REARRANGEMENTS OF ORGANOSILICON COMPOUNDS
I. THE MIGRATORY APTITUDES OF VARIOUS ORGANIC GROUPS IN THE ALUMINUM CHLORIDE-CATALYZED REARRANGEMENT OF (CHLOROMETHYL)TRIORGANOSILANES*

OMAR W. STEWARD, WILLIAM J. UHL AND BRUCE W. SANDS

*Department of Chemistry, Duquesne University, Pittsburgh, Pennsylvania 15219 (U.S.A.)*

(Received August 8th, 1968)

SUMMARY

The migratory aptitudes of various organic groups in the aluminum chloride-catalyzed rearrangement of (chloromethyl)triorganosilanes have been determined: Me, 1.00; Et, 2.07; n-Pr, 2.97; iso-Pr, $\ll$ 1.00; $ClCH_2$, $\ll$ 1.00. Migration of the organic group from silicon to carbon is facilitated by electron-release and inhibited, relative to methyl, by branching at the α-carbon. The migratory aptitudes determined in this study and obtained by other workers are discussed in terms of a mechanism involving synchronous intramolecular migration of the organic group and the chloride ion.

INTRODUCTION

The intramolecular rearrangement of (chloromethyl)trimethylsilane (eqn. 1) in the presence of aluminum chloride, a reaction analogous to the Wagner–Meerwein rearrangements of organic chemistry, was first reported by Whitmore, Sommer and Gold[1]. Subsequent studies have shown that other groups will rearrange from silicon

$$Me_3SiCH_2Cl \xrightarrow{AlCl_3} Me_2Si(Cl)CH_2Me \qquad (1)$$
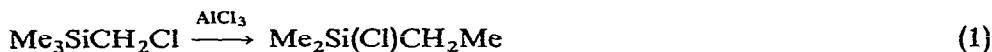
to carbon under similar conditions: Et[2], Me_3Si and $Me_2(Cl)Si$[3,4], Ph[5]. Ring expansion reactions (eqn. 2) have also been reported[6], where $n=4$ or 5. A closely related

$$(CH_2)_nSi(Me)CH_2Cl \xrightarrow{AlCl_3} (CH_2)_{n+1}Si(Me)Cl \qquad (2)$$
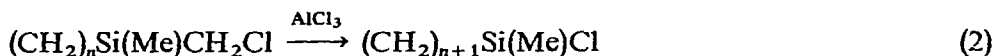
rearrangement of (hydroxymethyl)silicon compounds has been reported recently by Brook *et al.*[7], as exemplified in eqn. (3).

$$Ph_3SiC(Ph_2)OH \xrightarrow{BF_3} Ph_2Si(F)CPh_3 \qquad (3)$$
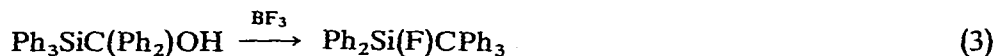
The relative order of reactivity of various organic groups in their ability to migrate from silicon to carbon has received limited attention. Eaborn *et al.*[5] observed

---

that electron-releasing substituent groups assist migration of the aryl group in the rearrangement of p-$XC_6H_4Si(Me_2)CH_2Cl$. Kumada et al.[3,4] observed that Me_3Si and $Me_2(Cl)Si$ groups migrate in preference to methyl in (chloromethyl)pentamethyldisilane and 1-(chloromethyl)-2-chlorotetramethyldisilane. They also reported that only methyl migration was observed when (chloromethyl)-tert-butyldimethylsilane was stirred with aluminum chloride[8].

This paper presents a systematic study of the ability of various organic substituent groups bonded to silicon in (chloromethyl)triorganosilanes to rearrange to carbon in the presence of aluminum chloride. Using (chloromethyl)triorganosilanes with two different organic substituent groups, the migratory aptitudes of these groups have been determined from the yields of the reaction products (eqn. 4). The results of these studies are discussed in terms of a concerted mechanism.

$$R_2R'SiCH_2Cl \xrightarrow[\text{CH}_2\text{Cl}_2]{\text{AlCl}_3} R_2Si(Cl)CH_2R' + RR'Si(Cl)CH_2R \tag{4}$$
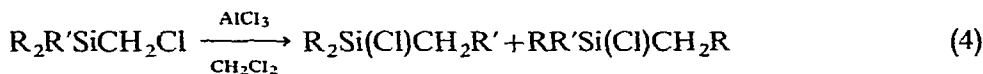
EXPERIMENTAL

Preparation of the (chloromethyl)triorganosilanes

(a) *General method.* (Chloromethyl)trimethylsilane, (chloromethyl)ethyldimethylsilane, (chloromethyl)diethylmethylsilane and (chloromethyl)-n-propyldimethylsilane were synthesized by the usual Grignard method[9] by adding (chloromethyl)-dimethylchlorosilane or (chloromethyl)methyldichlorosilane to an ether solution of the appropriate Grignard reagent. The yields and physical properties are given in Table 1.

. (b)*(Chloromethyl)isopropyldimethylsilane.*(Chloromethyl)dimethylfluorosilane, b.p. 82–84°, n_D^{25} 1.4002 (lit.[8], b.p. 84°, n_D^{25} 1.4000) was prepared in a 94% yield by treating 1,3-bis(chloromethyl)tetramethyldisiloxane with boron trifluoride etherate according to the method of Sommer and Ansul[15]. (Found: F, 15.0. C_3H_8ClFSi calcd.: F, 15.0%.) Isopropyllithium in pentane (Lithium Corporation of America), 1 mole, was added over a period of 2 h to (chloromethyl)dimethylfluorosilane, 127.8 g, 1.00 mole, dissolved in pentane, 50 ml. Throughout the reaction, a nitrogen atmosphere was maintained and the reaction flask was cooled in an ice-water bath. After it had been

TABLE 1

YIELDS AND PHYSICAL PROPERTIES OF THE (CHLOROMETHYL)TRIORGANOSILANES

Compound	Yield (%)	B.p. (°C) Found	B.p. (°C) Lit.	n_D(temp.) Found	n_D(temp.) Lit.	Ref.
Me_3SiCH_2Cl	62	97–97.6	97.1	1.4132(25)	1.4180(20)	10
$EtMe_2SiCH_2Cl$	60	126–127	127–127.8	1.4260(25)	1.4295(20)	11
$Et_2MeSiCH_2Cl$	60	155–156.3	155.2	1.4405(20)	1.4402(20)	11
n-$PrMe_2SiCH_2Cl$	64	147.4–148	151.7	1.4282(25)	1.4335(20)	12
iso-$PrMe_2SiCH_2Cl^a$	64	50/18 mm		1.4351(25)		
$Me_2Si(CH_2Cl)_2$	29	163–165	160/724 mm	1.4582(25)	1.4579(25)	13
					1.4573(25)	14

^{a} d_4^{25} 0.8832.

stirred at room temperature for 60 h, the reaction mixture was poured onto a mixture of cracked ice and concentrated hydrochloric acid, 40 ml. The resulting layers were separated and the water layer was extracted twice with 50-ml portions of pentane. The combined pentane solution was dried over anhydrous magnesium sulfate. The pentane was removed through a distillation column, and fractional distillation of the higher boiling material gave (chloromethyl)isopropyldimethylsilane. (Found: C, 47.67; H, 10.12. $C_6H_{15}ClSi$ calcd.: C, 47.84; H, 10.01.%.) The yield and physical properties are given in Table 1.

(c) *Bis(chloromethyl)dimethylsilane.* (Chloromethyl)trimethylsilane, 20.4 g, 0.49 moles, was chlorinated using chlorine gas, 0.5 moles, by the method of Speier[13]. Fractional distillation then gave: (dichloromethyl)trimethylsilane, 40.6 g, 0.26 mole, yield 51%, b.p. 133–134°, n_D^{25} 1.4425, (lit.[13] b.p. 133–134°, n_D^{25} 1.4430); bis(chloromethyl)dimethylsilane, 22.9 g, 0.15 mole. The yield and physical properties of the latter are given in Table 1.

Preparation of the trialkylchlorosilane

(a) *Ethyldimethylchlorosilane.* This compound was synthesized following the method of Shostakovskii et al.[16] by adding an ether solution of ethylmagnesium bromide to dimethyldichlorosilane: yield 31%, b.p. 89–90°, n_D^{25} 1.4016, (lit.[17] b.p. 90.5°/745 mm, n_D^{20} 1.4050). (Found: Cl, 28.7. $C_4H_{11}ClSi$ calcd.: Cl, 28.9%.)

(b) *Diethylmethylchlorosilane.* This compound was synthesized following the method of Shostakovskii et al.[16] by adding an ether solution of ethylmagnesium bromide to methyltrichlorosilane: yield 25%, b.p. 119–121°, n_D^{25} 1.4175, (lit.[16] b.p. 119–120°, n_D^{20} 1.4209). (Found: Cl, 25.6. $C_5H_{13}ClSi$ calcd.: Cl, 25.9%.)

(c) *n-Propyldimethylchlorosilane.* n-Propylmagnesium bromide, prepared in the usual manner from n-propyl bromide, 67.6 g, 0.55 moles, magnesium, 13.1 g, 0.54 moles, and ether, 400 ml, was added over a period of 1 h to dimethylethoxychlorosilane, 70.6 g, 0.51 moles, b.p. 96–97.3°, n_D^{25} 1.3887, (lit.[18] b.p. 95°, n_D^{25} 1.3898), prepared in a 93% yield by adding absolute ethanol, 23.3 g, 0.50 moles, to dimethyldichlorosilane, 64.5 g, 0.50 moles. The reaction mixture was heated at reflux for 2 h and then was poured onto a mixture of cracked ice and sodium bicarbonate, 84 g, 1.0 mole. The ether layer was separated and dried over anhydrous calcium sulfate. The ether was removed through a distillation column, and fractional distillation of the higher-boiling material gave n-propyldimethylethoxysilane, 43.1 g, 0.58 moles, yield 58%, b.p. 124–125°, n_D^{20} 1.3975, (lit.[19] b.p. 125°, n_D^{20} 1.3969).

n-Propyldimethylethoxylane, 42.7 g, 0.28 mole, and acetyl chloride, 44.2 g, 0.57 moles, and pyridine, a few drops, were heated to reflux for 6 h. Fractional distillation gave: acetyl chloride, 23.4 g, 0.29 moles, b.p.52–54° ; ethyl acetate, 13.3 g, 0.25 moles, b.p. 76° ; n-propyldimethylchlorosilane, 25.6 g, 0.15 moles, yield 53%, b.p. 113–115°, n_D^{20} 1.4132, (lit.[20] b.p. 115°, n_D^{20} 1.4133). (Found: Cl, 26.0. $C_5H_{13}ClSi$ calcd.: Cl, 25.9%.)

Rearrangement of the (chloromethyl)triorganosilanes

(a) *Materials.* Methylene chloride, Fisher Reagent Grade, was distilled from calcium hydride, b.p. 40–41°, and stored over molecular sieve. Aluminum chloride, A.C.S. Reagent Grade, was used without further purification. Toluene, *m*-xylene and mesitylene, Eastman Grade, were distilled and stored over anhydrous calcium sulfate.

(b) *Gas chromatography.* An Aerograph Autoprep, Model 700, gas chromatograph was used to separate and determine the yields of the products of the rearrangements. High-purity helium was used as the carrier gas. The following columns were employed: (1) an analytical-type column, 10 ft. × $\frac{1}{8}$ in., stainless steel, packed with 20% Silicone, D.C. 710, on 60–80 mesh Chromosorb W; (2) a preparative-type column, 12 ft. × $\frac{3}{8}$ in., stainless steel, with the above packing. The columns were conditioned by injections of dimethyldichlorosilane before being used for analytical purposes[21].

(c) *General procedure.* All reactions were carried out in a dry box under a nitrogen atmosphere. Methylene chloride was placed in an Erlenmeyer flask containing a magnetic stirring bar. The aluminum chloride catalyst was added, and the mixture was stirred until the catalyst dissolved. After the (chloromethyl)triorganosilane had been added, the reaction mixture was stirred for 2 h and allowed to stand for 48 h. In order to prevent further reaction during product analysis 20% excess of anhydrous sodium chloride was added to complex with the aluminum chloride. An internal standard (toluene, *m*-xylene or mesitylene) was added and a gas chromatogram was obtained.

The chromatographic peaks were identified by the following procedure. Peaks due to the internal standard and unreacted starting material, if present, were identified by comparison of the observed retention times with those obtained from the pure materials. Peaks due to the rearranged products were identified, after separation by preparative chromatography, by chemical and nuclear magnetic resonance spectral analysis (*cf.* Table 2). In runs No. 1 and 2 (*cf.* Table 2), the expected products of the rearrangement were synthesized by alternate routes and their retention times were compared with the retention times of the observed chromatographic peaks.

TABLE 2

REARRANGEMENT OF THE (CHLOROMETHYL)TRIORGANOSILANES[a]

Run No.	Reactants	Mole ratio silane[b]/AlCl₃	Products	Yield (%)
1	Me₃SiCH₂Cl	5	Me₂EtSiCl	96.4
2	Me₂EtSiCH₂Cl	5	MeEt₂SiCl	45.2
			Me₂PrSiCl	48.0
3	MeEt₂SiCH₂Cl	10	Et₃SiCl	18.4
			MeEtPrSiCl	73.8
4	Me₂PrSiCH₂Cl	5	MeEtPrSiCl	36.0
			Me₂BuSiCl	53.6
5	Me₂-iso-PrSiCH₂Cl	5	MeEt-iso-PrSiCl	98.0
6	Me₂Si(CH₂Cl)₂	3.5	MeEt(ClCH₂)SiCl	90.6

[a] Methylene chloride at room temperature. [b] 0.2–0.3 moles/l.

The yields of the rearrangement products were determined chromatographically by means of the internal standard. Solutions of known composition of the standard and products, obtained by preparative gas chromatography, were prepared. The constants relating the area ratios of the chromatographic peaks of the chlorosilanes and standard to the mole ratios were determined. The peak areas were measured by means of a planimeter. The yields of the products were calculated from the area ratios of the chromatogram of the reaction mixture containing the internal standard.

RESULTS

The reaction conditions and yields of the rearrangement products, determined by gas chromatography as described in the experimental section, are given in Table 2. In each case, the combined yield of the products is ~90% or greater. The variation in the mole ratio of the silane to catalyst reflects the sensitivity of the (chloromethyl)-triorganosilanes toward rearrangement in the presence of aluminum chloride.

Two methods were employed to identify the products. In the cases of (chloromethyl)trimethylsilane and (chloromethyl)ethyldimethylsilane, analyses were carried out by comparing the retention times and the chemical and physical properties of the isolated products with compounds of known structure synthesized by the Grignard method. The compounds synthesized were those expected to be the products of the rearrangements if simple alkyl migration from silicon to carbon had occurred.

The second method used to identify the products makes use of the chemical and spectral properties of the isolated products. The percentages of hydrolyzable chlorine were determined from which the empirical formulae of the products were assigned. The proton magnetic resonance spectra were used to elucidate the structures of the products. In most cases, the spectra were complex, but structural analysis was possible on the basis of chemical shift and relative peak area data. In all spectra, the peak due to CH_3Si is a singlet, δ 0.34–0.52, a position where no other peaks interfere. The peak area ratio, RSi/CH_3Si, where R represents all groups other than CH_3, is related directly to the structure of the compound. All analytical data are given in Table 3.

TABLE 3

NMR AND ANALYTICAL DATA OF THE PRODUCTS OF THE REARRANGEMENTS

Reaction No.	Products	$\delta(CH)^{a,b}$				Peak area ratio^c		Chlorine (%)^d	
		H^a	H^b	H^c	H^d	Calcd.	Found	Calcd.	Found
1	$(CH_3^a)_2(CH_3^cCH_2^b)SiCl$	0.45	0.73	1.00		0.83	0.86	28.9	28.7
2	$(CH_3^a)(CH_3^cCH_2^b)_2SiCl$	0.34	0.95			3.33	3.27	25.9	25.4
	$(CH_3^a)_2(CH_3^cCH_2^dCH_2^b)SiCl$	0.37	0.79	1.03	1.43	1.17	1.20	25.9	25.5
3	$(CH_3^cCH_2^b)_3SiCl$		0.70	1.00				23.5	23.4
	$(CH_3^a)(CH_3^cCH_2^b)(CH_3^cCH_2^dCH_2^b)SiCl$	0.34	0.95		1.38	4.00	4.07	23.5	23.3
4	$(CH_3^a)(CH_3^cCH_2^b)(CH_3^cCH_2^dCH_2^b)SiCl$	0.35	0.95		1.36	4.00	3.98	23.5	23.3
	$(CH_3^a)_2(CH_3^cCH_2^dCH_2^b)SiCl$	0.36	0.86		1.32	1.50	1.53	23.5	23.4
5	$(CH_3^a)(CH_3^cCH_2^b)[(CH_3^c)_2CH^d]SiCl$	0.35	0.85		1.20	4.00	3.97	23.5	23.7
6	$(CH_3^a)(CH_3^cCH_2^b)(ClCH_2^d)SiCl$	0.52	1.05		2.97	2.33	2.31	22.6	22.3

^{a} Spectra, determined in CCl_4, are given in ppm downfield from TMS, used as an internal standard, at 60 Mc. ^{b} For complex spectra, the value represents the center of the multiplet. ^{c} Peak area ratios, RSi/CH_3Si, where R represents groups other than CH_3. ^{d} Percent hydrolyzable chlorine.

The migratory aptitudes of the organic groups in the aluminum chloride-catalyzed rearrangement of (chloromethyl)triorganosilanes are given in Table 4. When the reactant contained two identical groups bonded to silicon, a statistical correction was made. For the compounds (chloromethyl)isopropyldimethylsilane and bis(chloromethyl)dimethylsilane, only methyl migration was observed. In the
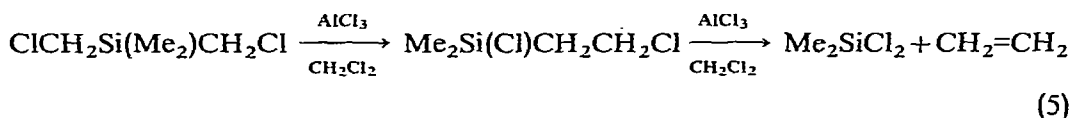
TABLE 4

MIGRATORY APTITUDES OF THE ORGANIC GROUPS

Group	Migratory aptitude[a]
Me	1.00[b]
Et	2.07[c]
n-Pr	2.97
iso-Pr	≪1.00[d]
ClCH$_2$	≪1.00[d]

[a] Estimated error, ±2%. [b] Me assigned the value 1.00. [c] Average value: rearrangement of (chloromethyl)-ethyldimethylsilane, 2.13; rearrangement of (chloromethyl)diethylmethylsilane, 2.01. [d] No migration detected relative to methyl.

case of bis(chloromethyl)dimethylsilane, migration of a chloromethyl group would lead to (2-chloroethyl)dimethylchlorosilane, a compound which under the reaction conditions would react further to yield dimethyldichlorosilane and ethylene[22]; however, no dimethyldichlorosilane was detected in the reaction mixture.

$$ClCH_2Si(Me_2)CH_2Cl \xrightarrow[CH_2Cl_2]{AlCl_3} Me_2Si(Cl)CH_2CH_2Cl \xrightarrow[CH_2Cl_2]{AlCl_3} Me_2SiCl_2 + CH_2{=}CH_2$$
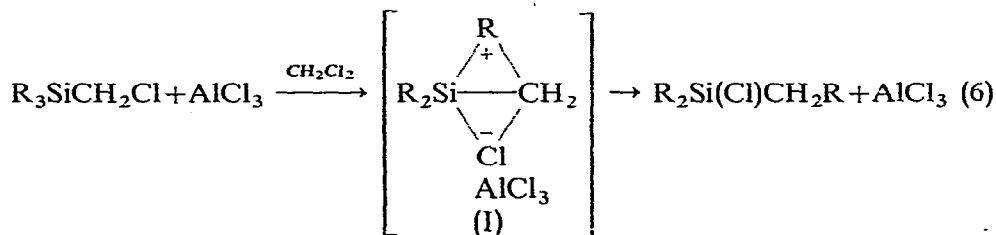
(5)

The consistency of the migratory aptitudes with structural changes in the (chloromethyl)triorganosilanes can be evaluated from studies of the rearrangement of (chloromethyl)triorganosilanes which have an identical pair of two different alkyl groups bonded to silicon. The migratory aptitude of the ethyl group was determined from the rearrangement of (chloromethyl)ethyldimethylsilane, 2.13, and (chloromethyl)diethylmethylsilane, 2.01. The deviation of these values from the arithmetic mean, 2.07, is only slightly greater than the estimated error. Thus, it seems reasonable to expect that the values obtained for the migratory aptitudes can be applied to other (chloromethyl)triorganosilanes containing primary alkyl groups.

DISCUSSION

Two trends are apparent from the migratory aptitudes of the organic groups in the aluminum chloride-catalyzed rearrangement of (chloromethyl)triorganosilanes. (1) + I effects facilitate migration from silicon to carbon; (2) branching at the α-carbon inhibits migration, relative to methyl. The first observation is in accord with the kinetic studies on the rearrangement of $p\text{-}XC_6H_4Si(Me_2)CH_2Cl$ by Eaborn et al.[5]. They reported the following order for para-substituent groups, Me > H > Cl. The second observation is in accord with the results of Kumada et al.[8] on the aluminum chloride-catalyzed rearrangement of (chloromethyl)-tert-butyldimethylsilane. They isolated only one product, tert-butylethylmethylchlorosilane (61.5%), which results from the migration of a methyl group.

Mechanisms for the aluminum chloride-catalyzed rearrangement of (chloromethyl)triorganosilanes have been proposed and discussed by Eaborn et al.[5]. Based on kinetic and structure-reactivity studies, they concluded that a concerted mechanism is most probable involving synchronous nucleophilic attack at silicon, migration of

the organic group with its electron pair and separation of chloride ion from carbon under electrophilic attack by aluminum chloride. Eaborn *et al.* also pointed out that

$$R_3SiCH_2Cl + AlCl_3 \xrightarrow{CH_2Cl_2} \left[\begin{array}{c} R \\ \diagup\!\!\!+\diagdown \\ R_2Si\!\!-\!\!-\!\!-CH_2 \\ \diagdown\!-\diagup \\ Cl \\ AlCl_3 \\ (I) \end{array} \right] \rightarrow R_2Si(Cl)CH_2R + AlCl_3 \quad (6)$$

the ability of silicon to expand its valence shell and other data on reactions involving silicon make this a much more acceptable process for the rearrangement of silicon compounds than it would be for the analogous carbon compounds (Wagner–Meerwein rearrangements). There may be considerable charge separation in the activated complex and/or intermediate since in a related rearrangement, the boron trifluoride-catalyzed rearrangement of α-silylcarbinols (reaction 3), Brook *et al.*[7] observed that two reaction paths are possible when the solvent is susceptible to electrophilic attack: (1) migrations of the organic group from silicon to carbon; (2) electrophilic attack of the activated complex or intermediate on the solvent.

The migratory aptitudes of the primary organic groups indicate that the inductive character of these groups plays an important role in the ease of migration from silicon to carbon—a $+I$ effect facilitates migration. Since mechanisms involving siliconium ion formation in the rate-determining step have been ruled out by structure-reactivity studies[5], the inductive effect on the migratory aptitudes is considered most reasonably in terms of the concerted mechanism or a closely related mechanism in which I is an unstable intermediate (eq. 6). Fig. 1 shows a free energy curve for a mechanism of the latter type for the aluminum chloride-catalyzed rearrangement,
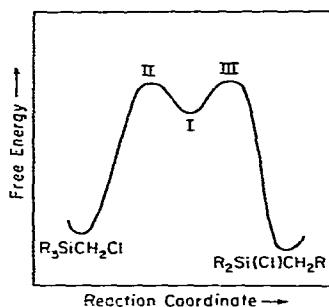

Fig. 1. Free energy curve for the mechanism involving an unstable intermediate for the rearrangement of (chloromethyl)triorganosilanes.

where I represents the free energy of the intermediate and II and III the transition states.

If the intermediate has appreciable stability relative to the activated complexes, either formation or destruction of the intermediate could be the rate-determining process. With respect to the migration of an organic group, transition state II primarily involves heterolytic cleavage of the C–Si bond and transition state III the formation of a C–C bond, a nucleophilic attack by the organic group on carbon.

Since $+I$ effects increase the nucleophilicity of the migrating organic group, it seems likely that the C–C bond formation, transition state III, is the rate-controlling process in the rearrangement of primary organic groups.

In spite of the fact that branching at the α-carbon of an organic group enhances the $+I$ effect of the group, migration of an isopropyl or tert-butyl group is not detected when methyl migration can occur. Steric effects perhaps could prevent migration of a secondary or tertiary alkyl group. However, two observations suggest that factors other than steric effects are involved: (1) the group is migrating from a tertiary silicon to a primary carbon; (2) Me_3Si and $Me_2(Cl)Si$ groups migrate to the exclusion of methyl migration. The significance of these observations is limited in the respect that silicon is larger than carbon. Steric requirements for the migration of a Me_3Si and a tert-butyl group may be quite different.

A plausible explanation of the relatively inert nature of secondary and tertiary alkyl groups toward migration can be developed in respect to the proposed mechanism involving the unstable intermediate (I). For these groups, heterolytic cleavage of the C–Si bond, transition state II, would be energetically less favorable than for a primary alkyl group since the migrating alkyl group is expected to develop considerable carbanion character. Carbanion stability of alkyl groups follow the order primary > secondary > tertiary[23]. Exclusive rearrangement of a methyl group relative to a secondary or tertiary alkyl group is expected if transition state II for the migration of a secondary or tertiary alkyl group is a much higher energy barrier than for the migration of a methyl group.

The facile rearrangement of Me_3Si and $Me_2(Cl)Si$ groups relative to methyl in (chloromethyl)pentamethyldisilane and 1-(chloromethyl)-2-chlorotetramethyl-disilane[3] is probably the result of a combination of factors: (1) the Si–Si bond energy is lower than the Si–C bond energy*; (2) the low energy d-orbitals on silicon allow for expansion of the valence shell during migration; (3) the trimethylsilyl group is more electron-releasing than an alkyl group. The combined result of these effects could appreciably lower the free energy of transition states II and III for the migration of a silyl group.
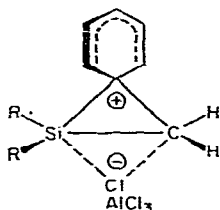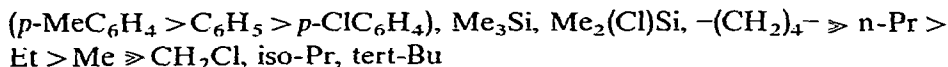

Fig. 2. Intermediate I for the rearrangement of an aryl group.

Kinetic studies by Eaborn et al.[5] on the rearrangement of p-$XC_6H_4Si(Me_2)$-CH_2Cl, where X = Me, H and Cl, in 1,2-dichloroethylene at $-20°$ show that only aryl group migration occurs under these conditions. Rough calculations based on these data and similar data on (chloromethyl)trimethylsilane at $25°$ indicate that phenyl migrates ~700 times faster than methyl. The facile migration of phenyl relative to

---

* Davidson and Stephenson[24], report the following bond dissociation energies: $Me_3SiSiMe_3$, $D(SiSi)$ 67 ± 2 kcal·mole^{-1}; Me_3SiMe, $D(SiC)$ 76 ± 2 kcal·mole^{-1}.

methyl is best explained in terms of the lowering of the energy requirements for migration of a phenyl group through charge delocalization. Intermediate I in this case would be related to an associated phenonium ion intermediate, of the type proposed in solvolytic displacement reactions at carbon where neighboring aryl group effects are observed[25], cf. Fig. 2.

The two-step mechanism involving an unstable intermediate presented above seems to be favored by the data available on the relative order of organic groups in their ability to migrate from silicon to carbon in the aluminum chloride-catalyzed rearrangement of (chloromethyl)triorganosilanes. A summary of data available on the relative migratory aptitudes of organic groups is given below:

$(p\text{-MeC}_6\text{H}_4 > \text{C}_6\text{H}_5 > p\text{-ClC}_6\text{H}_4)$, Me_3Si, $\text{Me}_2(\text{Cl})\text{Si}$, $-(\text{CH}_2)_4- \gg \text{n-Pr} >$
$\text{Et} > \text{Me} \gg \text{CH}_2\text{Cl}$, iso-Pr, tert-Bu

REFERENCES

1 F. C. WHITMORE, L. H. SOMMER AND J. GOLD, J. Amer. Chem. Soc., 69 (1947) 1976.
2 L. H. SOMMER, D. L. BAILEY, J. R. GOULD AND F. C. WHITMORE, J. Amer. Chem. Soc., 76 (1954) 801.
3 M. KUMADA, J. NAKAJIMA, M. ISHIKAWA AND Y. YAMAMOTO, J. Org. Chem., 23 (1958) 292.
4 M. KUMADA AND M. ISHIKAWA, J. Organometal. Chem., 1 (1964) 411.
5 R. W. BOTT, C. EABORN AND R. M. RUSHTON, J. Organometal. Chem., 3 (1965) 455.
6 V. M. VDOVIN, N. S. NAMETKIN, K. S. PUSHCHEVAYA AND A. V. TOPCHIEV, Bull. Acad. Sci. USSR, Div. Chem. Sci., (1962) 1057; (1963) 205; Izv. Akad. Nauk SSSR, Otd. Khim. Nauk, (1962) 1127; (1963) 274; N. S. NAMETKIN, V. M. VDOVIN, K. S. PUSHCHEVAYA AND A. N. EGOROCHKIN, Izv. Akad. Nauk SSSR, Ser. Khim., (1967) 2530.
7 A. G. BROOK, K. H. PANNELL, G. E. LEGROW AND J. J. SHEETO, J. Organometal. Chem., 2 (1964) 491.
8 M. KUMADA, M. ISHIKAWA, S. MAEDA AND K. IKURA, J. Organometal. Chem., 2 (1964) 146.
9 F. C. WHITMORE, L. H. SOMMER, P. A. DIGIORGIO, W. A. STRONG, R. E. VAN STRIEN, D. L. BAILEY, H. K. HALL, E. W. PIETRUSZA AND G. T. KERR, J. Amer. Chem. Soc., 68 (1946) 475.
10 F. C. WHITMORE AND L. H. SOMMER, J. Amer. Chem. Soc., 68 (1946) 481.
11 A. D. PETROV, V. F. MIRONOV, N. A. POGONKINA, Dokl. Akad. Nauk SSSR, 100 (1955) 81; Chem. Abstr., 50 (1956) 1573.
12 V. F. MIRONOV AND N. A. POGONKINA, Bull. Acad. Sci. USSR, Div. Chem. Sci., (1955) 161; Izv. Akad. Nauk SSSR, Otd. Khim. Nauk, (1955) 182.
13 J. L. SPEIER, J. Amer. Chem. Soc., 73 (1951) 824,
14 J. L. SPEIER AND B. F. DAUBERT, J. Amer. Chem. Soc., 70 (1948) 1400.
15 L. H. SOMMER AND G. R. ANSUL, J. Amer. Chem. Soc., 77 (1955) 2482.
16 M. F. SHOSTAKOVSKII, D. A. KOCHKIN, I. A. SHIKHIEV AND V. M. VLASOV, J. Gen. Chem. USSR, 25 (1955) 593; Zh. Obshch. Khim., 25 (1955) 622.
17 N. F. ORLOV, Dokl. Akad. Nauk SSSR, 114 (1957) 1033; Chem. Abstr., 52 (1958) 2742.
18 L. M. SHORR, J. Amer. Chem. Soc., 76 (1954) 1390.
19 H. WESTERMARK, Svensk Kem. Tid., 64 (1952) 283.
20 H. WESTERMARK, Acta Chem. Scand., 9 (1955) 947.
21 R. A. BENKESER, Y. NAGAI, J. L. NOE, R. F. CUNICO AND P. H. GUND, J. Amer. Chem. Soc., 86 (1964) 2446.
22 L. H. SOMMER, D. L. BAILEY AND F. C. WHITMORE, J. Amer. Chem. Soc., 70 (1948) 2869.
23 D. J. CRAM, Fundamentals of Carbanion Chemistry, Academic Press, New York, 1965, p. 21.
24 I. M. T. DAVIDSON AND I. L. STEPHENSON, J. Chem. Soc., A (1968) 282.
25 A. STREITWIESER, JR., Solvolytic Displacement Reactions, McGraw-Hill Book Co., New York, 1962, pp. 144–149.