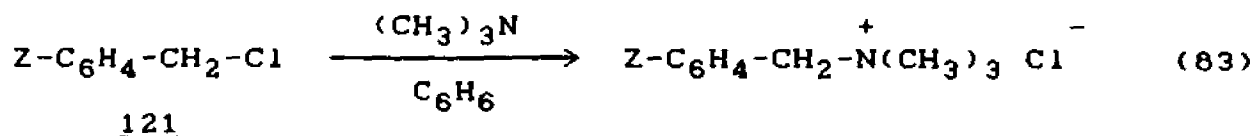
involve a transition state described primarily as 118-119. Since 118-119 is ylidic and essentially neutral, subsequent reorganization involving rearrangement would not have strong electronic demands and thus the rho values would be small. There is the further consideration that transition state 118-119 might incorporate accelerative pi electron participation from electron rich phenyl groups as in phenonium ion 120.⁸⁷



CHANGE IN TRANSITION STATE FEATURES

In the previous paragraphs the question has been raised that the non-linear Hammett correlations come from two different mechanisms for rearrangement of chloromethyl pentacoordinate silicanion intermediates. This author has enormous reservations as to the above mechanistic interpretation. It is also possible that the non-linearity of the Hammett plots are not due to changes in mechanism, but results from changes in the structures of the transition states leading to rearrangement-displacements.

Swain and Langsdorf⁸⁵ studied nucleophilic reactions of trimethylamine with substituted-benzyl chlorides 121 in benzene (Equation 83) and found a curved Hammett σ_p plot



Z = *p*-NO₂, *m*-Br, *p*-Br, H, *p*-CH₃, *p*-OCH₃

and that benzyl chloride (Z = H) reacted as the slowest halide. The curvature was explained in terms of relative amounts of nucleophile-carbon bond forming and carbon-chlorine bond rupture in the transition states. Electron-withdrawing groups which stabilize negative charge on benzylic carbon would favor bond-forming over bond-rupture. Electron-donating groups, on the other hand, would favor bond-rupture over bond-formation by stabilization of the developing positive charge.

As an alternate to two distinct mechanisms for rearrangement-displacement of 4 by fluoride ion it would appear more likely that the reactions occur by a single mechanistic continuum involving transition states with different contributions resulting from cleavage of aryl-silicon and carbon-chlorine bonds and formation of aryl-carbon bonds as in Figure 8.

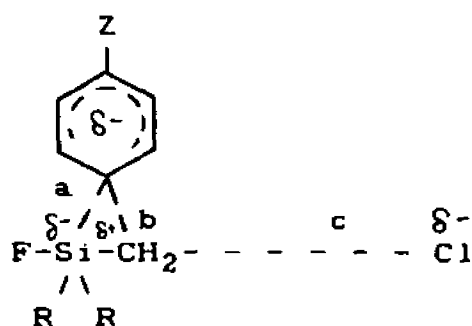


Figure 8. Structural representation of the transition state continuum proposed for rearrangement-displacement of pentacoordinate silyl intermediates 115.

In rearrangement-displacement of 4 to products, rupture of an aryl-silicon bond ("a" in Figure 8), formation of an aryl-carbon bond ("b" in Figure 8) and cleavage of a carbon-chlorine bond ("c" in Figure 8) occur. If the energies for cleavage of bonds *c* in 115 are essentially constant for all (chloromethyl)silanes studied, rupture of bond *a* will be favored by electron-withdrawing groups ($p_a > 0$) since the aryl group becomes more negatively charged. Formation of bond *b* would, on the other hand, be enhanced by electron-donating groups ($p_b < 0$) since electron-donation will make a migrating aryl group more nucleophilic. For there to be a linear free-energy correlation, the rho value must be constant for a series of substituted reactants and therefore the overall Hammett equation is a combination of the two effects:

$$\log (Ar/Ph) = (p_a + p_b)\sigma \quad (84)$$

The overall rho value for reaction ρ_r will thus be equal to the sum of ρ_a and ρ_b . If it is assumed that the absolute values of ρ_a and ρ_b are comparable and since silicon is negative $|\rho_a| > |\rho_b|$ a linear relationship between the logarithms of the migratory aptitudes and sigma constants is anticipated with a slope ($\rho_r = \rho_a + \rho_b$) greater than zero. This is indeed the case for the rearrangement-displacements at 25 °C, but does not explain the non-linearity of the lower temperature plots.

The Hammett equation assumes that the reaction constant, ρ , is independent of the substituent constant, σ . Swain and Langsdorf⁸⁵ argued that this might not be true. For example, electron-donating substituents should not only stabilize a transition state having a high positive charge but also increase the *capacity* of the reaction center (*including* substituent) for positive charge and therefore make rho more negative.

In the present rearrangement, there is no reason to assume that the requirements for cleavage of the carbon-chlorine bonds in 115 (bond *c*, Figure 8) are constant. An electron-donating group which destabilizes the negative charge on pentacoordinate silicon might cause increased stretching of bond *c* thus building partial positive charge on carbon which helps stabilize the negative-charge on silicon. The more electron-donating the group (the smaller the σ), the more bond *c* will stretch. The longer bond *c*,

the more positive carbon becomes and therefore the magnitude of p_b is increased. Since $p_b < 0$, $p_r (= p_a + p_b)$ should become increasingly smaller as the sigma value becomes smaller. Instead of two lines representing two mechanisms with two rho values, a curve is expected in which the rho value changes. Swain and Langsdorf have proposed a sigma-dependent rho value of (Equation 85):

$$\rho = \rho_0 + \tau \sigma \quad (85)$$

where ρ_0 is a reaction constant independent of the substituent, and τ is a measure of the difference between transition state and ground state resonance and dependent on the structure of the reaction center. If Equation 85 is placed into the Hammett equation for rearrangement, there is obtained (Equation 86):

$$\log (\text{Ar/Ph}) = (\rho_0 + \tau \sigma) \sigma \quad (86)$$

which upon expansion yields (Equation 87):

$$\log (\text{Ar/Ph}) = \rho_0 \sigma + \tau \sigma^2 \quad (87)$$

Equation 87 has the general formula (Equation 88) of a parabola.⁸⁸

$$y = A_0 + A_1 X + A_2 X^2 \quad (88)$$

Second-order least-square regression analyses⁶⁰ of the 0 and -20 °C reaction plots (logarithms of migratory aptitudes versus σ and σ°) are given in Table 9. All the

Table 9. Second-order Least-squares Regression Analysis Results from 0 °C and -20 °C Plots of Logarithms of Migratory Aptitudes Versus Sigma and Sigma-zero Values.

$$\log (\text{Ar/Ph}) = I + \rho_0 \sigma + \tau \sigma^2$$

Temp. (°C)	Sigma Type	I	ρ_0	τ	Correlation Coefficient	Relative % Error in Ar/Ph
0	σ	0.06	0.47	0.71	0.971	± 10
	σ°	0.05	0.41	0.85	0.961	± 12
-20	σ	0.05	0.52	0.76	0.976	± 10
	σ°	0.05	0.45	0.90	0.964	± 12

correlation coefficients are satisfactory⁶¹ and the curves calculated account for between 90 and 95% of the variance obtained. The relative errors in the curves are all within the errors calculated for the data. The quantitative meanings of ρ_0 and τ were not elaborated or discussed by Swain and Langsdorf. However, from ρ_0 and τ as calculated a rho value for each substituted-phenyl group (Table 10) can be

Table 10. Calculated Rho Values for the Substituted-phenyl Groups at 0 °C and -20 °C Using Data from Table 9 and Sigma and Sigma-zero Values.

$$\rho = \rho\sigma + \tau\sigma$$

Z	Sigma (σ)		Sigma-zero (σ^0)	
	0 °C	-20 °C	0 °C	-20 °C
<u>a</u> CF ₃	0.85	0.92	0.86	0.93
<u>b</u> Cl	0.65	0.70	0.62	0.67
<u>c</u> H	0.47	0.52	0.41	0.45
<u>d</u> CH ₃	0.37	0.41	0.30	0.33
<u>e</u> OCH ₃	0.27	0.31	0.31	0.35
<u>f</u> N(CH ₃) ₂	0.03	0.04	0.14	0.17

obtained. In Table 10 it is seen that the calculated rho values for migration of all phenyl groups are greater than zero, a correlation consistent with the premise that the transition state for rearrangement is always negative because it is derived from a negatively charged pentacoordinate silyl intermediate. The decrease in rho values as the sigma constants get larger implies that positive character increases in the rearrangement-displacement transition states. This is also consistent with the presumption of a longer carbon-chlorine bond (bond c, Figure 8). The longer bond c is stretched the more the transition state looks

like ylid 118-119 (Equation 82) which is essentially neutral and thus has minimal electronic demands.

Therefore, at 25 °C it can be argued that the rearrangements occur with very little change in the lengths of bonds *c* and thus ρ is a constant value and greater than zero. At lower temperatures, however, because slower rearrangement leads to more destabilization of the negative charge on silicon, the ease of stretching of bond *c* becomes more dependent on the substituents and thus causes a gradual decrease in the ρ values leading to curvature in the Hammett plots.

PSUEDOROTATION AND REARRANGEMENT

The interpretations that have as yet been presented in the present dissertation have all been based on traditional electrical and geometrical effects in carbon compounds. Since the present rearrangements occur however by nucleophilic attack on silicon, possible silicon stereochemistry can not be ignored. Thus it is widely known that nucleophilic attack on optically active silanes can proceed with inversion or retention of configuration.^{42f,89} Further nucleophilic attack on silicon has been postulated to lead to pentacoordinate silicon intermediates which are able to pseudorotate.^{42f,90,91}

The idea of pseudorotation was originated by Berry⁹² to explain the positional exchange of the fluorine atoms of PF_5 as indicated by its ^{19}F nmr spectra above -100°C . Since then considerable attention has been given to the stereochemical behavior of organophosphorus compounds.⁹¹⁻⁹⁶ Unfortunately, pseudorotation is not highly understood at present for any element.

Pseudorotation about silicon would be expected to involve the initial formation of a trigonal bipyramid (TBP) structure. Silicon in a pentacoordinate intermediate is expected to lie within a triangle defined by the three nearest bonding atoms in the basal plane of the TBP. Bonds between silicon and these three ligands are designated as "equatorial". Equatorial bonds have angles, in a totally symmetric structure, of 120° . The remaining two ligands, are located above and below the basal plane and are designated as "axial". In a symmetric structure the axial bonds are 90° to each of the equatorial bonds.

Pseudorotation in a pentacoordinate silicon intermediate is shown in Figure 9. A pair of equatorial ligands, B and C in 122a, move in a plane away from each other and expand the B-Si-C bond angle from 120° to 180° , thus making both B and C axial in 122b. Synchronously, axial ligands, D and E in 122a, move towards each other in a plane perpendicular to the equatorial plane, but away from pivot A. The D-Si-E angle is reduced from 180° to 120° in 122b and D and

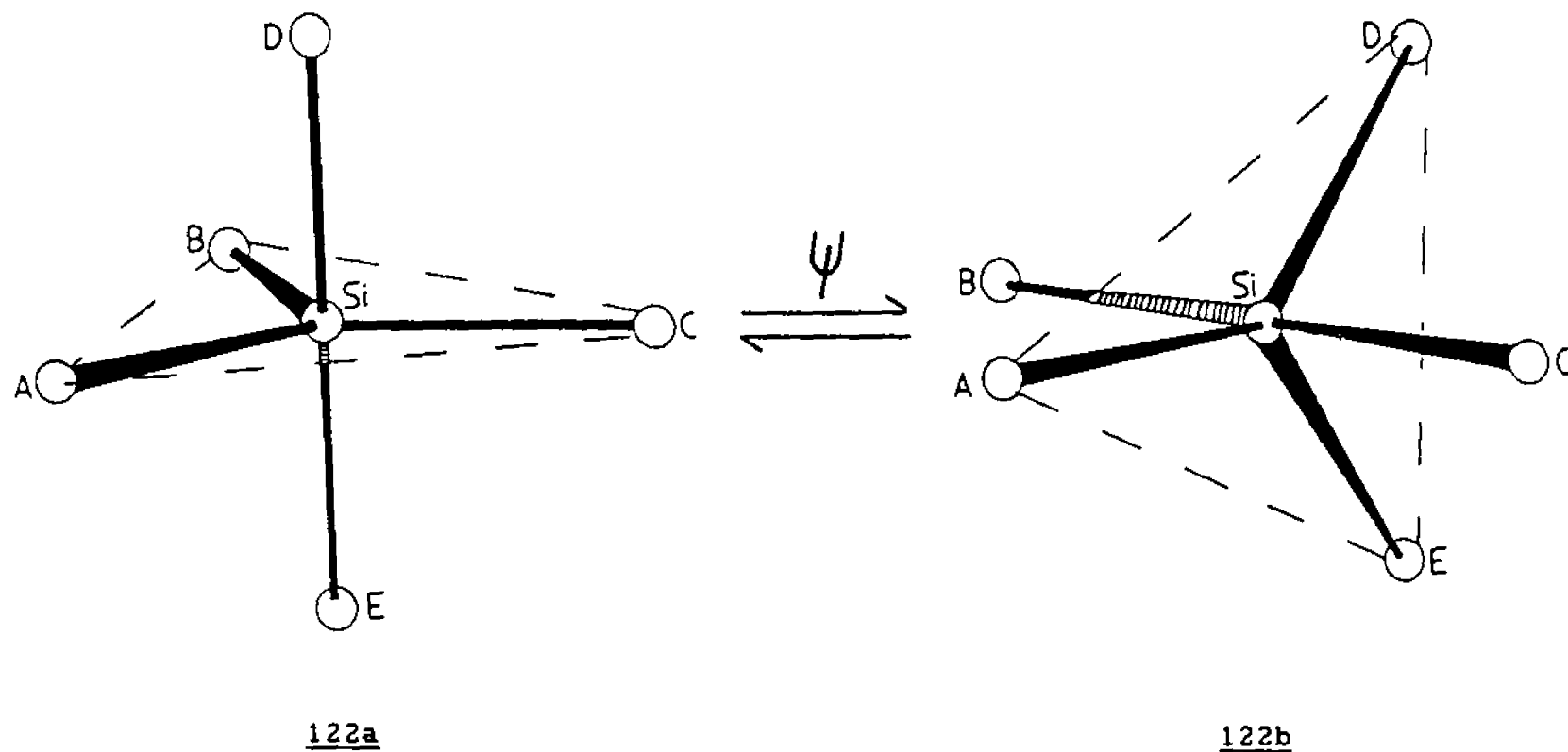


Figure 9. Pseudorotation in a trigonal bipyramidal silicon intermediate. In 122a, ligands A, B and C are equatorial and ligands D and E are axial. In 122b, ligands A, D and E are equatorial and ligands B and C are axial. Ligand A is the pivot.

E become equatorial. The pivot ligand, A in 122a, does not move and remains equatorial in 122b. A representation of the motions of the ligands in pseudorotation of 122a to 122b is given in Figure 10.

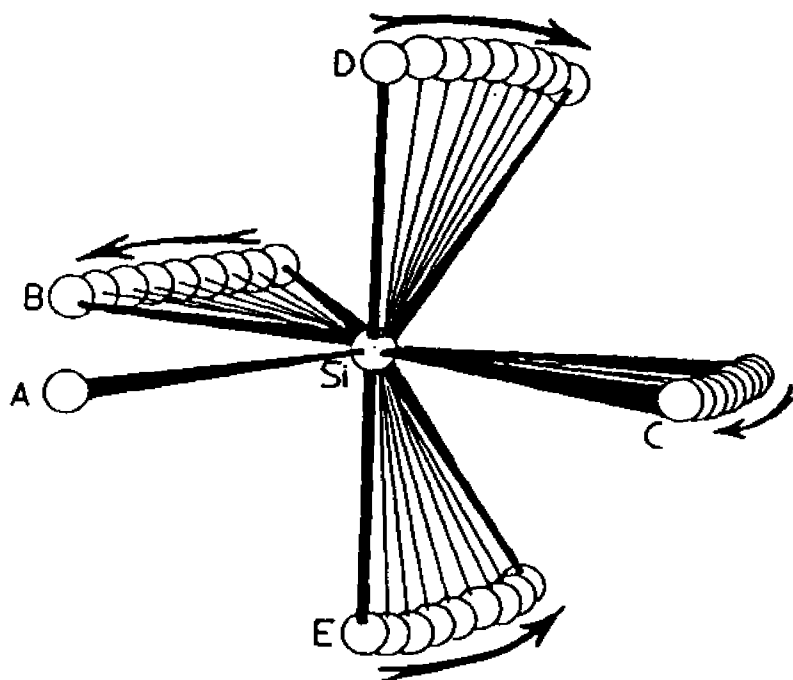
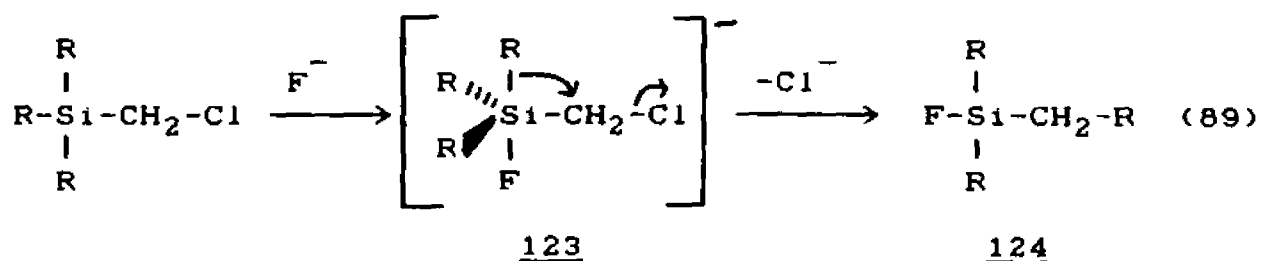


Figure 10. The motion involved in converting 122a to 122b via pseudorotation. Ligands B and C go from axial to equatorial. Ligands D and E go from equatorial to axial. The pivot ligand, A, remains equatorial in the process.

The concepts involved in the mechanistic aspects of pseudorotation in phosphorus^{91,93-96} are now to be extended to silicon:^{42f,90,91} (1) Since the axial bonds are presumably longer and weaker than equatorial bonds, the

intermediates are theorized to form by axial attack, (2) decomposition of an intermediate occurs by axial loss and (3) if the intermediates are sufficiently long-lived they undergo pseudorotation.

Therefore, when fluoride ion attacks (chloromethyl)silanes, a trigonal bipyramidal structure 123 is formed which migrates an axial group to the equatorial (chloromethyl) group with loss of chloride ion to yield rearrangement product 124 (Equation 89). If the factors that direct the



rearrangement to (chloromethyl) carbon are more important than those which result in pseudorotation, it is expected that stabilization of negative charge on pentacoordinate silicon as well as stabilization of the negative charge with which a group migrates will be controlling. Therefore, the electron-withdrawing groups should migrate better. On the other hand, if the factors that lead to pseudorotation become dominant, migration will be a function of the position of the groups around silicon. Groups which tend to go axial could thus migrate better. Therefore if

the abilities of groups to be axial were quite similar, migration could become statistically dependent and then substituent effects would not be important.

It can then be imagined that at 25 °C factors leading to rearrangement-displacement are greater than those for pseudorotation and thus electron-withdrawing groups migrate better than do electron-donors and a linear Hammett plot is obtained. At lower temperatures it can be presumed that rearrangement-displacement factors are more temperature dependent or are reduced at a faster rate than those leading to pseudorotation. It might then be proposed that for phenyls substituted by electron-withdrawing groups, the rearrangement factors are still more important than pseudorotation factors and a linear Hammett correlation for rearrangement-displacement is still observed. But for phenyls which are substituted by electron-donating groups, and thus do not rearrange as well as the withdrawing analogs, pseudorotation effects may have become more important than rearrangement factors and the migratory aptitudes are essentially statistically determined and thus independent of the sigma values for the phenyl substituents. Therefore, two lines might be obtained in a form similar to that noted in Figures 4-7.

Though there is no firm evidence for or against pseudorotation factors in this work, the premise is an exciting one. The idea of pseudorotation is of enormous

importance. Much more work needs to be done to understand further this phenomenon with reference to rearrangement-displacement in silyl intermediates and in the stereochemistry of silicon and phosphorus in general.

FUTURE AVENUES TO PURSUE

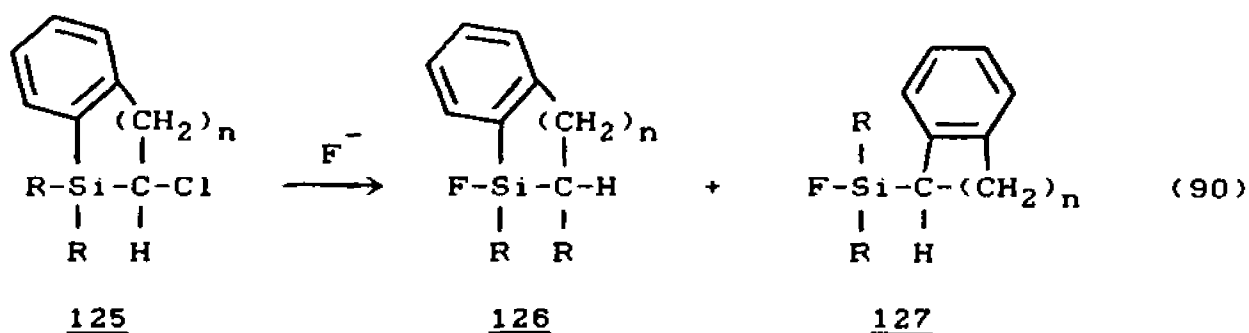
The results obtained in this research do not lead to a totally definitive understanding of rearrangement-displacements from pentacoordinate silicon. This problem is worth investigating in much greater detail whatever be the mechanistic details of such reactions.

The research in this dissertation has involved determinations of the migratory aptitudes of various substituted-phenyl groups relative to phenyl. It might be of value to actually study the rates of rearrangement-displacement by kinetic methods. Features might become apparent in a kinetic study which are not apparent from the migratory aptitudes.

Changing the leaving group from chlorine to bromine, iodine, tosylate etc., might give insight into leaving group effects. The results of this research support rearrangement-displacement transition states with variable carbon-chlorine bond lengths. Thus, leaving group effects might lend more support to this theory. With the proper leaving group, cationic features could become much more

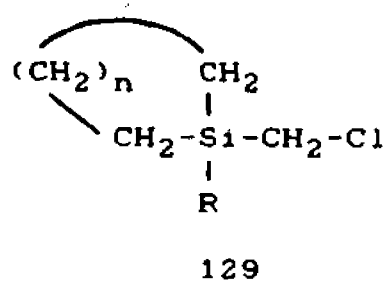
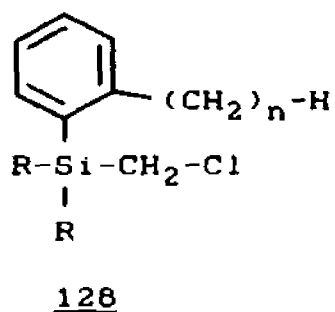
important than carbanionic features and thus the rho values for rearrangement-displacement might become negative.

Pseudorotation factors might be studied systematically in rearrangement-displacements using silanes 125 which have aryl groups bridged to chloromethyl carbon (Equation 90).



In phosphorus compounds which are bridged by four-membered and five-membered rings containing the phosphorus atom, the strained rings bridge one axial and one equatorial position in the subsequent pentacoordinate intermediate.⁹⁷ Six-membered rings prefer diequatorial placements of substituents.⁹⁷ One could study the axial-equatorial versus equatorial-equatorial rearrangements by varying the number of methylene units in the bridging chain and determining the extent and the rates of formation of the products. If axial migration is preferred, it would be expected that migratory aptitudes of aryl would be greater for the bridged aryl compound relative to the analogous unbridged

ortho-substituted aryl 128. Examining the bridged non-aromatic silanes 129 might also be of value to determine pseudorotation effects.



Chiral (halomethyl)silanes should be investigated to see if rearrangement-displacements proceed with retention or inversion of configuration. Studies could be conducted with silanes 130-132 having silicon, carbon or both silicon and carbon optically active as indicated (Figure 11).

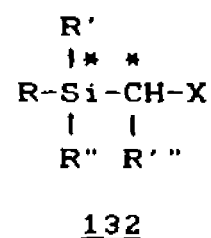
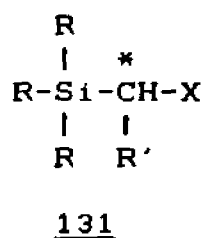
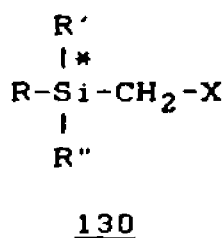
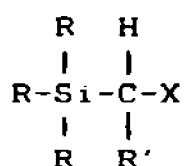


Figure 11. Possible chiral (halomethyl)silanes for further study of rearrangement-displacements.

Determining the electronics or other effects about (halomethyl)carbon might yield information with respect to

the rearrangement-displacement transition states. Thus, reactions might be conducted on (halosubstitutedmethyl)silanes 133 with varied substituents on halomethyl carbon.

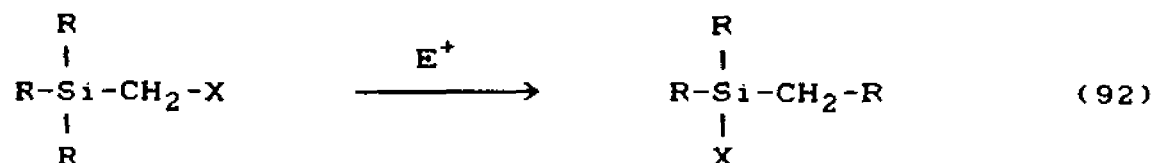
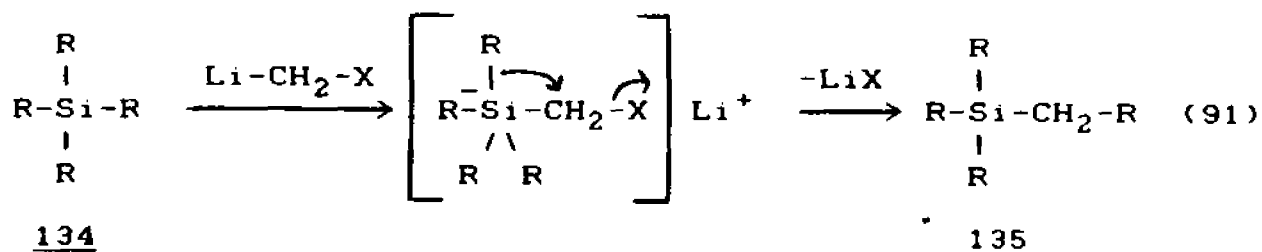


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It is possible that aryl(chloromethyl)diphenylsilanes 4 are too strained and that replacing one phenyl group by a methyl group might yield interesting results. It might also be instructive to study rearrangement-displacements with diaryl(halomethyl)silanes containing one phenyl group substituted with an electron-donor and a second phenyl group substituted with an electron-withdrawer.

The migratory aptitudes might be examined using other solvents or even higher reaction temperatures. Rearrangement-displacement with varied alkoxides could be attempted with varied (halomethyl)silanes.

Reacting halomethylolithiums with tetrasubstitutedsilanes 134 would be interesting to examine if rearrangement-displacement (Equation 91) occurs to yield (substitutedmethyl)silanes 135 and, if so, what the electronic effects are. Also, acid-catalyzed rearrangements (Equation 92)



might be conducted at low temperatures to study whether bent Hammett plots, similar to low temperature plots in this dissertation are obtained.

The evaluation of this work has lead to various conclusions about rearrangement-displacement transition states of pentacoordinate silicon. The results from this work also open the door to further studies on the mechanistic aspects of these and similar silyl intermediates.

CHAPTER V: SUMMARY AND CONCLUSIONS

A study has been made of fluoride ion induced rearrangement-displacements of aryl(chloromethyl)diphenylsilanes (4) in tetrahydrofuran at 25, 0 and -20 °C. Attack of fluoride ion presumably produces pentacoordinate silyl intermediates which rearrange with aryl (= *para*-substituted phenyl) or phenyl migration from negatively charged silicon to carbon with chloride expulsion. (Arylmethyl)-fluorodiphenylsilanes 109 and arylfluorophenyl(phenylmethyl)silanes 111 produced are cleaved quantitatively by fluoride ion to difluorodiphenylsilane (110c) and substituted-toluenes 33 and aryldifluorophenylsilanes 110 and toluene (33c), respectively.

Electronic effects in the rearrangement-displacements were studied by using various *para*-substituted-phenyl groups as aryl and determining the relative migratory aptitudes of aryl versus phenyl groups. At 25 °C the migratory aptitudes decrease in the order: $p\text{-CF}_3\text{-C}_6\text{H}_4 > p\text{-Cl-C}_6\text{H}_4 > \text{C}_6\text{H}_5 > p\text{-CH}_3\text{-C}_6\text{H}_4 > p\text{-CH}_3\text{O-C}_6\text{H}_4 > p\text{-(CH}_3)_2\text{N-C}_6\text{H}_4$. Hammett plots of the logarithms of the migratory aptitudes versus σ or σ° values yielded equally satisfactory correlations with calculated rho values of 0.64 and 0.84, respectively.

At 0 and -20 °C migratory aptitudes of decrease in the order: $p\text{-CF}_3\text{-C}_6\text{H}_4 > p\text{-Cl-C}_6\text{H}_4 > p\text{-(CH}_3)_2\text{N-C}_6\text{H}_4 \sim \text{C}_6\text{H}_5 \sim p\text{-CH}_3\text{-C}_6\text{H}_4 \sim p\text{-CH}_3\text{O-C}_6\text{H}_4$.

Various explanations have been postulated for the observed electronic effects. The mechanisms which have been considered include changes from rearrangement-displacement to ionization followed by rearrangement, pseudorotation at silicon and changes in the rearrangement-displacement transition states involving variable carbon-chlorine bond lengths. Quantitative analyses of these transition states gave rho values that depend on substituent constants and have values at 0 °C ranging from 0.85 for $p\text{-CF}_3\text{-C}_6\text{H}_4$ to 0.01 for $p\text{-(CH}_3)_2\text{N-C}_6\text{H}_4$ using sigma values, 0.86 for $p\text{-CF}_3\text{-C}_6\text{H}_4$ to 0.14 for $p\text{-(CH}_3)_2\text{N-C}_6\text{H}_4$ using sigma zero values. Calculated rho values at -20 °C range from 0.92 for $p\text{-CF}_3\text{-C}_6\text{H}_4$ to 0.04 for $p\text{-(CH}_3)_2\text{N-C}_6\text{H}_4$ using sigma values, and 0.93 for $p\text{-CF}_3\text{-C}_6\text{H}_4$ to 0.17 for $p\text{-(CH}_3)_2\text{N-C}_6\text{H}_4$ using sigma-zero values.

Aryl migrations from negatively charged silicon to carbon are favored by electron-withdrawing substituents on the aryl group. At 25 °C Hammett plots are linear but at lower temperatures mechanistic features involving increased positive character on the chloromethyl carbon and/or a greater significance of pseudorotation at silicon lead to a decreasing importance of electron-withdrawing stabilization and thus Hammett plots deviate from linearity.

CHAPTER VI: EXPERIMENTAL

GENERAL

General Procedures.

Reactions conducted under anhydrous conditions were effected under dry argon which had been passed through concentrated sulfuric acid, potassium hydroxide pellets and then anhydrous calcium sulfate (*Drierite*). Glassware was dried overnight at 100 °C and then flame-dried under argon immediately before use.

Boiling Points.

Boiling points were obtained at atmospheric pressure, unless otherwise noted, and are uncorrected. Temperatures are reported in degrees centigrade.

Melting Points.

Melting points were obtained on a Thomas Hoover *Uni-melt* capillary melting point apparatus and are uncorrected.

Proton Magnetic Resonance Spectra.

¹H nuclear magnetic resonance (NMR) spectra were obtained on a Varian Associates Models EM-390 nuclear magnetic resonance spectrometer. All chemical shifts,

unless otherwise stated, are reported in parts per million downfield from internal tetramethylsilane using carbon tetrachloride as solvent. Data are reported as follows: chemical shift [multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet), coupling constant (in Hertz), integration, interpretation].

Infrared Spectra.

Infrared spectra (IR) were obtained on a Perkin-Elmer Model 457 grating infrared spectrophotometer. Spectra of solids were obtained from potassium bromide pellets and those of liquids from either neat films on sodium chloride plates or from potassium bromide solution cells containing carbon tetrachloride. All spectra were calibrated against a polystyrene absorption peak at 1601 cm^{-1} and are reported in cm^{-1} (peak intensity (s = strong, m = medium, w = weak, b = broad)).

Mass Spectra.

Mass spectra (MS) were obtained with a Kratos Model MS-30 mass spectrometer at 70 eV at the Ohio State University Campus Chemical Instrument Center by C. R. Weisenberger. The parent peak and peaks with relative intensities greater than 10% are reported. Data are reported as follows: charge-to-mass ratio [interpretation (for parent and base peak), relative intensity].

Elemental Analysis.

Elemental analyses (Anal.) were performed by Micro-Analysis, Inc., P. O. Box 5088, Wilmington, DE 19808.

Gas Chromatograph/Mass Spectra.

Combined gas chromatograph/mass spectra (GC/MS) were obtained by David Chang at the Ohio State University Chemical Instrument Center with a Finnigan Model 4021 gas chromatograph/mass spectrum instrument.

Gas Chromatography.

General. Gas chromatography (GC) was effected on a Varian instrument *Aerograph* Model 920 with a four-filament, tungsten-rhenium WX hot wire type thermal conductivity detector. The filament current was set at 100 mA with helium as carrier gas. The products determined by GC were confirmed with the GC/MS or the IR of authentic samples. Frequently used columns and conditions, unless otherwise stated, were:

Column A: 10 ft x 1/4 in, 15% SE-30 on 100/120 mesh Gas-Chrom Q; Temperatures (°C): Injector (290), Column (230), Detector (285); Flow rate: 60 mL/min.

Column B: 6 ft x 1/4 in, 15% didecyl phthalate, 5% silicone oil W 98 on 60/80 mesh Chromosorb W; Temperatures (°C): Injector (150), Column (105), Detector (150); Flow rate: 60 mL/min.

Column C, 5 ft x 1/4 in, 10% didecyl phthalate on 80/100 mesh Chromosorb W HP; Temperatures (°C): Injector (155), Column (120), Detector (155); Flow rate: 75 mL/min.

GC Areas. Areas were determined as an average of four trials for each run by two methods considered equal in precision. The first method involved multiplication of the measured height by the measured width at half-height of the actual GC trace obtained on a Houston Instrument *Omniscribe* Model B-5217-1 10 inch strip chart recorder at a span width of 10 mV and chart speed of 10 cm/min.

The second method made use of a Spectra-Physics *Auto-lab Minigrator* Model 23000-111 electronic integrator with parameters set as: Peak Width (PW) = 12, Slope Sensitivity (SS) = 100, Baseline Test (BL) = 5, Tailing Peak (TP) = 25 and T1 = 75.

Tests for Detection of Grignard and Organolithium Reagents.

Color Tests. Qualitative color tests were used to determine completion of organometallic reactions. Color Test I (a.k.a. "The Gilman Test")⁹⁸ is a sensitive qualitative test for Grignard reagents and organolithium compounds. The test was administered as follows: to a 1 mL aliquot of the solution to be tested was added 1 mL of a 1% solution of 4,4'-bis(dimethylamino)benzophenone (Michler's ketone) in dry benzene. The solution was hydrolyzed with 1 mL of water and then acidified with 3-5 drops of a 0.2%

solution of iodine in glacial acetic acid. A greenish-blue color indicated presence of an organometallic reagent.

Color Test IIA⁹⁹ depends upon the greater reactivity of *n*-butyllithium over aryllithium compounds in halogen-metal interconversions. The procedure followed was: to a 1 mL aliquot of the solution to be tested was added 1 mL of a 15% solution of 4-bromo-*N,N*-dimethylaniline in dry benzene. One mL of a 15% solution of benzophenone in dry benzene was then immediately added to this. After a few seconds the mixture was hydrolyzed with water and acidified with concentrated hydrochloric acid. A red color in the water layer was a positive test for *n*-butyllithium.

Titration. After the preparations of the Grignards or the organolithium compounds were complete, the reagents were titrated to determine their concentration before use. Titration was accomplished¹⁰⁰ by adding a 1.0 mL aliquot of the organometallic solution to ~1 mg of the indicator, 1,10-phenanthroline, dissolved in ~1mL of dry benzene. The solution instantly turned deep-violet. Measurement of the volume of a 1.0 M solution of 2-butanol in xylenes to fade the color determines the molarity of the organometallic reagent.¹⁰¹

Preparation of Aryllithium Reagents

Aryllithium reagents were prepared by two methods depending on the substituent on the aryl group:

Method A: To a suspension of freshly-cut lithium chips (0.23 g, 33 mmol) in diethyl ether (5 mL) was added the substituted-phenyl bromide (98, 15 mmol) in diethyl ether (20 mL) at a rate (~30 min) to cause reflux. After the addition the reaction was refluxed 2 h.

Method B: A solution of *n*-butyllithium in hexanes (15 mmol) was added (~30 min) to a solution of the substituted-phenyl bromide (98, 15 mmol) in diethyl ether (20 mL) at -40 °C. The mixture was allowed to warm gradually to ~15 °C until Color Test IIA⁹⁹ indicated that all the *n*-butyllithium had reacted.

PREPARATION OF ARYL(CHLOROMETHYL)DIPHENYLSILANES 4

Preparation of Trichloro(chloromethyl)silane (96a).⁶⁴

Dry chlorine was bubbled into a mixture of trichloromethylsilane (95, 1750 mL, 2228 g, 14.9 mol) and 2,2'-azobisisobutyronitrile (AIBN, 4.5 g, 0.027 mol) at 60-65 °C. The reaction was monitored by NMR. When chlorination of 96a began to give trichloro(dichloromethyl)silane [96b], NMR: δ 5.00 (s, 1H, Si-CHCl₂), significantly at approximately 15-20 h, chlorination was stopped. Nitrogen was then

passed through the mixture for 0.5 h to purge hydrogen chloride.

The product mixture was distilled at atmospheric pressure through a 20 x 150 mm column packed with stainless steel staples. After approximately 1500 mL of 95 had been collected (bp 66 °C), the residue was distilled through a 10 x 320 mm column packed with stainless steel staples to obtain: (1) trichloromethylsilane (95, 13.6 g, total collected: 1909.2 g, 12.8 mol): bp 65 °C; (2) a mixture of 95 and 96a (12.8 g): bp 66-115 °C; (3) trichloro(chloromethyl)silane (96a, 112.1 g, 0.609 mol, 29% based on recovered 89): bp 115-117 °C [lit⁶⁴ 116-119 °C]. The spectral properties of 96a are as follows: NMR (CDCl₃) δ 3.30 (s, 2H, Si-CH₂-Cl); IR (CCl₄) 2920(m), 2820(w), 1380(m), 1100(b,m), 670(m), 600(s), 450(m) cm⁻¹; MS 184(13), 182(M⁺,10), 149(15), 147(16), 137(54), 135[M⁺ - (CH₂Cl), 100], 133(96), 113(14), 98(11), 65(23), 63(64), 49(19); exact mass calcd for CH₂³⁵Cl₄Si *m/e* 181.8683, found 181.8693.

Preparation of Chloro(chloromethyl)diphenylsilane (97).⁶⁵

A solution of phenylmagnesium bromide in anhydrous diethyl ether was prepared by dropwise addition of bromobenzene (96c, 75.0 ml, 112 g, 0.712 mol) in diethyl ether (100 mL) to a stirred suspension of magnesium turnings

(19.0 g, 0.782 mol) in diethyl ether (150 mL). After 98c had been added, the mixture was stirred for 2 h.

To a stirred solution of trichloro(chloromethyl)silane (96a, 54.1 g, 0.294 mol) in anhydrous diethyl ether (100 mL) was added dropwise (~2 h) phenylmagnesium bromide (250 mL of a 2.35 M solution in diethyl ether, 0.588 mol) over 2 h. The mixture was refluxed until Color Test I⁹⁸ was negative (~5 h).

The suspension was filtered through celite and then the magnesium salts were rinsed with anhydrous diethyl ether (5 x 50 mL). Concentration *in vacuo* followed by rapid, simple distillation of the liquid from the remaining magnesium salts gave a slightly-colored liquid (bp 96-155 °C/3 torr, which was redistilled through a 12 x 110 mm column packed with stainless steel staples to yield chloro-(chloromethyl)diphenylsilane (97, 53.3 g, 0.199 mol, 68%), a clear liquid: bp 136-140 °C/2.5 torr [lit⁶⁵ 187-192 °C/10 torr]; NMR (CDCl₃) δ 7.80-7.25 (m, 10H, 2 x Si-C₆H₅), 3.40 (s, 2H, Si-CH₂-Cl); IR (CCl₄) 3070(m), 3040(m), 3000(w), 2910(w), 1590(w), 1480(w), 1430(s), 1390(m), 1120(s), 690(s), 640(m), 550(s), 480(m), 434(m) cm⁻¹; MS 266(M⁺, 4), 227(24), 219(55), 218(27), 217[M⁺ - (CH₂Cl), 100], 183(15), 181(15), 91(12), 63(11); exact mass calcd for C₁₃H₁₂³⁵Cl₂Si *m/e* 266.0087, found 266.0164.

Preparation of (Chloromethyl)triphenylsilane (4c).

Addition of absolute ethanol (30 mL) to the pot residue in the distillation of 97 led to crystallization of an off-white solid.¹⁰² Recrystallization with low-boiling petroleum ether (2x) yielded (chloromethyl)triphenylsilane (4c, 3.2 g, 10 mmol, 4%) as white plates: mp 113-116 °C [lit⁶⁸ 112-115 °C]; NMR δ 7.65-7.25 (m, 15H, 3 x Si-C₆H₅); 3.45 (s, 2H, Si-CH₂-Cl); IR (CCl₄) 3060(m), 3040(m), 2920(w), 2820(w), 1590(w), 1480(w), 1425(s), 1390(m), 1260(w), 1200(m), 1110(s), 1050(m), 695(s), 680(w), 630(m), 500(s), 480(m), 430(m) cm⁻¹; MS 308(M⁺, 0.3), 261(11), 260(39), 259[M⁺ - (CH₂Cl), 100], 181(18), 105(13); exact mass calcd for C₁₉H₁₇³⁵ClSi *m/e* 308.0789, found 308.0745.

General Procedure for the Preparation of Aryl(chloromethyl)diphenylsilanes.

Aryl(chloromethyl)diphenylsilanes (4a, 4b, 4d, 4e and 4f) were prepared by the addition (~45 min) of the appropriate aryllithium reagent in diethyl ether or diethyl ether/hexanes (13 mmol) to a stirred solution of chloro(chloromethyl)diphenylsilane (97, 3.5 g, 13 mmol) in diethyl ether (10 mL). The aryllithiums prepared by Method A were added at room temperature and the mixtures refluxed until Color Test I⁹⁸ was negative (~1 h). Additions were effected at -40 °C for aryllithiums prepared by Method B, and

the mixtures were allowed to warm to room temperature (~1 h) until Color Test I⁹⁸ was negative.

After a reaction was complete, water (30 mL) was added, and the mixture was separated and extracted with diethyl ether (2 x 10 mL). The diethyl ether solutions were combined, washed with water (15 mL) and saturated sodium chloride (15 mL) and dried over anhydrous magnesium sulfate. After filtration and concentration *in vacuo*, crystals of the following previously unreported silanes were obtained:

(Chloromethyl)[4-(trifluoromethyl)phenyl]diphenylsilane (4a) was prepared by Method B and crystallization occurred spontaneously upon concentration of the diethyl ether. Recrystallization twice from hexane gave 4a as white needles: yield 51%; mp 98-100 °C; NMR δ 7.65-7.20 (m, 14H, Si-Ar-H), 3.45 (s, 2H, Si-CH₂-Cl); IR (KBr) 3080(w), 3060(w), 3015(w), 3000(w), 2920(w), 1610(w), 1590(w), 1485(w), 1430(m), 1390(m), 1330(s), 1270(w), 1175(m), 1160(m), 1135(s), 1120(s), 1110(s), 1060(m), 1020(m), 1000(w), 835(m), 790(w), 775(w), 755(m), 740(b,m), 710(m), 700(s), 645(w), 605(w), 515(s), 490(m), 455(w), 410(w), 370(w), 335(w) cm⁻¹; MS M⁺ undetected, 328(25), 327[M⁺ - (CH₂Cl), 100]; exact mass calcd for C₁₉H₁₄F₃Si [M⁺ - (CH₂Cl)] *m/e* 327.0817, found 327.0802. Anal. Calcd for C₂₀H₁₆ClF₃Si: C, 63.74; H, 4.25. Found: C, 64.00; H, 4.29.

(Chloromethyl)(4-chlorophenyl)diphenylsilane (4b), prepared by Method B, crystallized spontaneously upon concentration in diethyl ether. Recrystallization twice from hexane gave white needles of 4b: yield 54%; mp 84-45 °C; NMR δ 7.60-7.20 (m, 14H, Si-Ar-H), 3.40 (s, 2H, Si-CH₂-Cl); IR (KBr) 3080(w), 3040(w), 3020(w), 2920(w), 1590(m), 1480(m), 1430(s), 1380(m), 1340(w), 1310(w), 1260(w), 1180(w), 1120(s), 1105(m), 1080(s), 1015(m), 820(m), 785(w), 760(m), 740(b,m), 700(s), 640(m), 620(w), 535(w), 515(s), 480(m), 470(w), 460(w), 400(m), 350(w) cm⁻¹; MS 342(M⁺, 1), 295(38), 294(26), 293[M⁺ - (CH₂Cl), 100]; exact mass calcd for C₁₉H₁₆³⁵Cl₂Si [M⁺ - (CH₂Cl)] *m/e* 342.0400, found 342.0424. Anal. Calcd for C₁₉H₁₆Cl₂Si: C, 66.47; H, 4.66. Found: C, 65.99; H, 4.64.

(Chloromethyl)(4-methylphenyl)diphenylsilane (4d) was prepared by Method A. The product crystallized spontaneously from diethyl ether upon concentration. White needles of 4d were obtained after two recrystallizations from hexane: yield 54%; mp 76-79 °C; NMR δ 7.60-7.05 (m, 14H, Si-Ar-H), 3.40 (s, 2H, Si-CH₂-Cl), 2.40 (s, 3H, Ar-CH₃); IR (KBr) 3080(w), 3050(w), 3020(w), 2920(w), 1590(w), 1480(w), 1430(m), 1390(w), 1310(w), 1260(w), 1180(w), 1120(s), 1105(m), 1015(w), 805(m), 785(w), 750(m), 700(s), 640(m), 635(w), 605(w), 515(s), 480(m), 470(w), 425(w), 370(w), 340(w) cm⁻¹; MS M⁺ undetected, 274(24), 273[M⁺ - (CH₂Cl), 100]; exact mass calcd for C₁₉H₁₇Si [M⁺ -

(CH₂Cl)] m/e 273.1100, found 273.1096. Anal. Calcd for C₂₀H₁₉ClSi: C, 74.42; H, 5.89. Found: C, 74.73; H, 5.95.

(Chloromethyl)(4-methoxyphenyl)diphenylsilane (4e) was prepared by Method B. The syrup obtained after concentration was distilled to give a very viscous oil, bp 165-167 °C/0.25 torr which crystallized in diethyl ether/hexane overnight at -20 °C. Recrystallization twice from hexane gave 4e as white needles: yield 30%; mp 60-62 °C; NMR δ 7.65-6.80 (m, 14H, Si-Ar-H), 3.80 (s, 3H, Ar-O-CH₃), 3.40 (s, 2H, Si-CH₂-Cl); IR (KBr) 3080(w), 3050(w), 3020(w), 2920(w), 1590(s), 1560(w), 1490(m), 1440(m), 1390(w), 1310(w), 1280(m), 1255(m), 1180(w), 1115(s), 1020(m), 1000(w), 835(w), 820(w), 800(w), 770(w), 740(b,m), 700(s), 645(w), 605(w), 505(s), 480(w), 450(w), 420(w), 370(w) cm⁻¹; MS 338 (M⁺, 3), 290(26), 289[M⁺ - (CH₂Cl), 100]; exact mass calcd for C₂₀H₁₉³⁵ClOSi m/e 338.0895, found 338.0907. Anal. Calcd for C₂₀H₁₉ClOSi: C, 70.90; H, 5.61. Found: C, 71.21; H, 5.52.

(Chloromethyl)[4-(dimethylamino)phenyl]diphenylsilane (4f) was prepared by Method A and crystallized as a slightly yellow solid. Recrystallization from methylene chloride at -78 °C and then from hexane resulted in white needles of 4f: yield 30%; mp 106-110 °C; NMR δ 7.55-6.55 (m, 14H, Si-Ar-H), 3.40 (s, 2H, Si-CH₂-Cl), 2.95 [s, 6H, Ar-N(CH₃)₂]; IR (KBr) 3080(w), 3060(w), 3020(w), 2920(w), 1595(s), 1520(m), 1480(w), 1450(w), 1430(m), 1390(w),

1365(m), 1280(w), 1230(w), 1205(w), 1120(s), 1105(m), 1000(w), 945(w), 810(m), 780(m), 765(m), 730(b,m), 700(s), 640(m), 635(w), 600(w), 530(m), 490(w), 470(m), 400(w), 350(w) cm^{-1} ; MS 353(10), 351(M^+ , 24), 303(28), 302(M^+ - CH_2Cl), 100]; exact mass calcd for $\text{C}_{21}\text{H}_{22}^{35}\text{ClNSi}$ m/e 351.12127, found 351.1163. Anal. Calcd for $\text{C}_{21}\text{H}_{22}\text{ClNSi}$: C, 71.69; H, 6.26. Found: C, 71.49; H, 6.23.

REACTIONS OF 4 WITH FLUORIDE ION

Calculations of Product Yields.

Product yields were determined by GC using internal standard methodology in which a known amount of standard is added at the conclusion of the reaction and the GC areas of the compounds of interest are then compared to that of the standard. The average area from four analyses was used to determine the areas. The standard used in all cases was anisole and average areas were corrected for detector response. Yields determined by this method are accurate to approximately $\pm 5\%$ of the absolute value.⁷⁰ If the data produced a larger error than $\pm 5\%$ the larger error was used.

Determination of GC Detector Responses.

Detector responses were determined by injecting a mixture of known quantities of the standard (i.e. anisole) and the sample whose response is being determined into the

GC. Four runs were made, with four trials per run, for each sample with weight ratios (sample:standard) of approximately 1:4, 1:2, 3:4 and 1:1. The weight ratios (sample/standard) were then plotted versus the area ratios (sample/standard). The slope of the line determined by linear regression⁶⁰ is the detector response. The relative responses determined for substituted-toluenes 33 were:

4-(Trifluoromethyl)toluene (<u>33a</u>)	1.27 ± 0.04
4-Chlorotoluene (<u>33b</u>)	1.10 ± 0.03
Toluene (<u>33c</u>)	0.88 ± 0.03
4-Methyltoluene (<u>33d</u>)	0.90 ± 0.02
4-Methoxytoluene (<u>33e</u>)	1.01 ± 0.03
4-(Dimethylamino)toluene (<u>33f</u>)	1.07 ± 0.04

Preparation of Substituted-toluenes (33)

All of the substituted-toluenes were commercially available except for 4-(trifluoromethyl)toluene (33a). Available toluenes were purchased from The Aldrich Chemical Company and distilled immediately before use. 4-(Trifluoromethyl)toluene (33a) was prepared¹⁰³ as follows:

A solution of methyl iodide (14.8 g, 104 mmol) in anhydrous diethyl ether (25 mL) was added dropwise to a stirred solution 4-(trifluoromethyl)phenylmagnesium bromide in diethyl ether (prepared by the addition of 4-bromo-benzotrifluoride (98a, 7.4 g, 33 mmol) in anhydrous diethyl

ether (15 mL) to magnesium turnings (0.84 g, 35 mmol) in diethyl ether (20 mL)]. The reaction mixture was refluxed until Color Test I⁹⁸ was negative (~30 h).

After cooling, 10% sulfuric acid (25 mL) was added slowly to the reaction mixture followed by separation and extraction with diethyl ether (3 x 10 mL). The combined ethereal layers were washed with water (2 x 5 mL) and saturated sodium chloride (7 mL) and then dried over anhydrous magnesium sulfate. Filtration and concentration *in vacuo* gave an oil which was distilled through a short-path distillation apparatus containing Kurly-Kate to yield: (1) a mixture of 4-bromobenzotrifluoride, trifluoromethylbenzene, diethyl ether, and 4-(trifluoromethyl)toluene (33a, 0.72 g total, ~60% pure): bp 59-61 °C; (2) 33a (0.34g, ~95% pure): bp 101-103 °C [lit¹⁰³ 129 °C]. GC Prep (column B) of fractions 1 and 2 gave 4-(trifluoromethyl)toluene (33a, 0.69 g, 4.3 mmol, 13%), a clear liquid: retention time 160 s; NMR δ 7.55 (d, $J = 8$ Hz, 2H, 2 x *ortho*-CF₃ Ar-H), 7.25 (d, $J = 8$ Hz, 2H, 2 x *ortho*-CH₃ Ar-H), 2.50 (s, 3H, CF₃-C₆H₄-CH₃); IR (NaCl) 3040(m), 2930(m), 2860(w), 1910(w), 1800(w), 1760(w), 1660(w), 1640(m), 1610(m), 1450(b,m), 1410(m), 1380(m), 1330(b,s), 1240(m), 1215(m), 1160(b,s), 1130(b,s), 1070(s), 1020(s), 950(m), 820(s), 750(m), 730(b,m), 720(m) cm⁻¹; MS 160(M⁺, 70), 159(18), 141(11), 91[M⁺ - (CF₃), 100]; exact mass calcd for C₈H₇F₃ m/e 160.0500, found 160.0469.

Reaction of Aryl(chloromethyl)diphenylsilanes (4) with Tetrabutylammonium Fluoride.

The general reaction conditions were as follows:

To the aryl(chloromethyl)diphenylsilane (4, 0.2 mmol) in distilled tetrahydrofuran (0.3 mL) maintained at either 25, 0 or -20 °C was added, all at once, a 1.0 M solution of tetrabutylammonium fluoride (TBAF) in tetrahydrofuran (0.5 mmol). The mixture was stirred until reaction was complete (25 °C, ~8h; 0 and -20 °C, ~2 weeks), then water (2 mL) was added followed by pentane (0.2 mL). The mixture was separated and extracted with pentane (3 x 0.2 mL) and then analyzed by GC using column B or column C with anisole (retention time: column B, 310 s; column C, 250 s) as internal standard.

Reactions were conducted both by adding the standard (anisole) before the reaction started and after the reaction was worked-up. When the standard was added before the reaction started, the percent yield obtained from the total of measured toluene and substituted toluene was between 93 and 106%. Due to mechanical loss in the work-up when anisole was added afterwards yields were between 78 and 93%.

Typical results¹⁰⁴ are given below for each compound at 25 °C with column B. Chlorobenzene (~10%) was detected in the reactions of (chloromethyl)(4-chlorophenyl)diphenylsilane (4b) presumably from cleavage of (4-chlorophenyl)difluorophenylsilane (110b) with fluoride ion.

Substituted-benzenes from cleavages of other difluorosilanes 110 were not detected. Tributylamine (an impurity in tetrabutylammonium fluoride) was also detected in some runs. Retention times for toluenes 33 on column C were generally about 20% shorter:

(Chloromethyl)[4-(trifluoromethyl)phenyl]diphenylsilane (4a, 65.7 mg, 0.1743 mmol) with TBAF (0.44 mmol) gave in analysis: (1) toluene (33c, 7.0 mg, 0.076 mmol, 44%): retention time 120 s; (2) 4-(trifluoromethyl)toluene (33a, 17.1 mg, 0.107 mmol, 61%): retention time 160 s.

Reaction of (chloromethyl)(4-chlorophenyl)diphenylsilane (4b, 70.4 mg, 0.2051 mmol) with TBAF (0.51 mmol) gave: (1) toluene (33c, 10.2 mg, 0.111 mmol, 54%): retention time 120 s; (2) 4-chlorotoluene (33b, 10.4 mg, 0.082 mmol, 40%): retention time 390 s.

(Chloromethyl)triphenylsilane (4c, 300.8 mg, 0.9738 mmol) with TBAF (3.00 mmol) yielded: (1) toluene (33c, 92.0 mg, 1.00 mmol, 103%): retention time 120 s.

Reaction of TBAF (0.46 mmol) with (chloromethyl)(4-methylphenyl)diphenylsilane (4d, 59.9 mg, 0.1855 mmol) yielded: (1) toluene (33c, 11.8 mg, 0.128 mmol, 69%): retention time 120 s; (2) 4-methyltoluene (33d, 6.2 mg, 0.058 mmol, 31%): retention time 210 s.

(Chloromethyl)(4-methoxyphenyl)diphenylsilane (4e, 68.9 mg, 0.2033 mmol) with TBAF (0.51 mmol) resulted in: (1) toluene (33c, 14.1 mg, 0.153 mmol, 75%): retention

time 120 s; (2) 4-methoxytoluene (33e, 5.3 mg, 0.043 mmol, 21%): retention time 500 s.

The products of reaction of (chloromethyl)[4-(dimethylamino)phenyl]diphenylsilane (4f, 68.8 mg, 0.1955 mmol) with TBAF (0.49 mmol) were analyzed under slightly different GC conditions. Due to the retention of 4-(dimethylamino)toluene (33f) on the column, the column temperature was increased during each trial. Column temperature started at 105 °C and after the anisole had been measured (retention time 310 s) the column temperature was increased to 150 °C (rate -15 °C/min) until 33f had been measured. Typical analysis: (1) toluene (33c, 13.9 mg, 0.151 mmol, 77%): retention time 120 s; (2) 4-(dimethylamino)toluene (33f, 5.5 mg, 0.041 mmol, 21%): retention time 780 s.

Calculations of Relative Migratory Aptitudes for Substituted-phenyl Groups at Various Temperatures.

Relative migratory aptitudes were determined by division of mmoles of substituted toluenes 33 by mmoles of toluene (33c) for each reaction. The migratory aptitudes determined were then statistically corrected since (chloromethyl)silanes 4 contain two phenyl groups and one substituted-phenyl group. Minimum errors in migratory aptitudes are $\pm 10\%$.^{74,75} For each reaction at a given temperature the standard deviation of the mean for all runs was compared with the minimum error and the larger value used as

the error for the migratory aptitude. Corrected migratory aptitudes for the substituted phenyl groups at 25, 0 and -20 °C are given in Table 11.

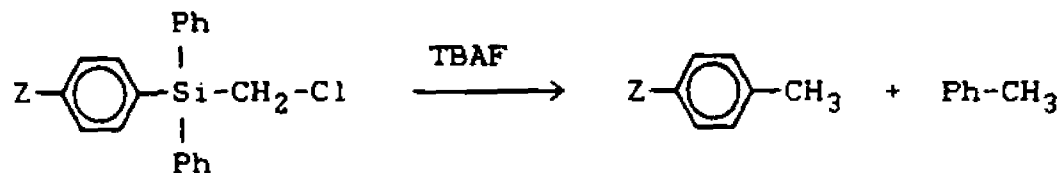
REACTIONS OF 4 WITH METHOXIDE ION

Reaction of (Chloromethyl)triphenylsilane (4c) with Sodium Methoxide in 1,4-Dioxane.

Dry sodium methoxide was prepared under argon by the addition of sodium metal (0.25 g, 10.9 mmol) to anhydrous methanol (5 mL) followed by removal of the excess methanol. The sodium methoxide prepared (assumed to be 10.9 mmol) was heated overnight at 150 °C at 30 torr.¹⁰⁵

After the sodium methoxide had been cooled and flushed with argon, anhydrous 1,4-dioxane (12 mL) and then (chloromethyl)triphenylsilane (4c, 1.50 g, 4.86 mmol) was added all at once. The mixture was refluxed (~72 h) until no 4c (retention time 1465 s) was detected by GC (column A). Addition of water (10 mL), separation and extraction with diethyl ether (2 x 5 mL), drying with magnesium sulfate, filtration and concentration *in vacuo* yielded an analyzable solution. Six products were noted by analysis on column A. Three of the components were very minor products (retention time 330 s) which could not be isolated in quantity. The major products (retention times 765, 990 and 1215 s) were obtained in very low yields and were unidentifiable. The

Table 11. Statistically Corrected Relative Migratory Aptitudes for Substituted-phenyl Groups at Various Temperatures.



Z	25 °C		0 °C		-20 °C	
	Migratory Aptitude	No. Runs	Migratory Aptitude	No. Runs	Migratory Aptitude	No. Runs
<u>a</u> CF ₃	2.72 ± 0.27	8	3.00 ± 0.30	5	3.20 ± 0.32	5
<u>b</u> Cl	1.67 ± 0.17	8	2.01 ± 0.21	4	2.02 ± 0.20	4
<u>c</u> H	1.00 ± 0.10	1 ^a	1.00 ± 0.10	1 ^a	1.00 ± 0.10	1 ^a
<u>d</u> CH ₃	0.906 ± 0.091	5	0.981 ± 0.098	4	0.974 ± 0.097	5
<u>e</u> OCH ₃	0.58 ± 0.12	11	0.974 ± 0.097	4	0.906 ± 0.091	4
<u>f</u> N(CH ₃) ₂	0.550 ± 0.095	6	1.13 ± 0.17	5	1.09 ± 0.19	5

^aRelative migratory aptitude must be unity. A run was made to confirm that reaction went to completion.

products contained no OCH₃ NMR peaks (δ 3-4 ppm) and do not match with any of the expected major products, methoxydiphenyl(phenylmethyl)silane (103c), dimethoxydiphenylsilane (102c), or methoxytriphenylsilane (104c) in retention time or spectra.

Authentic samples of 103c, 102c and 104c were stable to the GC conditions and work-up procedures used.

Reaction of (Chloromethyl)triphenylsilane (4c) with Sodium Methoxide in Methanol.

(Chloromethyl)triphenylsilane (4c, 1.00 g, 3.24 mmol) was added, all at once, to a solution of sodium methoxide in methanol prepared by the addition of sodium metal (0.15 g, 6.5 mmol) to anhydrous methanol (8 mL). The mixture was then refluxed (~55 h) until no 4c (retention time 1465 s) was detected by GC (column A). Addition of water (10 mL), separation and extraction with diethyl ether (2 x 5 mL), followed by drying with magnesium sulfate, filtration and concentration *in vacuo* yielded an analyzable product: (1) dimethoxydiphenylsilane (102c): retention time 350 s; (2) methoxydiphenyl(phenylmethyl)silane (103c): retention time 1090 s. The ratio of 102c:103c was approximately 1:2. The absolute yields were not determined.

Reaction of (Chloromethyl)(4-methylphenyl)diphenylsilane (4d) with Sodium Methoxide in Methanol.

To a solution of sodium methoxide in methanol, prepared by the addition of sodium metal (0.29 g, 12.6 mmol) to anhydrous methanol (8 mL), was added (chloromethyl)-(4-methylphenyl)diphenylsilane (4d, 1.00 g, 3.10 mmol) all at once. 1,4-Dioxane (1 mL) was also added to help dissolve 4d. The mixture was refluxed (~45 h) until no 4d (retention time 1800 s) was detected by GC (column A). Water (10 mL) was added and the layers separated. Extraction of the aqueous layer with diethyl ether (2 x 5 mL), followed by drying with magnesium sulfate, filtration and concentration *in vacuo* yielded: (1) dimethoxydiphenylsilane (102c): retention time 350 s; (2) dimethoxy(4-methylphenyl)phenylsilane (102d): retention time 410 s; (3) methoxy(4-methylphenyl)diphenylsilane (104d): retention time 1310 s; (4) mixture (~3:2:1 by NMR) of methoxy[(4-methylphenyl)methyl]diphenylsilane (101d), methoxy(4-methylphenyl)phenyl(phenylmethyl)silane (103d) and an unidentified methoxy compound: retention time 1540 s. The ratios of 102c:102d:104d:101d:103d were approximately 5:11:5:3:2. The absolute yields were not determined.

Reaction of (Chloromethyl)(4-chlorophenyl)diphenylsilane (4b) with Sodium Methoxide in Methanol.

(Chloromethyl)(4-chlorophenyl)diphenylsilane (4b, 1.06 g, 3.10 mmol) in 1,4-dioxane (1 mL) was added, all at once, to a solution of sodium methoxide in methanol [prepared with sodium metal (0.29 g, 12.6 mmol) and anhydrous methanol (8 mL)]. The mixture was refluxed (~45 h) until no 4b (retention time 1650 s) was detected by GC (column A). The reaction mixture was worked up by the addition of water (10 mL), separation and extraction with diethyl ether (2 x 5 mL), followed by drying with magnesium sulfate, filtration and concentration *in vacuo*. At least six products were detected by analysis on column A. The products seemed very similar to those noted in the reactions of 4c with sodium methoxide in 1,4-dioxane: low yields were obtained, products contained no OCH₃ NMR peaks (*o* 3-4 ppm) and the spectra did not match those of the expected major products, [(4-chlorophenyl)methyl]methoxydiphenylsilane (101b), dimethoxydiphenylsilane (102c), (4-chlorophenyl)methoxyphenyl-(phenylmethyl)silane (103b), (4-chlorophenyl)dimethoxyphenylsilane (102b) or (4-chlorophenyl)methoxydiphenylsilane (104b) in retention time or spectra.

Authentic samples of 101b, 102c, 103b, 102b and 104b were stable to the GC conditions and work-up procedures used.

PREPARATION OF AUTHENTIC METHOXYSILANES 101-104Preparation of Dimethoxyphenyl(phenylmethyl)silane (106).

Benzylmagnesium chloride in anhydrous diethyl ether was prepared by dropwise addition of benzyl chloride (40.0 ml, 44.0 g, 0.348 mol) in diethyl ether (50 mL) to a stirred suspension of magnesium turnings (10.0 g, 0.411 mol) in diethyl ether (150 mL). After addition of benzyl chloride, the mixture was refluxed for 2 h.

To a stirred solution of trimethoxyphenylsilane (105, 49.0 g, 0.247 mol) in anhydrous diethyl ether (100 mL) under argon was added dropwise (~2 h) the previously prepared benzylmagnesium chloride (175 mL of a 1.42 M solution in diethyl ether, 0.248 mol). The reaction mixture was then refluxed until Color Test 1⁹⁸ was negative (~5 h).

After the mixture had been cooled, water (150 mL) was added slowly followed by 10% hydrochloric acid (35 mL). The aqueous layer was separated and extracted with diethyl ether (3 x 50 mL). The combined extracts were washed with water (75 mL) and saturated sodium chloride (75 mL). After drying the extract over anhydrous magnesium sulfate, filtration and concentration *in vacuo* gave an oil which was distilled through a 12 x 110 mm column packed with stainless steel staples to yield a clear liquid dimethoxyphenyl-(phenylmethyl)silane (106, 34.55 g, 0.134 mol, 54%): bp 105-120 °C/0.4 torr [lit¹⁰⁶ 200-220 °C/10 torr]; NMR δ

7.50-6.90 (m, 10H, Ar-H), 3.50 (s, 6H, 2 x Si-O-CH₃), 2.30 (s, 2H, Si-CH₂-C₆H₅); IR (CCl₄) 3060(m), 3010(m), 2940(m), 2840(m), 1590(w), 1490(m), 1450(m), 1430(m), 1400(w), 1210(m), 1180(m), 1160(m), 1120(s), 1085(s), 1030(w), 900(m), 690(s), 640(w), 570(m), 500(s), 430(w) cm⁻¹; MS 258(M⁺, 3), 168(15), 167[M⁺ - (CH₂-C₆H₅), 100], 137(25), 107(11), 91(25); exact mass calcd for C₁₅H₁₈O₂Si *m/e* 258.1076, found 258.1082. Anal. Calcd for C₁₅H₁₈O₂Si: C, 69.77; H, 6.98. Found: C, 69.98; H, 6.89.

Preparation of Methoxydiphenyl(phenylmethyl)silane (103c).

A solution of phenylmagnesium bromide in anhydrous diethyl ether, prepared by the dropwise addition of bromobenzene (98c, 5.3 ml, 7.9 g, 50 mmol) in diethyl ether (15 mL) to a stirred suspension of magnesium turnings (1.44 g, 60.0 mmol) in diethyl ether (10 mL), was added (~2 h), under argon, to dimethoxyphenyl(phenylmethyl)silane (106, 10.0 g, 38.8 mmol) in anhydrous diethyl ether (10 mL). Color Test I⁹⁸ indicated that reaction was complete after reflux of ~90 h.

Water (15 mL) was slowly added after cooling the mixture, followed by acidification with 10% hydrochloric acid (5 mL). The combined organics obtained from separation and extraction with diethyl ether (3 x 10 mL) were washed with water (7 mL) and saturated sodium chloride (7 mL) and then dried over anhydrous magnesium sulfate. The oil obtained

after filtration and concentration *in vacuo* was distilled through a short-path distillation apparatus containing Kurly-Kate to yield methoxydiphenyl(phenylmethyl)silane (103c, 3.40 g, 11.2 mmol, 29%), a clear liquid: bp 175-178 °C/1.5 torr [lit¹⁰⁷ 159-161 °C/0.28 torr]; NMR δ 7.55-6.80 (m, 15H, Ar-H), 3.45 (s, 3H, Si-O-CH₃), 2.60 (s, 2H, Si-CH₂-C₆H₅); IR (CCl₄) 3060(m), 3040(m), 3010(m), 2915(m), 2830(m), 1590(m), 1490(m), 1450(m), 1425(m), 1400(w), 1330(w), 1300(w), 1205(m), 1180(m), 1110(s), 1080(s), 1030(m), 1000(w), 900(m), 690(s), 640(w), 570(m), 505(s), 480(m), 450(m), 385(w) cm⁻¹; MS 304(M⁺, 4), 214(21), 213[M⁺ - (CH₂-C₆H₅), 100], 183(32); exact mass calcd for C₂₀H₂₀OSi *m/e* 304.1284, found 304.1283.

General Procedure for the Preparation of Arylmethoxyphenyl-(phenylmethyl)silanes.

The aryllithium reagent (13 mmol in diethyl ether/hexane prepared by Method B) was added (~2 h) to a stirred solution under argon of dimethoxyphenyl(phenylmethyl)silane (106, 3.35 g, 13 mmol) in anhydrous diethyl ether (10 mL). The mixture was refluxed until reaction was complete (~90 h).

After cooling the mixture, water (15 mL) was added slowly followed by 10% hydrochloric acid (5 mL). The aqueous layer was extracted with diethyl ether (3 x 10 mL) after separation. Afterwards, the combined organic layers

were washed with water (7 mL) and saturated sodium chloride (7 mL) and dried over magnesium sulfate followed by filtration and concentration *in vacuo*. Distillation through a short-path apparatus containing Kurly-Kate gave the following previously unreported compounds:

(4-Chlorophenyl)methoxyphenyl(phenylmethyl)silane

(103b): yield 22%; bp 178-180 °C/0.5 torr; NMR δ 7.50-6.70 (m, 14H, Ar-H), 3.35 (s, 3H, Si-O-CH₃), 2.50 (s, 2H, Si-CH₂-C₆H₅); IR (CCl₄) 3060(m), 3020(m), 2930(m), 2830(w), 1580(w), 1480(w), 1450(w), 1430(w), 1400(w), 1380(w), 1210(b,m), 1160(m), 1110(m), 1085(s), 1020(m), 900(w), 700(s), 570(w), 530(m), 510(s), 440(m), 420(m), 380(w) cm⁻¹; MS 338(M⁺, 3), 249(36), 248(19), 247[M⁺ - (CH₂-C₆H₅), 1001, 219(13), 217(26); exact mass calcd for C₂₀H₁₉³⁵ClOSi *m/e* 338.0895, found 338.0877.

Methoxy(4-methylphenyl)phenyl(phenylmethyl)silane

(103d): yield 55%; bp 145-146 °C/0.4 torr; NMR δ 7.65-6.85 (m, 14H, Ar-H), 3.50 (s, 3H, Si-O-CH₃), 2.65 (s, 2H, Si-CH₂-C₆H₅), 2.40 (s, 3H, Si-C₆H₄-CH₃); IR (CCl₄) 3060(m), 3020(m), 2920(m), 2830(w), 1950(w), 1930(w), 1900(w), 1875(w), 1825(w), 1810(w), 1730(w), 1640(w), 1590(m), 1490(m), 1450(m), 1430(m), 1400(w), 1390(m), 1310(w), 1260(w), 1210(m), 1180(b,m), 1160(m), 1110(b,s), 1085(b,s), 1030(m), 900(m), 690(s), 670(m), 610(m), 600(w), 570(m), 510(s), 480(b,m), 440(m), 380(w) cm⁻¹; MS 318(M⁺, 2), 228(21), 227[M⁺ - (CH₂-C₆H₅), 1001, 197(27), 193(11),

137(13); exact mass calcd for $C_{21}H_{22}OSi$ m/e 318.1441, found 318.1477.

Preparation of Dimethoxydiphenylsilane (102c).

To a stirred solution under argon of trimethoxyphenylsilane (105, 110 mL, 117g, 0.590 mol) in anhydrous diethyl ether (100 mL) was added dropwise (~6 h) phenylmagnesium bromide (345 mL of a 1.80 M solution in diethyl ether, 0.621 mol). When Color Test I⁹⁸ was negative (~15 h) reaction was complete.

Water (150 mL) and 10% hydrochloric acid (35 mL) were added after cooling the mixture. Separation, extraction with diethyl ether (3 x 50 mL), washing with water (75 mL) and saturated sodium chloride (75 mL), drying with magnesium sulfate followed by filtration and concentration *in vacuo* gave an oil which was distilled through a 12 x 110 mm column packed with stainless steel staples to yield dimethoxydiphenylsilane (102c, 94.04 g, 0.385 mol, 65%), a clear liquid: bp 128-136 °C/0.6 torr [lit¹⁰⁸ 102-104 °C/0.1 torr]; NMR δ 7.75-7.20 (m, 10H, 2 x Si-C₆H₅), 3.60 (s, 6H, 2 x Si-O-CH₃); IR (CCl₄) 3060(m), 3040(m), 3000(w), 2915(m), 2830(m), 1590(w), 1480(w), 1425(m), 1190(w), 1125(s), 1115(s), 1080(s), 700(s), 660(w), 525(s), 480(w) cm⁻¹; MS 244(M⁺, 23), 168(14), 167[M⁺ - (C₆H₅), 100], 166(34), 154(28), 137(37), 107(23), 91(27); exact mass calcd for $C_{14}H_{16}O_2Si$ m/e 244.0920, found 244.0913.

General Procedure for the Preparation of Aryldimethoxyphenylsilanes.

To a stirred solution under argon of trimethoxyphenylsilane (105, 2.61 g, 13 mmol) in anhydrous diethyl ether (10 mL) was added dropwise (~2 h) arylmagnesium bromide (13 mmol in diethyl ether). The mixture was refluxed until Color Test I⁹⁸ was negative (~90 h).

After cooling the mixture, water (15 mL) was added slowly followed by 10% hydrochloric acid (5 mL). The layers were separated and the aqueous layer extracted with diethyl ether (3 x 10 mL). The combined organics were washed with water (7 mL) and saturated sodium chloride (7 mL) and dried over anhydrous magnesium sulfate. Filtration and concentration *in vacuo*, followed by distillation through a short-path apparatus containing Kurly-Kate gave the following previously unreported silanes:

(4-Chlorophenyl)dimethoxyphenylsilane (102b): yield 42%; bp 111-114 °C/0.2 torr; NMR δ 7.70-7.20 (m, 9H, Si-Ar-H), 3.60 (s, 6H, 2 x Si-O-CH₃); IR (CCl₄) 3070(w), 3040(w), 2920(m), 2840(m), 1900(w), 1640(w), 1570(b,w), 1480(m), 1425(m), 1380(m), 1190(m), 1120(s), 1110(s), 1080(s), 1015(m), 700(m), 680(w), 560(m), 505(m), 470(w), 450(b,w), 400(w) cm⁻¹; MS 280(13), 278(M⁺, 35), 203(19), 202(12), 201(48), 200(13), 188(13), 171(16), 168(16), 167[M⁺ - (C₆H₄-Cl), 100], 166(32), 141(11), 137(23),

107(16), 91(23), 59(28), 40(11); exact mass calcd for $C_{14}H_{15}^{35}ClO_2Si$ *m/e* 278.0530, found 278.0513.

Dimethoxy(4-methylphenyl)phenylsilane (102d): yield 36%; bp 129-133 °C/2.0 torr; NMR δ 7.75-7.10 (m, 9H, Si-Ar-H), 3.65 (s, 6H, 2 x Si-O-CH₃), 2.40 (s, 3H, Si-C₆H₄-CH₃); IR (CCl₄) 3070(w), 3030(b,w), 2980(b,w), 2920(m), 2840(m), 1590(b,w), 1430(m), 1390(w), 1190(m), 1120(s), 1110(s), 1080(s), 1015(m), 700(m), 610(w), 515(m), 490(w), 420(w) cm⁻¹; MS 259(13), 258(M⁺, 58), 182(16), 181[M⁺ - (C₆H₅), 100], 180(10), 168(37), 166(51), 165(14), 153(21), 151(32), 137(19), 121(19), 107(17), 105(32), 91(20), 59(30); exact mass calcd for $C_{15}H_{18}O_2Si$ *m/e* 258.1076, found 258.1097.

General Procedure for the Preparation of (Arylmethyl)methoxydiphenylsilanes.

(Arylmethyl)magnesium chloride (13 mmol in diethyl ether) was added dropwise (~2 h) to a stirred solution under argon of dimethoxydiphenylsilane (102c, 2.61 g, 13 mmol) in anhydrous diethyl ether (10 mL). Refluxing of the mixture was conducted until Color Test I⁹⁸ was negative (~90 h).

Water (15 mL) was added slowly after cooling the mixture followed by addition of 10% hydrochloric acid (5 mL). Separation, extraction with diethyl ether (3 x 10 mL), washing with water (7 mL) and saturated sodium chloride (7

mL) and drying over anhydrous magnesium sulfate, followed by filtration and concentration *in vacuo* yielded an oil which was distilled through a short-path distillation apparatus containing Kurly-Kate to give the following previously unreported compounds:

[(4-Chlorophenyl)methyl]methoxydiphenylsilane (101b):

yield 38%; bp 167-172 °C/0.2 torr; NMR δ 7.65-7.10 (m, 10H, 2 x Si-C₆H₅), 7.00 (d, J = 8 Hz, 2H, 2 x *ortho*-Cl Ar-H), 6.75 (d, J = 8 Hz, 2H, 2 x *ortho*-CH₂ Ar-H), 3.45 (s, 3H, Si-O-CH₃), 2.50 (s, 2H, Si-CH₂-C₆H₄-Cl); IR (CCl₄) 3060(m), 3040(m), 3000(b,w), 2920(m), 2820(w), 1980(w), 1580(w), 1480(m), 1430(m), 1400(w), 1300(w), 1210(b,m), 1150(m), 1110(s), 1085(b,s), 1020(m), 860(w), 700(s), 660(m), 630(w), 520(m), 480(m), 440(w), 380(m) cm⁻¹; MS 338(M⁺, 2), 214(20), 213[M⁺ - (CH₂-C₆H₄-Cl), 100], 183(31), 105(11); exact mass calcd for C₂₀H₁₉³⁵ClOSi *m/e* 338.0895, found 338.0859.

Methoxy[(4-methylphenyl)methyl]diphenylsilane (101d):

yield 34%; bp 156-160 °C/0.3 torr; NMR δ 7.75-7.15 (m, 10H, 2 x Si-C₆H₅), 7.85 (bs, 4H, CH₂-C₆H₄-CH₃), 3.50 (s, 3H, Si-O-CH₃), 2.60 (s, 2H, Si-CH₂-C₆H₄-CH₃), 2.40 (s, 3H, CH₂-C₆H₄-CH₃); IR (CCl₄) 3060(m), 3040(m), 3020(m), 3000(m), 2930(b,m), 2830(m), 1950(w), 1880(w), 1820(w), 1765(w), 1650(w), 1610(w), 1590(w), 1510(m), 1480(w), 1450(w), 1430(s), 1400(w), 1380(m), 1320(w), 1300(w), 1260(w), 1210(m), 1180(b,m), 1160(m), 1110(b,s), 1085(b,s),

1030(w), 935(m), 700(s), 640(w), 600(w), 540(s), 490(b,s), 450(m), 400(w) cm^{-1} ; MS 318(M^+ , 5), 214(20), 213(M^+ - $(\text{CH}_2-\text{C}_6\text{H}_4-\text{CH}_3)$, 100), 183(27); exact mass calcd for $\text{C}_{21}\text{H}_{22}\text{OSi}$ m/e 318.1441, found 318.1464.

Preparation of Methoxytriphenylsilane (104c).

To a stirred solution under argon of dimethoxydiphenylsilane (102c, 10.0 g, 40.9 mmol) in anhydrous diethyl ether (10 mL) was added dropwise (~2 h) phenylmagnesium bromide (21 mL of a 2.00 M solution in diethyl ether, 42.0 mmol). After refluxing the mixture until completion of the reaction (~135 h), the mixture was cooled, diluted with water (15 mL) and acidified with 10% hydrochloric acid (5 mL). The aqueous layer was extracted with diethyl ether (3 x 10 mL) after separation. The combined ethereal layers were washed with water (7 mL) and saturated sodium chloride (7 mL), dried over magnesium sulfate and then filtered and concentrated *in vacuo* to yield an oil which was crystallized with absolute ethanol then recrystallized twice with absolute ethanol to yield methoxytriphenylsilane (104c, 2.93 g, 10.1 mmol, 25%) as white plates: mp 52-54 °C [lit¹⁰⁹ 52-55 °C]; NMR δ 7.70-7.25 (m, 15H, 3 x Si-C₆H₅), 3.65 (s, 3H, Si-O-CH₃); IR (CCl₄) 3060(m), 3040(m), 3010(b,m), 2930(m), 2830(m), 1950(w), 1885(b,w), 1820(w), 1650(w), 1590(w), 1480(w), 1425(s), 1330(w), 1300(w), 1250(w), 1180(m), 1120(s), 1110(m), 1090(s), 1030(w),

1000(w), 700(s), 660(w), 520(m), 510(s), 480(w), 430(w) cm^{-1} ; MS 291(15), 290(M^+ , 56), 214(20), 213($\text{M}^+ - (\text{C}_6\text{H}_5)$, 100), 183(45), 181(17), 136(49), 105(14), 59(12); exact mass calcd for $\text{C}_{19}\text{H}_{18}\text{OSi}$ m/e 290.1127, found 290.1145.

General Procedure for the Preparation of Arylmethoxydiphenylsilanes.

To a stirred solution under argon of dimethoxydiphenylsilane (102c, 3.2 g, 13 mmol) in anhydrous diethyl ether (10 mL) was added dropwise (45 min) the aryllithium reagent (13 mmol) in either diethyl ether or diethyl ether/hexanes. Additions were done at room temperature for aryllithiums prepared by Method A and then refluxed until Color Test I⁹⁸ was negative (~2 h). Additions were done at -40 °C for aryllithiums prepared by Method B, followed by warming to room temperature and stirring until Color Test I⁹⁸ was negative (~1 h).

Water (15 mL) was then added slowly followed by 10% hydrochloric acid (5 mL). The aqueous layer was separated and extracted with diethyl ether (3 x 10 mL). The combined organic layers were washed with water (7 mL) and saturated sodium chloride (7 mL) and then dried over anhydrous magnesium sulfate. Filtration and concentration *in vacuo* yielded the following previously unreported compounds:

(4-Chlorophenyl)methoxydiphenylsilane (104b) was prepared by Method B and was distilled through a short-path

distillation apparatus packed with Kurly-Kate to obtain 104b as a clear liquid: yield 24%; bp 167-169 °C/0.9 torr; NMR δ 7.50-7.15 (m, 14H, Si-Ar-H), 3.60 (s, 3H, Si-O-CH₃); IR (CCl₄) 3060(m), 3020(m), 3000(b,w) 2930(b,m), 2830(m), 1950(w), 1905(w), 1885(w), 1820(w), 1650(w), 1575(b,m), 1480(m), 1430(m), 1380(m), 1240(m), 1180(m), 1120(m), 1085(s), 1015(m), 860(m), 700(s), 680(w), 555(m), 520(m), 470(w), 410(m) cm⁻¹; MS 326(38), 325(23), 324(M⁺, 86), 249(38), 248(20), 247[M⁺ - (C₆H₅), 100], 219(28), 217(48), 215(15), 214(19), 213(89), 183(30), 181(17), 172(12), 170(34), 152(10), 136(30), 105(24), 91(20), 69(18), 63(14), 59(40); exact mass calcd for C₁₉H₁₇³⁵ClOSi *m/e* 324.0738, found 324.0736.

Methoxy(4-methylphenyl)diphenylsilane (104d) was prepared by Method A and was crystallized at 0 °C with absolute ethanol and recrystallized twice with absolute ethanol at -20 °C to obtain 104d as white plates: yield 12%; mp 48-50 °C; NMR δ 7.65-6.95 (m, 14H, Si-Ar-H), 3.60 (s, 3H, Si-O-CH₃), 2.40 (s, 3H, Si-C₆H₄-CH₃); IR (CCl₄) 3060(w), 3020(w), 3000(w), 2930(w), 2830(w), 1590(w), 1430(m), 1390(w), 1310(w), 1260(w), 1180(b,m), 1110(s), 1085(b,s), 695(s), 685(m), 610(m), 510(s), 500(b,m), 430(w) cm⁻¹; MS 305(13), 304(M⁺, 51), 228(19), 227[M⁺ - (C₆H₅), 100], 213(24), 197(44), 195(11), 183(18), 150(21), 136(39), 105(25), 59(27); exact mass calcd for C₂₀H₂₀OSi *m/e* 304.1284, found 304.1261.

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