

THE REACTION OF (α -HALOALKYL)SILANES WITH LEWIS ACIDS*

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SUMMARY

The kinetics for the reaction of three (α -haloalkyl)silanes with antimony pentafluoride in nitromethane have been studied using NMR to follow the reaction. For tertiary (α -haloalkyl)silanes, the reaction is stepwise with the intermediate formation of a charged species. The rearrangement-elimination reaction of this intermediate is sensitive to the Lewis acid used and to the inductive character and size of the alkyl groups attached to silicon. The kinetic and thermodynamic data are consistent with a mechanism involving nucleophilic attack at silicon before or during the rate determining alkyl migration or alkene elimination.

INTRODUCTION

We have previously reported the reaction of 2-(trimethylsilyl)-2-chloropropane (I) and 1-(trimethylsilyl)-1-chloroethane (III) with antimony pentafluoride in nitromethane¹. For the tertiary halide (I), ionization is followed by a combination of rearrangement and β -elimination. Each step can be directly observed using nuclear magnetic resonance. For the secondary halide (III), the initial ionization is rate determining and only resonances due to the starting halide and the elimination product, trimethylfluorosilane, are observed. The ionization of (I) follows second-order kinetics, first-order in (I) and first-order in antimony pentafluoride. The rearrangement-elimination of the ion (IV) follows competitive second-order kinetics, first-order in (IV) and first-order in hexahaloantimonate ion. These data indicate that the rearrangement-elimination reaction requires nucleophilic attack at silicon. This is in contrast to the four-centered intramolecular mechanism previously described for the reaction of primary (α -haloalkyl)silanes with aluminum chloride².

RESULTS AND DISCUSSION

We now wish to report further studies of this important reaction. Kinetic investigations have been made for three (α -haloalkyl)silanes at several temperatures and the thermodynamic data determined. The reaction of (I) with boron trifluoride

* For a preliminary report of this work see ref. 1.

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and antimony pentachloride has also been studied.

The reaction of (I) with antimony pentafluoride results in the appearance of new methyl resonances at δ 0.32 and 1.69 ppm (integrated intensities: 3.0/2.0; Fig. 1a).

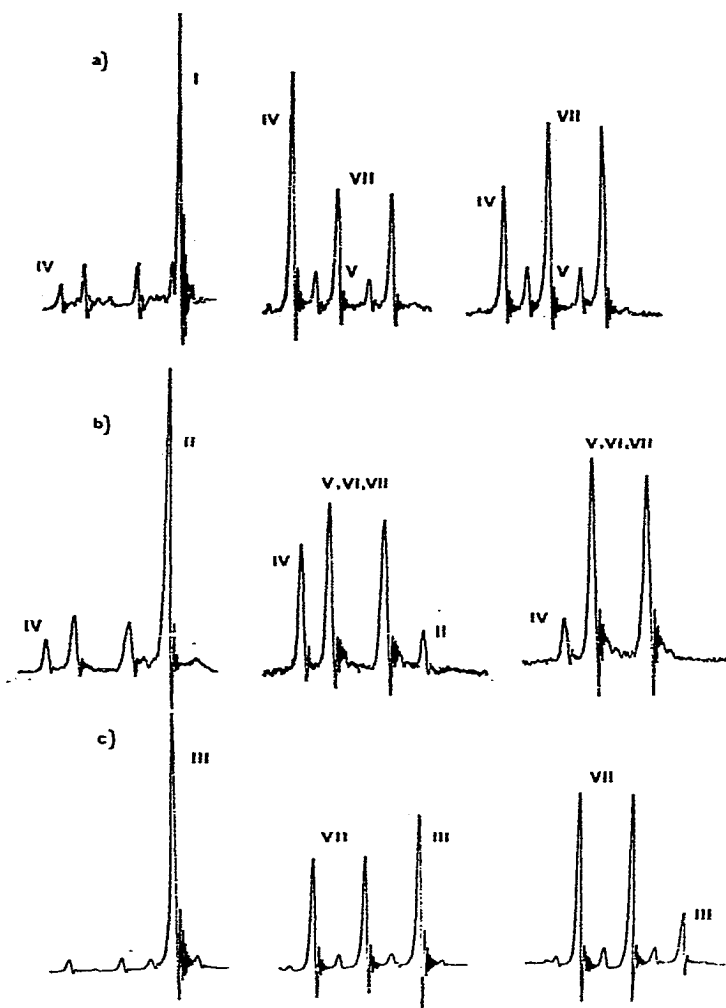
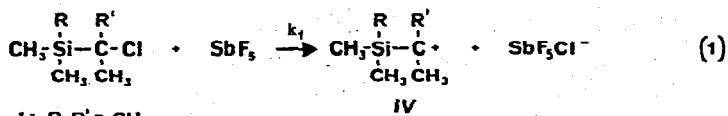


Fig. 1. Changes in the methyl-silicon resonances during the ionization and rearrangement-elimination reactions: (a) reaction of (I); (b) reaction of (II); (c) reaction of (III) [resonances on either side of doublet due to (VII) are ^{29}Si satellite peaks].

Kinetic data were obtained by integrating the appropriate resonances in the NMR spectra as a function of time. The ionization of (I) followed second-order kinetics through about 55% of the reaction. The rate then appeared to slowly increase as the regeneration of the Lewis acid from the second reaction became significant (Fig. 2). The species (IV) then reacted to form the rearranged product, tert-butyl-dimethyl-fluorosilane [(V) or (VI), eqn. (2)] and the β -elimination product, trimethylfluoro-



- I: R, R' = CH₃
 II: R = C₂H₅; R' = CH₃
 III: R = CH₃; R' = H

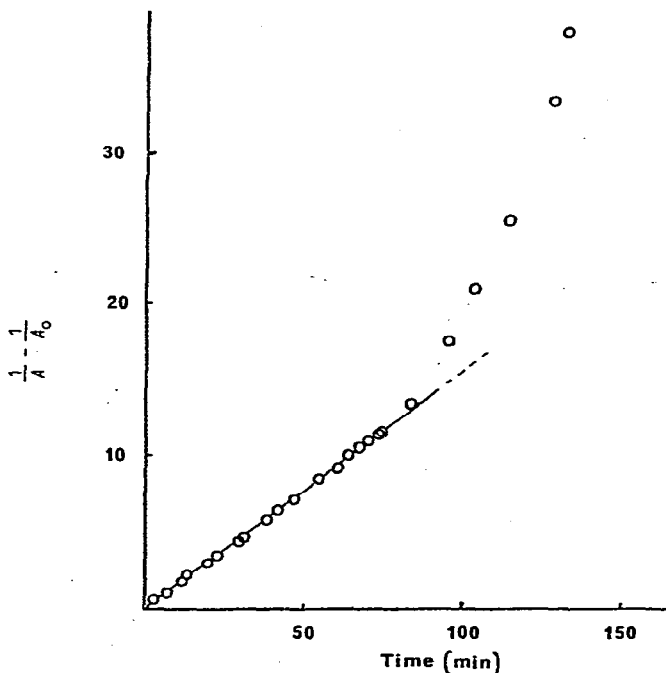
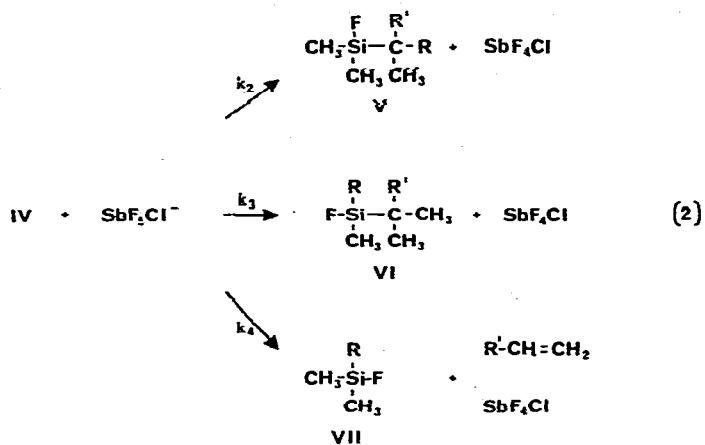


Fig. 2. Second-order plot of the reaction of (I) with SbF₅.

silane [(VII), eqn. (2)]. The rearrangement-elimination occurred in a second-order manner, first-order in (IV) and first-order in hexahaloantimonate ion. The first-order dependence upon hexahaloantimonate ion was verified by the addition of potassium hexafluoroantimonate to the reaction. Second-order rate constants were obtained in these runs if the concentration of hexahaloantimonate used in the rate calculation was the sum of the concentration resulting from the ionization reaction and the added potassium hexafluoroantimonate concentration. Kinetics for the rearrangement-elimination were determined by integration of the NMR after the completion of the ionization reaction.

The reaction of 2-(ethyldimethylsilyl)-2-chloropropane (II) occurred in a manner similar to (I) except that two rearranged products, (V) and (VI), were obtained so that, with the β -elimination product, (VII), three fluorosilanes were formed. For (I), the two products had methyl-silicon resonances sufficiently separated to allow kinetic data and product distribution to be determined from the proton spectra (Fig. 1a). However, for (II), the three products had methyl-silicon resonances which overlapped, making it impossible to determine the product distribution from the proton spectra (Fig. 1b). It was necessary to integrate the fluorine-19 spectra at the end of the reaction to determine the exact product distribution.

When the halide is secondary, ionization becomes rate determining. Kinetic data does not yield mechanistic information concerning the rapid elimination-rearrangement step following ionization. The reaction of 1-(trimethylsilyl)-1-chloroethane (III) with antimony pentafluoride showed only resonances due to (III) and the elimination product, trimethylfluorosilane [(VII); Fig. 1c]. Pseudo first-order plots were obtained for the reaction of (III) (Fig. 3). The value of the rate constant depended upon the antimony pentafluoride concentration. This confirms that the ionization of (III) is a second-order process. The ionization of the tertiary halide, (I), is about thirteen times faster than the secondary halide, (III). Chemical shift and coupling constant data for the reactions of (I), (II) and (III) are presented in Table 1.

TABLE 1

NMR DATA FOR REACTIONS OF (α -HALOALKYL)SILANES WITH LEWIS ACIDS^a

Reactant		Intermediate (IV)		Products						
No.	CH ₃ -Si $\delta(^1\text{H})$	C-CH ₃ $\delta(^1\text{H})$	CH ₃ -Si $\delta(^1\text{H})$	C-CH ₃ $\delta(^1\text{H})$	No.	CH ₃ -Si $\delta(^1\text{H})$	C-CH ₃ $\delta(^1\text{H})$	F-Si $\phi(^{19}\text{F})$		
						$J(\text{H-F})$	$J(\text{H-F})$			
I)	0.14(1)	1.57(1)	0.33(1)	1.69 b	(V)	0.22(2)	7.6	0.98(2)	1.0	171.0
					(VII)	0.32(2)	7.5			155.3
II)	0.12(1) -CH ₂ CH ₃ : 1.01 m	1.59(1)	0.30(1)	1.71 b	(V)	0.22(2)	7.6	0.95(2)	1.0	165.9
					(VI)	0.22(2)	7.6			176.6
					(VII)	0.22(2)	7.6			163.8
III)	0.21(1) -SiCHCl:	1.94(2) 3.94(4)			(VII)	0.32(2)	7.5			155.3

^a ¹H shifts reported in ppm downfield from TMS (internal); figures in parentheses represent multiplicity of peaks: b, broad singlet; m, complex multiplet; fluorine-19 chemical shifts were measured from C₆F₆ (internal) and converted into ppm upfield from CCl₃F (ϕ) using the relationship $\phi = \phi(\text{C}_6\text{F}_6) + 162.3$.

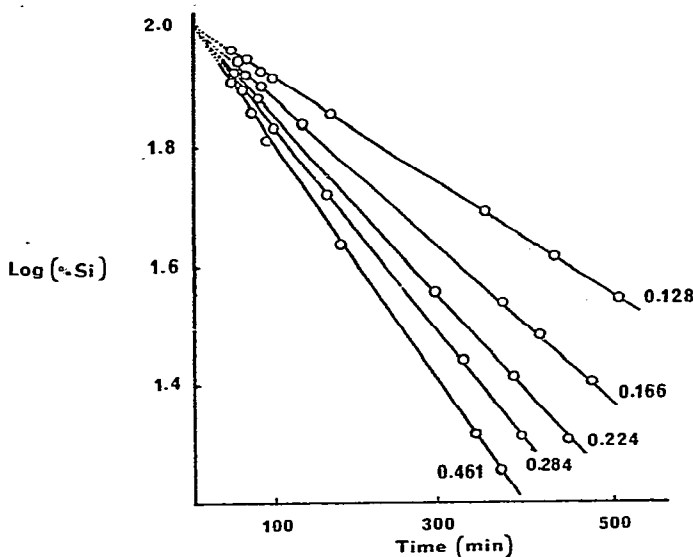
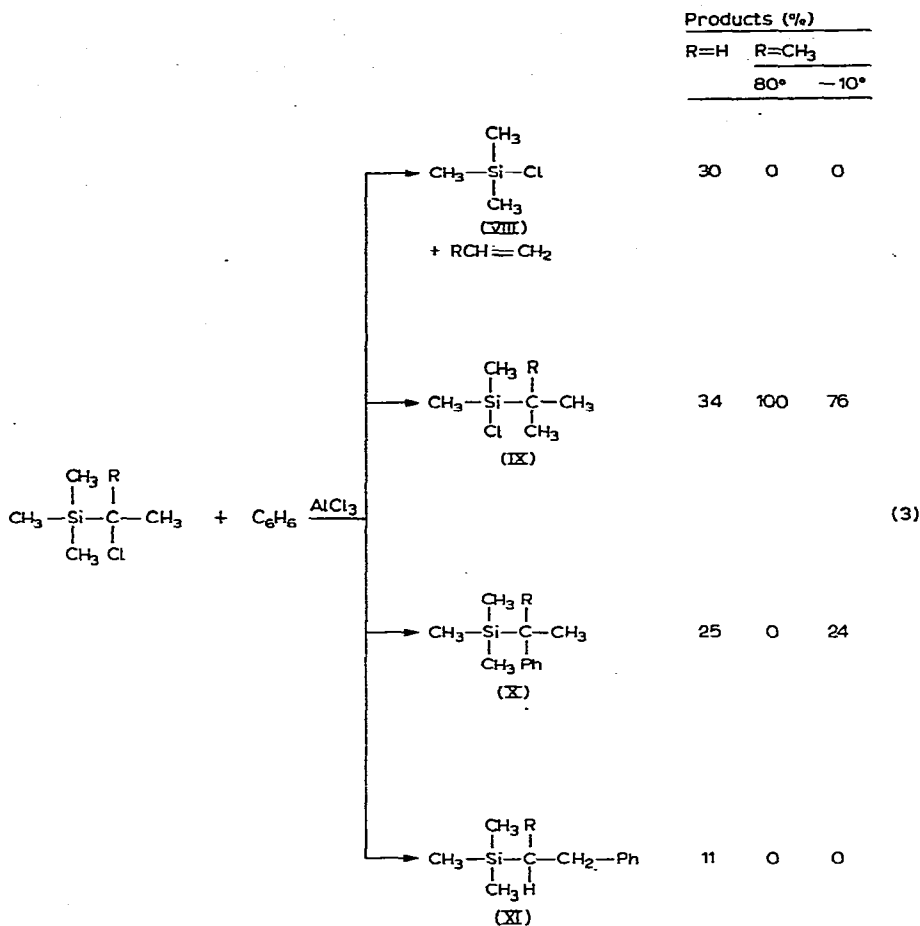


Fig. 3. Pseudo first-order plots of the reaction of (III) at different concentrations of SbF_5 .

The primary halide, (chloromethyl)trimethylsilane, was studied under similar conditions (0.2 M in silane and SbF_5 , 40°). The ionization reaction was so slow that no product formation was observed even after eight hours.

The existence of an α -silylcarbonium ion in rearrangements of this type has previously been suggested^{3,4}. The initially formed species (IV) is perhaps best described as a tightly bound ion pair rather than a free carbonium ion because of the small downfield chemical shifts for both the silicon-methyls and the carbon-methyls compared to the resonances of the starting (α -haloalkyl)silanes (approximately δ 0.19 and 0.12 ppm, respectively). Olah has reported downfield chemical shifts of δ 3.05 ppm for trimethylcarbonium ion generated from tert-butyl fluoride in neat antimony pentafluoride and a shift of δ 2.77 ppm for the same carbonium ion in sulfur dioxide solution⁵. However, to our knowledge no one has used nitromethane as solvent for the NMR characterization of carbonium ions and the degree of solvation in this medium is unknown. Regardless of the exact nature of (IV), it should be emphasized that it represents a distinct chemical species and the presence of this intermediate shows the stepwise nature of the reaction.

Since this species reacts not only to give rearranged products but also β -elimination products, it is reasonable to assume that the positive charge on the α -carbon is substantial enough to promote hydride shift from the β -carbon. Other, indirect evidence is available to indicate the presence of substantial positive charge on the α -carbon. Other investigators have found ring alkylation occurs when (α -hydroxyalkyl)silanes are ionized by Lewis acids in the presence of benzene⁶. We found similar results for the reaction of (I) and (III) with benzene and aluminum chloride. (I) reacts with benzene and aluminum chloride at reflux to yield only the rearranged product (IX) [eqn. (3)]. However, at lower temperatures (-10°) diluted with sulfur dioxide,



an appreciable yield of the α -alkylation product (X) is formed. The reaction of (III) with benzene and aluminum chloride yields the two alkylation products (X) and (XI) in addition to the elimination and rearrangement products (VIII) and (IX). However, aromatic silylation products were *not* detected. These reactions show that the intermediate is electrophilic and can be intercepted by the nucleophile, benzene.

Attempts were made to characterize the intermediate α -silylcarbonium ion (IV) under conditions which have been found suitable for observing stable carbonium ions. When (I) was dissolved in sulfur dioxide/antimony pentafluoride solution at low temperatures (-30 to -70°), only the starting and final product resonances were observed. Even at these low temperatures, the overall rate of the reaction was *increased* ($t_{\frac{1}{2}}$, $-60^\circ = \sim 10$ min) when compared to the reaction at 40° in nitromethane. Apparently, this more polar medium not only enhances carbonium ion formation but also the presence of a greater positive charge α to silicon promotes a great increase in the rate of alkyl group migration. This may prevent the observation of an appreciable concentration of the α -silylcarbonium ion.

Kinetic measurements

Rate data were obtained for the rearrangement-elimination reaction of (I) and (II) at several temperatures and for the ionization of (III) at 40.0°. These data and the product distributions are presented in Table 2. Thermodynamic data for the rear-

TABLE 2

KINETIC DATA FOR THE REACTION OF (α -HALOALKYL)SILANES WITH LEWIS ACIDS

Reactants No. Acid	Temp. (°C)	$k_1 \cdot 10^5$ (l·mole ⁻¹ ·sec ⁻¹)	$(k_2 + k_3 + k_4) \cdot 10^5$ (l·mole ⁻¹ ·sec ⁻¹)	Product distribution		
				%CH ₃ migration	%Elimi- nation	%CH ₃ CH ₂ migration
(I) SbF ₅	20.0	255 ± 6	84 ± 2	81	19	
	30.0		128 ± 11	85	15	
	40.0		245 ± 7	90	10	
	50.0		413 ± 18	92	8	
(I) SbCl ₅	40.0	262 ± 12				
(I) BF ₃	40.0	245 ± 16		94	6	
(II) SbF ₅	30.0		136 ± 3	13	30	57
	40.0		245 ± 17	14	21	65
	50.0		390 ± 6	17	17	66
	60.0		573 ± 28	20	14	66
Reactants No. Acid	SbF ₅ (mole·l ⁻¹)	$k \cdot 10^5$ (sec ⁻¹)	$k_1 \cdot 10^5$ (l·mole ⁻¹ ·sec ⁻¹)	%Elimi- nation		
(III) SbF ₅	0.1279	2.52	19.7 ^a	~98		
	0.1657	3.32	20.1	~98		
	0.2241	4.53	20.2	~98		
	0.2835	5.67	20.0	~98		
	0.4612	9.59	20.8	~98		

^a The value reported originally¹ for this constant was incorrect due to a computational error.

rangement-elimination reaction of (I) and (II) were determined from the rate constants derived by multiplying the total rate constant ($k_2 + k_3 + k_4$) by the appropriate product distribution. These data are collected in Table 3. The activation energy plots for the reactions of (I) and (II) are shown in Fig. 4.

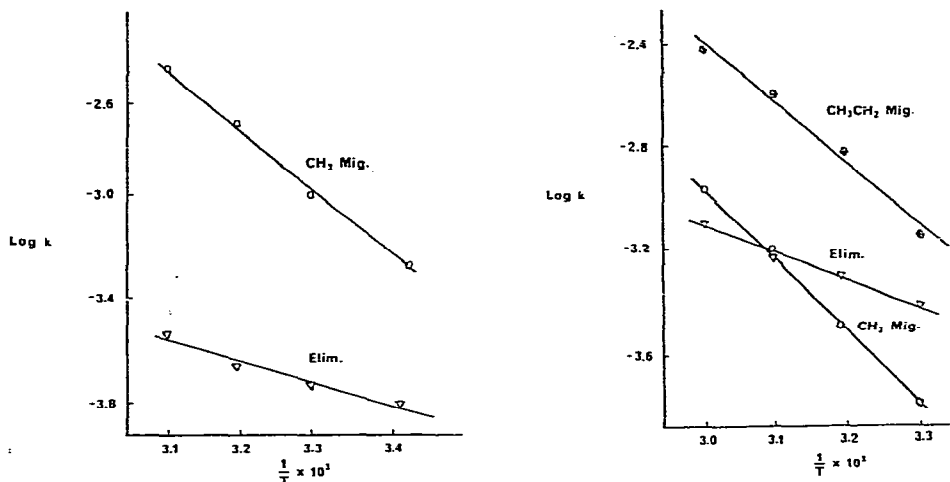
For the tertiary halides (I) and (II), the rearrangement-elimination step showed first order dependence upon hexahaloantimonate ion concentration. This implies that this ion attacks at silicon during or before the rate determining step. Therefore, the rearrangement-elimination reaction may be discussed mechanistically as a nucleophilic substitution at silicon combined with either alkyl migration or β -alkene elimination.

The importance of the nature of the nucleophile was demonstrated by the use of other Lewis acids in the reaction. When either boron trifluoride or antimony pentachloride were used in place of antimony pentafluoride, the rate of ionization (k_1) remained the same within experimental error (Table 2). This indicates that nitro-

TABLE 3

ACTIVATION PARAMETERS, 40°

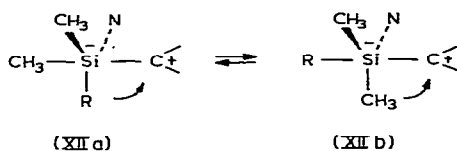
Reactions	E_a (kcal·mole ⁻¹)	ΔH^\ddagger (kcal·mole ⁻¹)	ΔG^\ddagger (kcal·mole ⁻¹)	ΔS^\ddagger (cal·deg ⁻¹ ·mole ⁻¹)
(I)				
CH ₃ migration	10.8 ± 0.8	10.2 ± 0.8	22.1 ± 1.6	-38.1 ± 2.9
Elimination	4.6 ± 1.6	4.0 ± 1.6	23.5 ± 1.6	-62.4 ± 4.6
(II)				
CH ₃ migration	12.5 ± 0.7	11.9 ± 0.7	23.3 ± 1.6	-36.6 ± 1.8
C ₂ H ₅ migration	10.5 ± 2.4	9.9 ± 2.4	22.4 ± 1.6	-39.9 ± 7.6
Elimination	4.5 ± 0.6	3.9 ± 0.6	23.1 ± 1.6	-61.3 ± 1.9

Fig. 4. Activation energy plots for the reactions of (I) and (II) with SbF₅.

methane interacts with the Lewis acid to produce a leveling effect on the strength of the acid. However, the rearrangement-elimination rate varied greatly depending on the Lewis acid used. With antimony pentachloride, the rate of the rearrangement-elimination was extremely slow. The ionization was complete after approximately 1 h but no appreciable further reaction took place even after eight hours. This is quite a striking effect when it is compared to the half-life of a typical reaction of (IV) with antimony pentafluoride ($t_{1/2} = \sim 70$ min). In sharp contrast, the rearrangement-elimination was greatly speeded up when (I) was reacted with boron trifluoride. In this reaction a small, steady-state concentration of the ion (IV) was observed and it is estimated from calculations of k_1 that $(k_2 + k_4)$ is approximately one hundred times greater than for the reaction with antimony pentafluoride. If the attacking nucleophile is the negative ion of the Lewis acid in each case, it appears that the rearrangement-elimination process is extremely sensitive to the size of the nucleophile.

Table 3 presents thermodynamic data for the rearrangement and elimination reactions of (I) and (II) determined from kinetic runs at several temperatures. The rearrangement of ethyl and methyl groups proceeds with large negative entropies of

activation. This is probably due to steric requirements in the activated complex. Similar large negative entropies were recently reported for the reaction between trichlorosilane and aromatic sulfoxides⁷. A pentacoordinate transition state was proposed for this reaction. Treating the rearrangement as a nucleophilic attack at silicon, the kinetic and thermodynamic data are consistent with a transition state (XII) in



which the nucleophile attacks *before or during* alkyl migration and in which little positive charge develops on silicon. If a siliconium ion were present, a positive entropy change would be expected for the neutralization of this charge by the nucleophile.

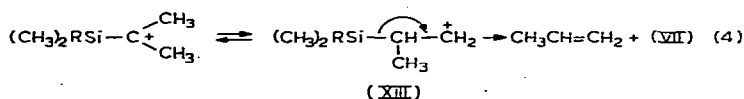
The first-order dependence of the reaction of (IV) upon hexahaloantimonate ion for *tertiary* (α -haloalkyl)silanes does not necessarily rule out the four-centered intermediate proposed by Eaborn² and supported by Steward, Uhl and Sands⁸ for *primary* (α -haloalkyl)silanes because of the expected marked difference in the stability of the tertiary versus the primary carbonium ion produced. However, it is the feeling of the authors that such a four-centered intermediate has not yet been supported by determination of the effect of the negative ion of the Lewis acid on the kinetics of the reaction of primary (α -haloalkyl)silanes. The difficulty in determining the effect of added negative ion of the Lewis acid for the reaction of primary (α -haloalkyl)silanes is pointed out by the kinetic data presented here. The ionization step becomes rate determining in going from tertiary to secondary and it would be expected that this would also be true for primary (α -haloalkyl)silanes.

The greater amount of ethyl compared to methyl migration in the rearrangement of (II) shows that the inductive character of the migrating group is important for migration from silicon to carbon for small alkyl groups. The migratory aptitude of ethyl compared to methyl found for the reaction of (II) ($k_2/2k_3=9.3$ at 40°) is similar to the migratory aptitude found by Steward, Uhl and Sands (ethyl/methyl=2.07)⁸. These authors studied the product distribution for the reaction of various (chloromethyl)trialkylsilanes with aluminum chloride and found that n-propyl migrates faster than ethyl and ethyl faster than methyl. Surprisingly, they found that isopropyl and tert-butyl did not migrate at all. We feel that these results can be explained by the mechanism presented here. Although five other distinguishable pentavalent intermediates can be drawn like (XIa) and (XIb) with differing arrangements of the four different groups around the central silicon, (XII) will be used to conveniently represent the steric control of the rearrangement reaction which may be taking place as one of the alkyl groups becomes larger. For the model we have chosen, if it is assumed that rearrangement occurs only from the planar position to the apical positive charge and that the larger group prefers the other apical position, the failure of isopropyl and tert-butyl to migrate can be rationalized. For methyl, ethyl and n-propyl, migration is controlled by the inductive nature of the migrating group while for larger (or branched) groups, (XIIb) is favored and migration is sterically controlled.

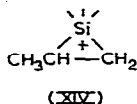
It should be emphasized that these conclusions should be treated as tentative

at best. The restrictions which we have placed on the intermediate are somewhat arbitrary since the present evidence does not allow a conclusion concerning whether the nucleophile attacks "rearward" or "flank". Also, Kumada has found that the bulky trimethylsilyl group in (chloromethyl)pentamethyldisilane rearranges in the presence of aluminum chloride rather than a methyl group⁹.

For the elimination, the reaction appears to be even more entropy dependent. This lower entropy may reflect the decrease in entropy associated with the formation of the more highly solvated primary carbonium ion, (XIII), in addition to the entropy associated with nucleophilic attack on this carbonium ion at silicon and elimination [eqn. (4)].



Another possibility may involve participation of the silicon with the primary carbonium ion center and the formation of a silacyclopropenium ion (XIV). The possible existence of such species has recently been postulated to account for the



highly stereospecific solvolysis of (2-haloalkyl)silanes¹⁰ and for deuterium scrambling in the solvolysis of the bromide, $(\text{CH}_3)_3\text{SiCH}_2\text{CD}_2\text{Br}$ ¹¹.

EXPERIMENTAL

General

All NMR spectra were obtained using a Varian Associates Model HA-100 Spectrometer equipped with a variable temperature probe. Proton chemical shifts are reported in ppm downfield from tetramethylsilane (internal). Fluorine-19 spectra were obtained using the HA-100 spectrometer with a V-4311 radio frequency unit operating at 94.1 MHz. Fluorine chemical shifts were measured using sidebands generated by a Hewlett-Packard Model 200CD audio oscillator and are reported in ppm upfield from CCl_3F (internal).

Nitromethane was carefully purified for the kinetic runs¹². Spectroscopic grade nitromethane was washed three times with a solution containing 2.5% sodium bicarbonate and 2.5% sodium bisulfite and then washed with 5% sulfuric acid, distilled water and 5% sodium carbonate. The nitromethane was then dried with Drierite and then with molecular sieves. It was then distilled through a four foot, vacuum jacketed, glass helix packed column. The center cut boiling at 100–101° was collected. The purified nitromethane was freshly distilled immediately before each kinetic run. Antimony pentafluoride was purified by distilling it in an atmosphere of dry nitrogen just prior to use. Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn.

Kinetic studies

Samples were prepared by mixing the appropriate silane with nitromethane and cooling to -76° . Antimony pentafluoride was dissolved in nitromethane, cooled and added to the cold silane solution. The sample was then warmed to the melting point of nitromethane (-28°) and the components mixed thoroughly and cooled again to -76° . Kinetic runs were carried out by allowing samples prepared in this manner to warm to the desired temperature in the NMR probe.

The rate of ionization (k_1) was determined by following the disappearance of the starting silane as a function of time. When the ionization was complete, the rate of rearrangement-elimination ($k_2 + k_3 + k_4$) was determined by following the disappearance of the ion peak. Product distribution for 2-(ethyltrimethylsilyl)-2-chloropropane (II) was determined by integration of the fluorine-19 spectrum. The individual rates of rearrangement and elimination were calculated by multiplying the total rate ($k_2 + k_3 + k_4$) by the product distribution.

Slopes were plotted for all kinetic runs using the method of least squares with the aid of a Hewlett-Packard Model 2161A/2114A computer. An estimate of the errors within an individual run was determined by measuring the root mean square deviation from the least square slopes for each point. Table 4 presents the average

TABLE 4

ERROR WITHIN INDIVIDUAL KINETIC RUNS

Compound	Temp. (°C)	No. of runs	$(k_2 + k_3 + k_4) \cdot 10^3$ (l · mole ⁻¹ · sec ⁻¹)	RMSD
(I)	20	2	0.84	± 0.02
	30	3	1.28	± 0.01
	40	7	2.45	± 0.01
	50	2	4.13	± 0.07
(II)	30	2	1.36	± 0.07
	40	4	2.45	± 0.11
	50	3	3.90	± 0.20
	60	4	5.73	± 0.04

root mean square deviations for all runs at a given temperature. It is believed that the most serious errors arise from the temperature control in the NMR probe ($\pm 0.5^\circ$) and, for (II), in the precision of the integrated fluorine-19 spectra used to determine product distribution.

Energy of activation slopes were calculated by the method of least squares. The error presented (Table 3) is that which results from a propagation of errors calculation using a Taylor Series as described by Bevington¹³. Errors used in the calculation were root mean square deviations from least square plots of activation energies, standard deviations from rate constants and the estimated temperature deviations within the runs.

*Syntheses**2-(Trimethylsilyl)-2-chloropropane (I).*

Preparation of (I) was carried out in a manner similar to that described by

Sommer¹⁴. To a two liter flask was added 750 ml of ether and magnesium turnings (72.0 g, 3.0 g-atoms). 2-Bromopropane (369.0 g, 3 moles) was added to the flask over a 3 h period. The Grignard solution was then added slowly to a solution of silicon tetrachloride (700.0 g, 3.95 moles) in 500 ml of ether at a rate to maintain gentle reflux. Distillation of the reaction mixture gave isopropyltrichlorosilane (268 g, 1.5 moles, 50.5% yield, b.p. 116–120°/756 mm, lit.¹⁴: 120.3°/748 mm). The product was divided into two parts and the following reactions were carried out on both parts.

A solution of isopropyltrichlorosilane (134 g, 0.76 mole), sulfuryl chloride (100 g, 0.74 mole) and benzoyl peroxide (1.0 g) was heated at reflux until evolution of sulfur dioxide and hydrogen chloride ceased. Distillation through a glass helix packed column gave 2-(trichlorosilyl)-2-chloropropane (39.7 g, 0.19 mole, 25% yield, b.p. 148–152°/756 mm, lit.¹⁵: 151°/744 mm) and 2-(trichlorosilyl)-1-chloropropane (101.0 g, 0.48 mole, 65% yield, b.p. 163–165°/756 mm, lit.¹⁵: 164°/744 mm). 2-(Trichlorosilyl)-1-chloropropane (100.0 g, 0.47 mole) was dehydrochlorinated with quinoline and distilled directly from the reaction flask (b.p. 110–180°). Distillation from a 20 cm glass helix packed column gave 2-(trichlorosilyl)propene (56.2 g, 0.32 mole, 68% yield, b.p. 112.5–114.0°/756 mm, lit.¹⁵: 113.5°/731 mm).

2-(Trimethylsilyl)propene was prepared by adding 2-(trichlorosilyl)propene (50.0 g, 0.29 mole) to a solution of excess methylmagnesium bromide (1.14 moles) in ether. The reaction mixture was refluxed for 12 h, poured into ice water and neutralized with dilute hydrochloric acid. The ether layer was dried over calcium chloride and distilled through a 50 cm vacuum jacked vigreux column to give 2-(trimethylsilyl)propene (20.1 g, 0.19 mole, 68% yield, b.p. 81.5–82.5°/756 mm, lit.¹⁵: 82°/730 mm). 2-(Trimethylsilyl)propene (15.0 g, 0.14 mole) was stirred with 150 ml of concentrated hydrochloric acid at 50° for 17 h. The flask was cooled and the crystals that precipitated were filtered immediately. Sublimation gave 2-(trimethylsilyl)-2-chloropropane (I) (4.8 g, 0.032 mole, 22% yield, m.p. 96–97°, lit.¹⁴: 95–97°).

2-(Ethyldimethylsilyl)-2-chloropropane (II)

Ethylmagnesium bromide was prepared by the reaction of ethyl bromide (30.0 g, 0.27 mole) with magnesium turnings (6.6 g, 0.27 g-atom) in 200 ml of ether. The ethylmagnesium bromide solution was added slowly to a solution of 2-(trichlorosilyl)propene (48.0 g, 0.27 mole) in 200 ml of ether. After the addition was complete, the reaction mixture was stirred for 2 h. Distillation gave 2-(ethyldichlorosilyl)propene (35.6 g, 0.21 mole, 77% yield, b.p. 141–144°/758 mm). Excess methylmagnesium chloride (0.60 mole) in 200 ml of ether was added to a solution of 2-(ethyldichlorosilyl)propene (35.6 g, 0.21 mole) in ether. The reaction mixture was stirred at reflux for 24 h, poured into ice water, neutralized with dilute hydrochloric acid and the ether layer dried over calcium chloride. Distillation through a 20 cm helix packed column gave 2-(ethyldimethylsilyl)propene (20.5 g, 0.16 mole, 77% yield, b.p. 114–115°/758 mm). 2-(Ethyldimethylsilyl)propene (15 g, 0.12 mole) was stirred with concentrated hydrochloric acid for 4 days. The organic layer was separated and the aqueous layer washed with 50 ml of ether. The combined organic layers were then washed repeatedly with distilled water until neutral, dried with calcium chloride and vacuum distilled to give 2-(ethyldimethylsilyl)-2-chloropropane (II) (11.0 g, 0.007 mole, 57.2% yield, b.p. 76–78°/26 mm). (Found: C, 50.95; H, 10.30; Cl, 21.29; Si, 17.25. C₇H₁₇ClSi calcd.: C, 51.03; H, 10.40; Cl, 21.52; Si, 17.05%.)

1-(Trimethylsilyl)-1-chloroethane (III)

The preparation of (III) was carried out in a manner similar to that described by Sommer and Whitmore¹⁶. A solution of ethyltrichlorosilane (50.0 g, 0.31 mole), sulfur chloride (41.0 g, 0.29 mole) and benzoyl peroxide (1.0 g) was heated until the evolution of sulfur dioxide and hydrogen chloride ceased. Distillation separated the product into four components: ethyltrichlorosilane (7.0 g, 0.43 mole, b.p. 100–102°/760 mm, lit.¹⁶: 100.5°/734 mm), 1-(trichlorosilyl)-1-chloroethane (20.0 g, 0.10 mole, 33% yield, b.p. 135–137°/760 mm, lit.¹⁶: 136.4°/734 mm), 2-(trichlorosilyl)-1-chloroethane (25.0 g, 0.13 mole, 41% yield, b.p. 151–153°/760 mm, lit.¹⁶: 152°/734 mm) and higher boiling material which did not distill (4.7 g). 1-(Trichlorosilyl)-1-chloroethane (20.0 g, 0.10 mole) was added slowly to a solution of an excess of methylmagnesium bromide (0.40 mole) dissolved in 200 ml of ether and the reaction mixture was refluxed for 12 h. The reaction mixture was poured into ice water, washed with dilute acid, distilled water and the organic layer dried over calcium chloride. Distillation gave 1-(trimethylsilyl)-1-chloroethane (III) (8.9 g, 0.065 mole, 65% yield, b.p. 117–119°/760 mm, lit.¹⁶: 117.5°/735 mm).

Alkylation reactions

Gas chromatographic analyses were carried out using a Varian Aerograph Series 1700 Chromatograph with a four foot 1/4" SAE-40 column and a Sargent Model SRC Recorder equipped with a disc integrator.

Reaction of 1-(trimethylsilyl)-1-chloroethane with benzene

1-(Trimethylsilyl)-1-chloroethane (13.7 g, 0.10 mole), benzene (15.6 g, 0.20 mole) and freshly sublimed aluminum chloride (0.25 g) was added to a flask equipped with a reflux condenser and a gas trap containing bromine. A very vigorous reaction occurred with the evolution of a gas. The gas evolved was identified as ethylene through the isolation of 1,2-dibromoethane from the gas trap. Gas chromatographic analysis of the reaction mixture showed the presence of the following silicon-containing products: trimethylchlorosilane (30%), isopropyldimethylchlorosilane (34%), (β -phenylethyl)trimethylsilane (11%) and (α -phenylethyl)trimethylsilane (25%). The reaction mixture was fractionally distilled and the boiling points and retention times of the products were compared to pure samples. The (α -phenylethyl)- and (β -phenylethyl)trimethylsilanes were prepared from 1-bromo-1-phenylethane and 1-bromo-2-phenylethane by the reaction of the Grignard reagents of these compounds with trimethylchlorosilane.

Reaction of 2-(trimethylsilyl)-2-chloropropane with benzene

(a) 2-(Trimethylsilyl)-2-chloropropane (1.0 g, 0.007 mole) was added to a solution of benzene (1.0 g, 0.013 mole) and freshly sublimed aluminum chloride (0.24 g). A vigorous reaction occurred. The reaction mixture was refluxed for 20 min. Gas chromatographic analysis showed the presence of only one product, tert-butylchlorosilane.

(b) In a similar manner, 2-(trimethylsilyl)-2-chloropropane (1.0 g, 0.007 mole), benzene (1.0 g, 0.013 mole) and aluminum chloride (0.16 g) were diluted with sulfur dioxide (15 ml) at -76° . The reaction mixture was allowed to reflux (-10°) for 20 min. Removal of the sulfur dioxide and gas chromatographic analysis showed the

presence of t-butyldimethylchlorosilane (76%) and 2-(trimethylsilyl)-2-phenylpropane (24%).

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