***n*-Butoxide–Methylmercaptide Exchange Reactions.** Lithium and sodium *n*-butoxides were prepared by heating lithium or sodium metal and *n*-butyl alcohol in benzene except for V-1. As an example, a procedure for V-1 is described. Lithium *n*-butoxide was prepared from 1.95 mmol of *n*-butyllithium (1.60 *M* in hexane) and 0.30 ml of *n*-butyl alcohol in 12 ml of benzene. The solution was stirred for 1 hr at room temperature. Into the solution, which remained clear, 1.70 mmol of (−)$R_3Si^*SCH_3$ (0.50 g), $[\alpha]_D$ −10.0° (*c* 2.44, pentane), was added in 3 ml of benzene. No apparent change was observed and it was refluxed for 22 hr, during which time a suspension (CH_3SLi?) appeared. The reaction mixture was worked up in the usual manner. An infrared spectrum of the crude product (0.51 g) showed that the reaction was complete. It was chromatographed in the manner mentioned before. The recovered (+)-R_3Si^*O-*n*-Bu (0.41 g) had $[\alpha]_D$ +2.95° (*c* 4.59, pentane).

Isopropoxide–Methylmercaptide Exchange Reactions. As a typical example, a procedure for VI-2 is described. Lithium isopropoxide was prepared by heating 15.4 mg of lithium (2.22 mmol) and 7.5 ml of isopropyl alcohol in 5 ml of benzene for 0.5 hr. At room temperature, 1.70 mmol of (−)$R_3Si^*SCH_3$ (0.50 g), $[\alpha]_D$ −9.6° (*c* 0.91, pentane), was added dissolved in benzene. There was a small amount of solid suspended (*i*-PrOLi?). This suspension soon disappeared and the solution became clear. The solution was stirred for 2.5 hr. An infrared spectrum of the crude product showed that the reaction was complete and the products were chromatographed in the manner mentioned before. The recovered (+)R_3Si^*O-*i*-Pr (0.31 g) had $[\alpha]_D$ +2.18° (*c* 2.89, pentane).

***n*-Butoxide–Fluoride Exchange Reactions.** As a typical example, a procedure for VII-3 is described. Lithium *n*-butoxide was prepared by heating 18 mg of lithium metal and 7.5 ml of *n*-butyl alcohol in 5 ml of benzene. When the solution was cooled to room temperature, the solution became opaque because of a suspension, presumably lithium *n*-butoxide. Into the solution, 1.9 mmol of (+)R_3SiF (0.51 g), $[\alpha]_D$ +38.9° (*c* 1.20, pentane), was added in 2.5 ml of benzene. The solution immediately cleared and started to become cloudy again. Presumably, lithium *n*-butoxide dissolved in the initial stage and lithium fluoride started to appear. Although the reaction seemed fast, it was magnetically stirred for 2.5 hr at room temperature. The reaction mixture was worked up in the usual manner. The crude product was chromatographed in the manner mentioned before. The recovered (−)R_3Si^*O-*n*-Bu (0.39 g) identified by an infrared spectrum had $[\alpha]_D$ −6.47° (*c* 4.06, pentane).

Isopropoxide–Fluoride Exchange Reactions. As a typical example, a procedure for VIII-5 is described. Sodium isopropoxide was prepared by heating 51.9 mg of sodium (2.26 mmol) and 7.5 ml of isopropyl alcohol in 10 ml of benzene. In 2 hr, sodium was dissolved and the solution was cooled to room temperature. The solution remained clear. A solution of 0.51 g of (+)R_3Si^*F (1.9 mmol), $[\alpha]_D$ +38.9° (*c* 1.20, pentane), in 2.5 ml of benzene was added into the solution. The solution immediately became cloudy and was magnetically stirred for 2.5 hr. The reaction mixture was worked up in the usual manner. An infrared spectrum of the crude product showed it to be exclusively isopropoxysilane except for some silanol. It was chromatographed in the manner mentioned before and the recovered (−)R_3Si^*O-*i*-Pr had $[\alpha]_D$ −2.61° (*c* 3.44, pentane).

Stereochemistry of Asymmetric Silicon. XIV. The SN2*–Si Mechanism and Racemization of an Optically Active Fluorosilane without Displacement of Fluoride Ion[1,2]

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Abstract: A kinetic study of the alcohol-induced racemization of optically active α-naphthylphenylmethylfluorosilane, R_3Si^*F, has been carried out. The data have been rationalized in terms of mechanism SN2*–Si which involves the equilibrium formation of an expanded-octet addition complex between the reagent and the fluorosilane.

As proposed in previous publications, mechanism SN2–Si commonly operates for stereospecific *inversion* reactions of optically active R_3Si^*X, and mechanism SNi–Si is usual for *retention* of configuration at an asymmetric silicon center in triorgano monofunctional silanes. Furthermore, neither of these mechanisms involve formation of a full-fledged *Si-5* intermediate having *five full bonds to central silicon.*[3–6]

The extensive evidence for operation of mechanisms SN2–Si and SNi–Si in a very large number (~100) of stereospecific reactions of α-NpPhMeSi*X and PhMeRSi*X (R = neopentyl, benzhydryl, or ethyl) stands in interesting contrast to the elegant studies by Frye which have resulted in isolation of special structures containing pentacoordinate silicon.[7] These substances comprise nitrilotriethoxysilanes, Z-$Si(OCH_2CH_2)_3N$, and related pentacoordinate silicon derivatives of 2,2′,2″-nitrilophenol, $(o\text{-}HOC_6H_4)_3N$, in which the silicon is part of *neutral* triptych structures having transannular dative bonding between nitrogen and silicon, and pentacoordinate silicon derivatives of catechol in which the silicon is part of the *anionic* component of salts. However, these structures, which are formally analogous to expanded-octet intermediates derived from addition of an

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(1) For the preceding paper in this series see L. H. Sommer and H. Fujimoto, *J. Am. Chem. Soc.*, **91**, 7040 (1969).

(2) For a report of preliminary results obtained at the Pennsylvania State University, see L. H. Sommer and P. G. Rodewald, *ibid.*, **85**, 3898 (1963).

(3) For a recent detailed treatment of mechanism SN2–Si, see L. H. Sommer, G. A. Parker, N. C. Lloyd, C. L. Frye, and K. W. Michael, *ibid.*, **89**, 857 (1967).

(4) For a recent paper on mechanism SNi–Si, see L. H. Sommer and H. Fujimoto, *ibid.*, **90**, 982 (1968).

(5) For general treatments of mechanisms SN2-Si and SNi–Si, see L. H. Sommer, "Stereochemistry, Mechanism, and Silicon," McGraw-Hill Book Co., Inc., New York, N. Y., 1965.

(6) It should be noted that, as defined in ref 5, mechanisms SN2–Si and SNi–Si may or may not involve formation of an unstable intermediate whose structure and free energy closely approximate the structures and free energies of the transition state maxima which precede and follow it along the reaction coordinate. In short, for SN2–Si or SNi–Si an unstable intermediate is a shallow minimum having long and weak bonds between Si and the entering and leaving groups.

(7) C. L. Frye, G. E. Vogel, and J. A. Hall, *J. Am. Chem. Soc.*, **83**, 996 (1961); C. L. Frye, *ibid.*, **86**, 3170 (1964); C. L. Frye, G. A. Vincent, and G. L. Hanschildt, *ibid.*, **88**, 2727 (1966).

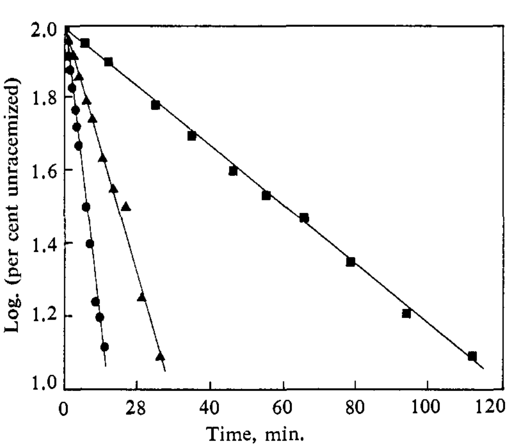

Figure 1. First-order rate plots for the racemization of R_3Si*F (0.0470 *M*) at 24.4° in $MeOH/CCl_4$ solvent systems: ●, 20% MeOH; ▲, 15% MeOH; ■, 10% MeOH.

anion or a neutral molecule to a tetravalent silicon reaction center, *contain a maximum of one organic group* directly bonded to silicon. Four or five electronegative groups (relative to R or Ar) are apparently *usually* necessary to confer the stability necessary for isolation of pentacoordinate silicon compounds in such cases.[8] Of course, the extreme example of expanded-octet stability conferred upon silicon by highly electronegative substituents is the very stable SiF_6^{2-} ion.

The high bond dissociation energy of Si–F in Me_3-Si–F (>150 kcal/mol),[9] the high electronegativity of fluorine and its small size, plus the above considerations, suggested to us that optically active α-NpPhMeSi*F, designated R_3Si*F below, might, under favorable conditions, give racemization by mechanism SN2*–Si.

For the general case, mechanism SN2*–Si has been defined[10] as involving formation of a full-fledged pentacoordinate silicon intermediate, five full bonds to central Si, in a rapid equilibrium step, followed by rate-controlling conversion of the intermediate to products. For an optically active reactant, mechanism SN2*–Si can be formulated so as to include the possibility of racemization by expanded-octet (EO) return. In eq 1, Y is a nucleophile and R_3Si*XY is an intermediate whose structure and free energy *differ significantly* from those of the transition state maxima which precede and follow it along the reaction coordinate. Racemization of

$$\begin{tikzcd}
(+)\mathrm{R_3Si*X} + \mathrm{Y} \arrow[r, shift left, "k_1"] & \mathrm{R_3Si*XY} \arrow[l, shift left, "k_{\mathrm{ret}}"] \arrow[r, "k_2", "\text{inv or ret}"'] \arrow[d, shift left, "k_1"] & \mathrm{R_3Si*Y} + \mathrm{X} \quad (1) \\
 & (-)\mathrm{R_3Si*X} + \mathrm{Y} \arrow[u, shift left, "k_{\mathrm{inv}}"] &
\end{tikzcd}$$

R_3Si*F by mechanism SN2*–Si would involve $k_{inv} > k_2$ in mechanism 1, and prior to the initiation of the present work stereospecific reactions of R_3Si*F were known which could not involve mechanism 1 having $k_{inv} \sim k_{ret} > k_2$. However, these stereospecific reactions all employed strong bases as nucleophilic reagents. For example, reactions 2 and 3 proceed with good *inversion* of configuration[11,12] and reactions 4 and 5 proceed with good *retention* of configuration.[12,13]

$$(+)R_3Si*F + LiAlH_4 \xrightarrow[\text{inv}]{\text{ether}} (-)R_3Si*H \qquad (2)$$

$$(+)R_3Si*F + Ph_2CHLi \xrightarrow[\text{inv}]{\text{ether}} (-)R_3Si*CHPh_2 \qquad (3)$$

$$(+)R_3Si*F + i\text{-}PrLi \xrightarrow[\text{ret}]{\text{ether}} (+)R_3Si*\text{-}i\text{-}Pr \qquad (4)$$

$$(+)Ph_2CHPhMeSi*F + \alpha\text{-}NpLi \xrightarrow[\text{ret}]{\text{ether}} (+)Ph_2CHPhMeSi*\text{-}\alpha\text{-}Np \qquad (5)$$

Concerning reactions 2–5, there are grounds for preferred assignment of mechanism SN2–Si to (2) and (3), and mechanism SNi–Si to (4) and (5).[12] For example, operation of SN2*–Si for reaction 5 should give optically inactive mixed organosilicon products, since expanded-octet return in a fast equilibrium process would clearly result in displacement of the more stable benzhydryl anion by the less stable α-naphthyl anion, and *this is not observed.*[13] Nevertheless, racemization of R_3Si*F by mechanism SN2*–Si has, we believe, been realized in the present work by using reagents which are *mild* nucleophiles and whose nature does not permit the formation of salts such as lithium fluoride to furnish an additional powerful driving force for reaction of the strong silicon–fluorine bond by mechanism SN2–Si.

Results and Discussion

Optically active α-naphthylphenylmethylfluorosilane (R_3Si*F) racemizes quite rapidly in low molecular weight alcohols such as methanol and ethanol. It was found that dilution of the alcohol with an inert solvent such as carbon tetrachloride slowed the racemization to a rate which could conveniently be followed using conventional polarimetric techniques. It is with the carbon tetrachloride/methanol solvent system that the bulk of the data presented here is concerned.

The racemization process displays good pseudo-first-order kinetics and was treated as an irreversible transformation of one of the enantiomers into the racemic modification.[14] Typical first-order rate plots for runs in 10, 15, and 20 vol % methanol in carbon tetrachloride are presented in Figure 1. Infrared spectroscopy showed the racemization product to be pure fluorosilane within the limits of the sensitivity of the method. Analysis of known mixtures showed that as little as 3% $R_3Si*OMe$ could be detected in a sample of R_3Si*F. This is in agreement with previous results which showed that an equilibrium is established when a fluorosilane is dissolved in an alcohol.[15] In these cases of tri-*n*-butyl-

$$R_3SiF + R'OH \rightleftharpoons R_3SiOR' + HF \qquad (6)$$

fluorosilane and triphenylfluorosilane, the equilibrium position in absolute ethanol was reported to correspond to less than 2% reaction.

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(8) For a report of a *cation* containing three phenyl groups and two nitrogens bonded to silicon, see J. Y. Corey and R. West, *J. Am. Chem. Soc.*, **85**, 4043 (1963).

(9) G. G. Hess, F. W. Lampe, and L. H. Sommer, *ibid.*, **87**, 5327 (1965).

(10) See ref 5, pp 179–180.

(11) L. H. Sommer, C. L. Frye, G. A. Parker, and K. W. Michael, *J. Am. Chem. Soc.*, **86**, 3271 (1964).

(12) L. H. Sommer, W. D. Korte, and P. G. Rodewald, *ibid.*, **89**, 862 (1967).

(13) L. H. Sommer, K. W. Michael, and W. D. Korte, *ibid.*, **89**, 868 (1967).

(14) E. L. Eliel, "Stereochemistry of Carbon Compounds," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p 34.

(15) C. Eaborn, *J. Chem. Soc.*, 2846 (1952).

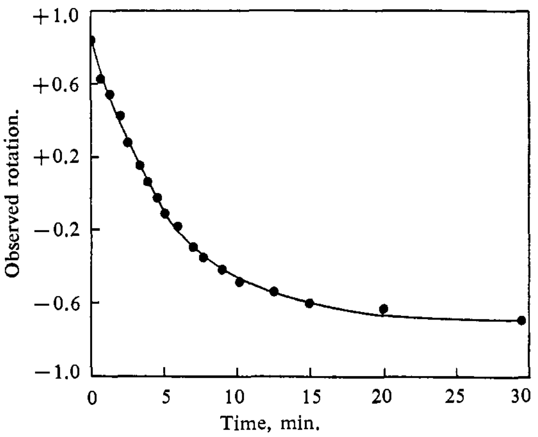

Figure 2. Plot of rotation *vs.* time for the racemization of R_3Si^*F (0.0470 *M*) at 24.4° in 20% MeOH/CCl_4 in the presence of R_3Si^*-OMe (0.0376 *M*).

Rate constants for the racemization in various methanol/carbon tetrachloride mixtures are listed in Table I. Rate constants derived from individual runs usually deviated by no more than 10% from the average value obtained from three or more runs. It should be noted that division of each pseudo-first-order rate constant by the cube of the methanol concentration yields a fourth-order rate constant which deviates remarkably little over the complete range of solvent mixtures studied. Evidence will first be presented which eliminates three intuitively obvious mechanistic possibilities for the racemization process. A mechanism will then be proposed by which all of the data presented can be rationalized.

Table I. Rate Constants for the Racemization of R_3Si^*F (0.0470 *M*) at 24.4° in Methanol–Carbon Tetrachloride Solvents

MeOH, vol %	[MeOH], *M*	k_1, sec^{-1}	$k_1/[MeOH]^3$, $M^{-3}\ sec^{-1}$
50.0	12.3	4.3×10^{-2}	2.3×10^{-5}
40.0	9.85	2.2×10^{-2}	2.3×10^{-5}
30.0	7.39	1.1×10^{-2}	2.8×10^{-5}
25.0	6.16	5.8×10^{-3}	2.5×10^{-5}
20.0	4.93	3.2×10^{-3}	2.5×10^{-5}
17.5	4.31	2.0×10^{-3}	2.5×10^{-5}
15.0	3.69	1.1×10^{-3}	2.2×10^{-5}
12.5	3.07	8.4×10^{-4}	2.8×10^{-5}
10.0	2.46	3.2×10^{-4}	2.1×10^{-5}
7.5	1.84	1.8×10^{-4}	2.9×10^{-5}
5.0	1.23	5.0×10^{-5}	2.7×10^{-5}

Racemization is not a result of the macroscopic formation of R_3Si^*OMe in an equilibrium (6) unfavorable to its isolation. If the substitution product were a partner in an equilibrium which resulted in the racemization of its precursor, it would also be racemized in the process. An experiment in which $(+)R_3Si^*F$ and $(-)R_3$-Si^*OMe were dissolved in 20 vol % methanol in carbon tetrachloride led to the racemization of the fluorosilane at a rate which was not altered by the presence of the other silicon compound. *During this period of time the methoxysilane retained its original optical purity.* Indeed, after the fluorosilane was completely racemized, the rotation due to the methoxysilane remained constant for 24 hr. This experiment is graphically illustrated in Figure 2 in which the observed rotation for the experiment described is plotted as a function of time.

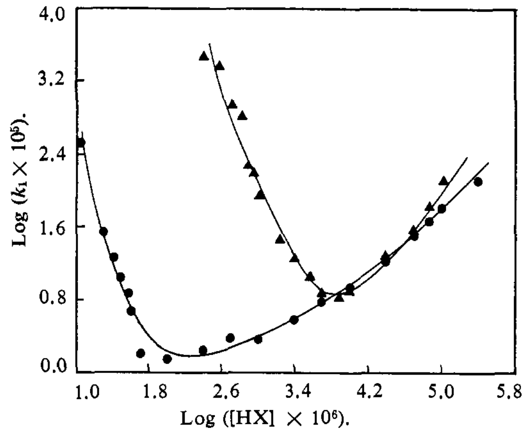

Figure 3. Plot of log ($k_1 \times 10^5$) *vs.* log ([HX]) $\times 10^6$) for the racemization of R_3Si^*F (0.0470 *M*) at 24.4° in 50% MeOH/CCl_4 with added HX: ●, HCl; ▲, HF.

Racemization can be envisioned as being the result of a fluoride–fluoride exchange process resulting from the formation of small amounts of HF in an equilibrium such as (6). If this hypothesis were correct, one might expect to observe an induction period during which a steady state concentration of HF was established. At no time was such a phenomenon observed. Furthermore, a detailed study of the effect of anhydrous HF and HCl on the rate of racemization was carried out. The results presented in Table II show that in the concentration range which would be appropriate assuming from 1 to 10% solvolysis, HF actually inhibits the rate of racemization. Furthermore, introduction of adventitious *very* small amounts of HF and/or fluoride ion by *varied* preparation and purification procedures for R_3Si^*F did not change the racemization rate. These facts seem to rule out rigorously, in these experiments, any mechanism requiring HF or fluoride ion as a racemization catalyst. The data of Table II are illustrated in the form of a log–log plot in Figure 3; however, a discussion of the structure of the plots will be postponed until they can be considered in relation to the mechanism to be proposed.

Table II. Rate Constants for the Racemization of R_3Si^*F (0.0470 *M*) at 24.4° in 50% Methanol–50% Carbon Tetrachloride with Added Anhydrous HF and HCl

[HF], *M*	k_1, sec^{-1}	[HCl], *M*	k_1, sec^{-1}
3.75×10^{-4}	2.2×10^{-2}	1.00×10^{-5}	2.3×10^{-3}
5.00×10^{-4}	8.3×10^{-3}	3.75×10^{-5}	7.3×10^{-5}
6.50×10^{-4}	6.0×10^{-3}	5.00×10^{-5}	1.6×10^{-5}
8.75×10^{-4}	1.5×10^{-3}	2.50×10^{-4}	1.8×10^{-5}
1.00×10^{-3}	8.3×10^{-4}	5.00×10^{-4}	2.3×10^{-5}
2.50×10^{-3}	1.7×10^{-4}	2.50×10^{-3}	3.8×10^{-5}
5.00×10^{-3}	7.2×10^{-5}	5.00×10^{-3}	6.0×10^{-5}
7.50×10^{-3}	6.8×10^{-5}	7.50×10^{-3}	8.2×10^{-5}
1.00×10^{-2}	7.7×10^{-5}	2.50×10^{-2}	1.7×10^{-4}
5.00×10^{-2}	3.7×10^{-4}	7.50×10^{-2}	4.3×10^{-4}
1.00×10^{-1}	1.1×10^{-3}	2.50×10^{-1}	1.2×10^{-3}

It is interesting to observe that although hydrogen fluoride does not catalyze the racemization, more ionic fluoride sources do cause a significant increase in the rate of racemization. In Table III are presented data which illustrate the effect of cyclohexylammonium fluoride on the racemization rate. The rate is very

Table III. Rate Constants for the Racemization of R_3Si^*F (0.0470 *M*) at 24.4° in 5% Methanol–95% Carbon Tetrachloride with Added Cyclohexylammonium Fluoride

$[c\text{-}C_6H_{11}NH_3F]$	k_1, sec^{-1}	$k_1/[c\text{-}C_6H_{11}NH_3F]$
5.0×10^{-4}	4.3×10^{-2}	86
4.4×10^{-4}	3.8×10^{-2}	86
3.5×10^{-4}	2.8×10^{-2}	80
2.5×10^{-4}	2.0×10^{-2}	80
2.0×10^{-4}	1.6×10^{-2}	80
1.5×10^{-4}	1.2×10^{-2}	80
1.0×10^{-4}	7.2×10^{-3}	72
8.0×10^{-5}	6.2×10^{-3}	77
5.0×10^{-5}	3.0×10^{-3}	60
2.5×10^{-5}	1.3×10^{-3}	52
1.0×10^{-5}	5.3×10^{-4}	53
5.0×10^{-6}	2.3×10^{-4}	46
	6.7×10^{-5}	

Table IV. First-Order Rate Constants (Sec^{-1}) for the Racemization of R_3Si^*F (0.0470 *M*) at 24.4° in Alcohol–Carbon Tetrachloride Mixtures

	Alcohol concentration, *M*				
Alcohol	12.3	9.85	7.39	4.93	3.69
MeOH	3.3×10^{-2}	2.2×10^{-2}	1.2×10^{-2}	3.2×10^{-3}	1.2×10^{-3}
EtOH	1.0×10^{-2}	8.8×10^{-3}	3.8×10^{-3}	5.0×10^{-4}	1.2×10^{-4}
n-PrOH	7.2×10^{-3}	5.3×10^{-3}	2.2×10^{-3}	2.3×10^{-4}	3.8×10^{-5}
n-BuOH		7.8×10^{-3}	2.5×10^{-3}	1.5×10^{-4}	2.8×10^{-5}
i-BuOH		1.8×10^{-3}	5.7×10^{-4}	2.2×10^{-5}	
i-PrOH	4.3×10^{-4}	1.5×10^{-4}	5.3×10^{-5}		
t-BuOH		1.7×10^{-5}			

nearly directly proportional to the total available fluoride concentration. The second-order rate constants obtained by dividing the observed pseudo-first-order rate constants by the total salt concentration vary by only a factor of 2 while the salt concentration is being changed by two powers of ten. A plot of log k_1 *vs.* log [salt] yields a good straight line of slope 1.2. The fractional order greater than one can conceivably be the result of a positive salt effect as no attempt was made to adjust the ionic strength of the medium to a constant value. Racemization catalyzed by cyclohexylammonium fluoride is felt to be the result of an S_N2–Si fluoride–fluoride exchange mechanism. However, definitive experiments designed to test this hypothesis have not yet been carried out. An attempt to gain some information about the effect of salts on the rate of solvent induced racemization was made by adding cyclohexylammonium chloride to the reaction mixture. This proved unpractical because small amounts of cyclohexylammonium fluoride from HF generated over the course of the racemization now acted as an effective racemization catalyst and autocatalytic kinetics were observed.

A mechanism for solvent-induced racemization involving the formation of a cationic silicon intermediate seems highly unlikely for several reasons. First, the high bond dissociation energy of Si–F is very unfavorable for an ionization process. Second, if racemization were the result of a rate-controlling ionization, addition of anhydrous HF and HCl to the medium would be expected to facilitate the process by favoring removal of fluoride ion from silicon through the formation of HF_2^- and $HFCl^-$.[16] This should be especially true in the case of added HF with the heat of formation of the bifluoride ion having been determined to have a minimum value of 37 kcal/mol.[17] Last, the rate of racemization is slow in high dielectric constant good dissociating solvents such as formic acid, dimethyl sulfoxide, and nitromethane. The rate in either formic acid or dimethyl sulfoxide is equivalent to that produced by a solution containing only 5 vol % of methanol in carbon tetrachloride. The dielectric constant of the latter solution is only 2.82.[18] This should be compared with the values of 2.25 for pure carbon tetrachloride,[18] 58.5 for formic acid,[19] and 48.9 for dimethyl sulfoxide.[20] The rate in pure nitromethane is so slow as to amount to only about 6% reaction after 120 hr.

Table V. $k_1(\mathrm{MeOH})/k_1(\mathrm{ROH})$ for the Racemization of R_3Si^*F (0.0470 *M*) at 24.4° in $ROH\text{–}CCl_4$ Mixtures

	Alcohol concentration, *M*				
Alcohol	12.3	9.85	7.39	4.93	3.69
EtOH	3.6	2.3	3.1	6.3	10
n-PrOH	4.6	4.1	5.5	14	32
n-BuOH		2.8	4.7	21	43
i-BuOH		12	21	150	
i-PrOH	77	150	190		
t-BuOH		1300			

In Table IV are presented data which illustrate the effect of branching in the alcohol on the rate of racemization. For easy comparison, the data of Table IV are shown in Table V as the ratio of the rate constants observed with methanol to the rate constants characteristic of the alcohol in question at equivalent concentrations. Although the order of the reaction with respect to alcohol concentration clearly changes somewhat from alcohol to alcohol, a definite trend is apparent. The rate slowly decreases as the length of the chain of the unbranched alcohols is increased. Branching in the β position causes a somewhat more pronounced decrease in rate, while branching in the α position causes a more drastic decrease in rate. These data seem to indicate that the alcohol is intimately associated with the silicon compound in the formation of the rate-controlling activated complex.

In view of these data and the fact that the three other most attractive mechanistic pathways have been shown to be unlikely, one attractive choice remains. This mechanism involves the equilibrium formation of an

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(16) D. W. A. Sharp, *J. Chem. Soc.*, 2558 (1958).

(17) S. A. Harrell and D. H. McDaniel, *J. Am. Chem. Soc.*, **86**, 4497 (1964).

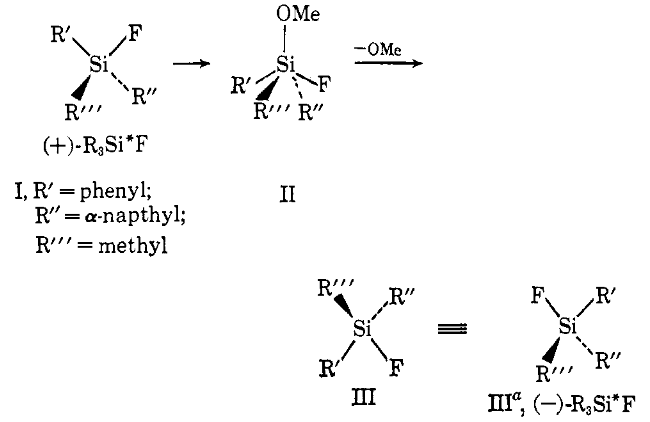
(18) H. Sadek and R. M. Fuoss, *ibid.*, **76**, 5897 (1954).

(19) A. A. Maryott and E. A. Smith, "Table of Dielectric Constants of Pure Liquids," National Bureau of Standards Circular 514, U. S. Government Printing Office, Washington, D. C., August 10, 1951.

(20) "Dimethyl Sulfoxide," Technical Bulletin, Crown Zellerbach Corp.

expanded-octet addition complex between the alcohol and the fluorosilane. This complex must be either optically inactive, optically unstable, or capable of collapsing to give both enantiomers of the tetrahedral fluorosilane. If the addition complex is assumed to be pentacoordinate, it will likely display one of two probable geometric arrangements depending on which d orbital is hybridized with the sp^3 system. Theoretical calculations carried out to deduce the most probable arrangement of five electrons with parallel spin indicate a trigonal bypyramidal geometry ($sp^3d_{z^2}$) to be only 3–4% more probable than a tetragonal pyramidal geometry ($sp^3d_{x^2-y^2}$).[21] Depending upon whether one assumes the trigonal bipyramid or the tetragonal pyramid to be of preferred geometry for the intermediate whose structure may or may not parallel those of known[22,23] ground-state structures, several schemes can be envisaged which would lead to racemized fluorosilane. The scheme which contains the least number of steps was outlined partially in a preliminary communication.[2] It is shown in detail in Chart I and involves (a) front-edge attack (attack at an Si tetrahedron edge containing F) to give tetragonal pyramid II, (b) movement upward toward OMe of the two groups not originally present in the front edge in a, and expulsion of OMe. The methoxide in Chart I and other schemes may be considered to come from a methylonium–methoxide ion pair from autoprotolysis of methanol ($MeOH_2^+$—MeO^-).

Chart I

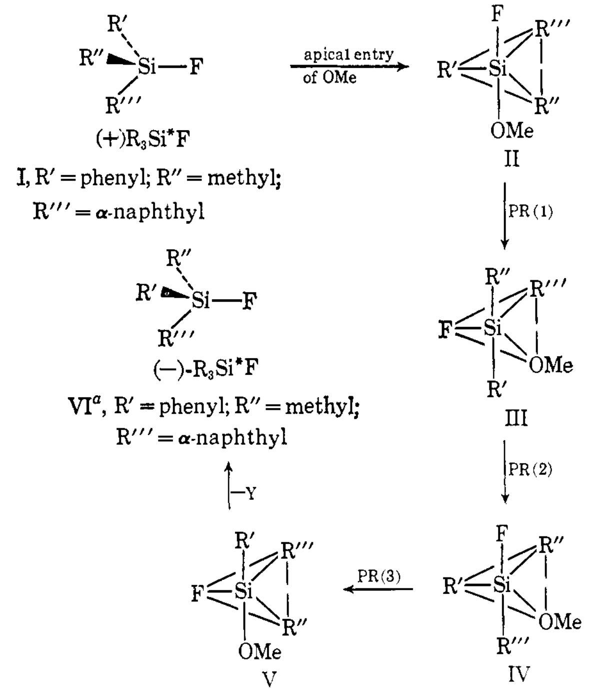


^{a} The silicon has been inverted.

In Chart II a pseudorotation scheme is presented which utilizes trigonal bipyramids as interconverting intermediates and requires five steps for racemization. In this pseudorotation (PR) formation we assume with Westheimer[24] that entry and exit of –OMe are apical.

For nmr evidence that pseudorotation occurs in SiF_5^- and $RSiF_4^-$, but not in $Ph_2SiF_3^-$, due to incursion of rapid intermolecular F–F exchange, and for evidence that $R_3SiF_2^-$ is too unstable to exist as a ground-state species under the conditions used to prepare the former species, a recent elegant study by Klanberg and Muetterties provides valuable data.[25]

Chart II



^{a} The silicon has been inverted. PR = pseudorotation.

The exact sequence of steps leading to the formation of the intermediate silicon species, and its nature, are of necessity somewhat obscure. The resulting complex is probably also solvated by a sphere of methanol molecules. A third-order dependence on methanol concentration should then not be surprising.

The exact role played by acids present at low concentration in inhibiting the rate of racemization remains somewhat uncertain. They presumably serve to protonate the addition complex, destroying it before the racemization process has a chance to occur.

Consideration of Figure 3 shows HCl to be effective as a racemization inhibitor at lower concentration than is the case for HF. It seems that this fact can be rationalized in terms of the greater acidity of the former acid. The rate of racemization in 50% methanol in carbon tetrachloride is slowed to the same extent by 5.2×10^{-4} *M* HF and by 7.2×10^{-6} *M* HCl. For HCl to be completely dissociated at this concentration would require only that the dissociation constant be greater than 10^{-4} in this medium. This is quite reasonable, the dissociation constant for HCl in pure methanol being 0.059.[26] For a 5.2×10^{-4} *M* solution of HF to yield this concentration of protons would require a dissociation constant of 10^{-7}. This is the value found for HF in absolute ethanol although at somewhat larger concentrations.[27]

It is extremely important to recognize that solvent-induced racemization of R_3Si^*F represents a significant departure from the normal behavior of R_3Si^*X and the many highly stereospecific reactions observed at asymmetric silicon. Occurrence of a facile equilibrium formation of an expanded-octet complex in one case cer-

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[21] J. W. Linnett and C. E. Mellish, *Trans. Faraday Soc.*, **50**, 665 (1954).

[22] For structural studies using X-ray diffraction which define pentacoordinate, near-trigonal-bipyramidal geometry for $PhSi(OCH_2CH_2)_3N$ and for $PhSi(OC_6H_4)_3N$, see J. W. Turley and F. P. Boer, *J. Am. Chem. Soc.*, **90**, 4026 (1968); F. P. Boer, J. W. Turley, and J. L. Flyn, *ibid.*, **90**, 5102 (1968).

[23] For an X-ray diffraction study showing dimethylsilylamine pentamer, $(-SiH_3N(CH_3)_2-)_5$, to be composed of pentacoordinate, trigonal-bipyramidal silicons, see R. Rudman, W. C. Hamilton, S. Novick, and T. D. Goldfarb, *ibid.*, **89**, 5157 (1967).

[24] For microscopic reversibility arguments supporting apical entry and exit of entering and leaving groups in the hydrolysis of phosphate esters, see F. H. Westheimer, *Accounts Chem. Res.*, **1**, 70 (1968).

[25] F. Klanberg and E. L. Muetterties, *Inorg. Chem.*, **7**, 155 (1968).

[26] T. Shedlovsky and R. L. Kay, *J. Phys. Chem.*, **60**, 151 (1956).

[27] E. Nachbur, *Montash.*, **91**, 749 (1960).

Figure 4. Variation in reaction profile of racemization and methanolysis of R_3Si^*F with increasing acid concentration.

tainly does not demonstrate this to be the preferred path for substitution in all silicon compounds. Indeed, other energetically more favorable pathways may exist for the displacement of fluoride from silicon. It is noted in Figure 3 that while small concentrations of added HCl and HF retard the rate of racemization, larger concentrations cause the rate to again approach that seen in neutral solution. The rate of hydrolysis of triphenylfluorosilane in 33.3% aqueous acetone has been found to be directly proportional to the concentration of added nitric acid.[28] This being true, it is possible that the increased rates of racemization at higher acid concentration are the result of an enhanced rate of methanolysis of R_3Si^*F in equilibrium 6, accompanied by acid-catalyzed racemization of formed R_3Si^*-OMe. Two experiments were carried out in an attempt to test this hypothesis. In the first, both R_3Si^*F and R_3Si^*OMe were dissolved in a medium consisting of 50 vol % methanol in carbon tetrachloride 0.1 *M* in HCl. The R_3Si^*OMe was completely racemic in less than 1 min, indicating that if it were formed in a solution of high acid content, it would be rapidly racemized. The second experiment was designed to estimate the rate of the forward reaction of eq 6. Here, a reaction was carried out in 50 vol % methanol in carbon tetrachloride containing R_3Si^*F (0.0470 *M*), HCl (0.101 *M*), and $Th(NO_3)_4$ (0.130 *M*).[29] At the end of 90 min there existed a mixture of 30% racemic R_3Si^*F and 70% racemic R_3Si^*OMe. While not conclusive these results indicate that at high acid concentration a substantial amount of racemization probably occurs *via* an equilibrium process. It is assumed that acids act as electrophilic catalysts helping to break the silicon–fluorine bond. In terms of transition state theory, as the acid concentration is increased, the rate-controlling transition state for solvolysis becomes lower and lower while that for racemization (intermediate formation) becomes higher. Thus, a limit will be reached at which the total reaction profile will take on the appearance of a direct displacement reaction (SN2–Si) (see Figure 4).[30]

Experimental Section

Solvents. Mallinckrodt analytical reagent carbon tetrachloride was fractionally distilled, the first 10% of the distillate containing the aqueous azeotrope being discarded.

Mallinckrodt analytical reagent methanol was fractionally distilled after refluxing for 12 hr with its magnesium salt. Subsequent distillation from sulfanilic acid, tartaric acid, or silver nitrate did not alter the observed rate of racemization. Anhydrous ethanol obtained from Commercial Solvents Corp. was treated in the same manner as described for methanol. *n*-Propyl alcohol and isobutyl alcohol (Eastman White Label), isopropyl alcohol (Mallinckrodt analytical reagent), *n*-butyl alcohol (Baker and Adamson ACS reagent), and *t*-butyl alcohol (Baker ACS analyzed reagent) were all fractionally distilled twice with the first and last 15% of the distillate which contained the aqueous azeotrope being discarded. Subsequent distillation of the *n*-propyl alcohol from its magnesium salt produced no change in the observed kinetics.

Reagents and Starting Materials. (+)- or (−)-α-naphthylphenylmethylfluorosilane was prepared using three different procedures all of which have been described in detail.[3,11,30] The crude fluorosilane resulting from each procedure was crystallized twice from pentane. The resulting material was passed over a column of silica gel using a mixture of 10 vol % benzene in pentane as eluent. After removal of solvents, the residue was dissolved in pentane and allowed to crystallize at room temperature. The method of preparation of the fluorosilane had no effect on the observed kinetics.

(−)-α-Naphthylphenylmethylmethoxysilane was prepared by the procedure described in ref 11.

Cyclohexylammonium fluoride was prepared by the action of anhydrous HF on a pentane solution of cyclohexylamine. The resulting precipitate was evacuated at 0.5 mm for 24 hr. A satisfactory neutralization equivalent was obtained using a standard solution of potassium isopropoxide in isopropyl alcohol as the base and thymolphthalein as the indicator.

Racemization of R_3Si^*F in $MeOH/CCl_4$ Solvent Mixtures. In this section, the general procedure used for all racemization experiments will be described. A stock hexane solution of the fluorosilane was prepared. Just prior to a racemization experiment an aliquot of the stock hexane solution of fluorosilane was put into a jacketed polarimeter tube using an oven dried syringe. The hexane was then removed under reduced pressure and the tube and its contents were evacuated at 0.5 mm for 30 min. Dry N_2H was allowed to pass into the evacuated tube *via* a two-way stopcock. The fluorosilane was then dissolved in the appropriate amount of anhydrous carbon tetrachloride, the jacket of the tube was connected to a circulating constant temperature bath, and the contents of the tube were allowed to equilibrate for 5 min. The proper amount of anhydrous methanol, previously equilibrated at the racemization temperature, was added using an oven-dried syringe. The contents of the tube were mixed thoroughly and the rotation of the solution followed as a function of time. In this series of experiments, the concentration of the fluorosilane was held constant at 0.0470 *M* and the temperature maintained at 24.4 ± 0.05°. The solvent compositions are expressed as volume per cent methanol in carbon tetrachloride. In all cases, deviations from direct additivity of the separate volumes were quite small and were neglected. The racemization product was characterized by comparing its infrared spectrum (CCl_4 solution) with that of an authentic sample of fluorosilane. In no case was it possible to detect any solvolysis product in the racemic fluorosilane. Analysis of known mixtures using the same method showed that as little as 3% methoxysilane could be detected in a sample of fluorosilane.

Optical Stability of R_3Si^*OMe under the Racemization Conditions. The racemization of (+)-fluorosilane (0.0470 *M*) in 20% methanol in carbon tetrachloride was carried out at 24.4° in the presence of (−)-methoxysilane (0.0376 *M*). The rotation of the solution was observed to decrease from the initial positive value to a negative value due to the methoxysilane in the solution. The rotation remained constant at this value for at least 24 hr. The rate of racemization of the fluorosilane was not altered by the presence of the methoxysilane.

Effect of Acids on the Rate of Racemization. Standard methanolic solutions of hydrogen fluoride and hydrogen chloride were prepared by bubbling the gas into anhydrous methanol followed by titration of an aliquot of the resulting solution with standard base. More dilute solutions were prepared by successively diluting aliquots of the original solution. The variation of the pseudo-first-order rate constant for the racemization of (+)-fluorosilane (0.0470 *M*) at 24.4° in 50% methanol in carbon tetrachloride was studied as a function of acid concentration. Comparison of the infrared spectrum of the racemization product with those of known mixtures showed that no more than 3% solvolysis occurred during any experiment.

Racemization of R_3Si^*F and R_3Si^*OMe in the Presence of HCl. The rotation of a solution of (+)-fluorosilane (0.0272 *M*) in 50% methanol in carbon tetrachloride in the presence of (−)-methoxy-

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[28] L. H. Sommer and M. C. Musolf, unpublished work; see M. C. Musolf, Ph.D. Thesis, The Pennsylvania State University, 1960.

[29] Th(IV) is a strong complexing agent for fluoride and will remove any HF formed from the solvolysis of the fluorosilane.

[30] For a review of previous studies on the hydrolysis of optically inactive R_3SiF compounds which do not permit a decision as to whether mechanism SN2*–Si is operating, see ref 5, pp 139–142; C. Eaborn, "Organosilicon Compounds," Academic Press, New York, N. Y., 1960, pp 110–113.

silane (0.0280 *M*) and hydrogen chloride (0.08 *M*) at 24.4° was followed as a function of time. From the magnitude of the initial positive rotation and from the linearity of the resulting first-order rate plot, it was clear that the methoxysilane was essentially completely racemic before the first reading could be taken (~1 min).

Acid-Catalyzed Reaction of R_3Si^*F with MeOH in the Presence of $Th(NO_3)_4$. To a 25-ml glass-stoppered flask were added R_3Si^*F (0.250 g, 0.940 mmol), thorium nitrate (1.30 g, 2.61 mmol), 10 ml of carbon tetrachloride, 8.6 ml of dry methanol, and 1.4 ml of a 1.45 *M* solution of hydrogen chloride in methanol. After mixing thoroughly, the resulting solution was allowed to stand for 90 min. At the end of the reaction period, the solution was diluted with ether (50 ml) and washed well with water, then dried over anhydrous sodium sulfate. Volatiles were removed at reduced pressure, the residue was dissolved in 2 ml of carbon tetrachloride, and an infrared spectrum was taken. Comparison of this spectrum with those of known mixtures showed the reaction product to consist of about 70% methoxysilane and 30% fluorosilane. Both were racemic.

Racemization of R_3Si^*F Catalyzed by *c*-$C_6H_{11}NH_3F$. Standard methanolic solutions of cyclohexylammonium fluoride were prepared. The variation of the pseudo-first-order rate constant for the racemization of (−)-fluorosilane (0.0470 *M*) at 24.4° in 5% methanol in carbon tetrachloride was studied as a function of cyclohexylammonium fluoride concentration.

Racemization of R_3Si^*F in ROH/CCl_4 Solvent Mixtures. In this series of experiments, the rate of racemization of (+)-fluorosilane (0.0470 *M*) was determined in mixtures of different alcohols in carbon tetrachloride at 24.4°, all at equivalent concentrations. The procedure was the same as that already described.

Stereochemistry of Asymmetric Silicon. XV. Stereospecific Hydrosilation and Exchange Reactions of $R_3Si^*H(D)$ Catalyzed by Group VIII Metal Centers[1,2]

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Abstract: The addition of R_3Si^*H to olefins (hydrosilation) catalyzed by transition metal centers proceeds with *retention* of configuration as do Si*H–Si*D isotopic-exchange reactions. The data are accommodated by the general mechanistic conclusion that the initial process in these reactions involves stereospecific *retentive* interaction of the Si*–H bond with the reactive transition metal center to form a metal–silicon bond which then reacts in a variety of ways with complete retention of configuration in hydrosilation and isotopic exchange reactions.

The first example of hydrosilation, addition of a silicon hydride to an olefin, involved reaction of trichlorosilane with 1-octene in the presence of diacetyl peroxide and was reported in 1947.[3] During the next two decades hydrosilation became an exceedingly important laboratory and industrial process, and it was discovered that platinum–charcoal and chloroplatinic acid are very effective catalysts.[4]

$$\equiv SiH + CH_2{=}CHR \xrightarrow[\text{or } H_2PtCl_6]{Pt\text{–}C} \equiv SiCH_2CH_2R \qquad (1)$$

Beginning with the observation that primary alkylsilanes often result from reactions involving nonterminal olefins, as in reaction 2,[5] Speier and coworkers have engaged in an intensive study of the mechanism of reactions 1.[6] This work revealed that platinum-catalyzed hydrosilation is often accompanied by olefin isomerization which is significantly altered by the presence of silane,[6a–c] and that hydrosilation carried out with Cl_3SiD results in extensive exchange between Si–D and C–H of the olefin plus the formation of adducts having deuterium widely distributed in their structures as in reaction 3.[6c] It was also demonstrated that the silicon–hydrogen bond is extremely labile in the presence of platinum[7] and chloroplatinic acid,[6c] resulting in SiH–SiD exchange at room temperature (4).

$$Cl_2(CH_3)SiH + CH_3CH{=}CHCH_2CH_3 \xrightarrow{H_2PtCl_6} CH_3(CH_2)_3CH_2Si(CH_3)Cl_2 \qquad (2)$$

$$3.56Cl_3SiD + CH_2{=}C(CH_3)_2 \xrightarrow{H_2PtCl_6} Cl_3SiC_4H_{6.5}D_{2.5} + 1.5Cl_3SiH + Cl_3SiD \qquad (3)$$

$$R_3SiD + R_3'SiH \underset{\text{or } H_2PtCl_6}{\overset{Pt\text{–}C}{\rightleftharpoons}} R_3SiH + R_3'SiD \qquad (4)$$

In a significant extension of the above studies, Chalk and Harrod[8] have reported that a Pt(II)–olefin complex, $((C_2H_4)PtCl_2)_2$, provides homogeneous catalysis of hydrosilation and concurrent olefin isomerization, and that the presence of silane markedly affects the olefin isomerization profile. It is also found[8] that the Pt(II)–olefin catalyst gave results very similar to those obtained with chloroplatinic acid. In addition, it was reported that a phosphine complex of iridium(I) cleaved a variety of

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[1] For the preceding paper in this series, see L. H. Sommer and D. L. Bauman, *J. Am. Chem. Soc.*, **91**, 7045 (1969).

[2] In its initial stages this work was supported by a grant from Dow Corning Corp. and carried out in part at the Pennsylvania State University.

[3] L. H. Sommer, E. W. Pietrusza, and F. C. Whitmore, *J. Am. Chem. Soc.*, **69**, 188 (1947).

[4] For an excellent review up to about 1959, see C. Eaborn, "Organosilicon Compounds," Academic Press, New York, N. Y., 1960, pp 45–64.

[5] J. L. Speier, J. A. Webster, and G. H. Barnes, *J. Am. Chem. Soc.*, **79**, 974 (1957).

[6] (a) J. L. Speier and J. C. Saam, *ibid.*, **80**, 4104 (1958); (b) *ibid.*, **83**, 1351 (1961); (c) J. W. Ryan and J. L. Speier, *ibid.*, **86**, 895 (1964); (d) M. C. Musolf and J. L. Speier, *J. Org. Chem.*, **29**, 2519 (1964); (e) J. W. Ryan and J. L. Speier, *ibid.*, **31**, 2698 (1966).

[7] V. A. Ponomarenko, *et al.*, *Dokl. Akad. Nauk SSSR*, **131**, 321 (1960).

[8] A. J. Chalk and J. F. Harrod, *J. Am. Chem. Soc.*, **87**, 16 (1965).