Reduction of VIII with LiAlH$_4$[5b] gave (+)-α-naphthylphenylmethylsilane, $[\alpha]_D$ +33° (*c* 2.1, pentane).

To establish that VII was formed exclusively, VIII and (+)-α-naphthylphenylmethyl-1-phenylethoxysilane (IX) were each prepared by the catalytic method in pentane, see Table I. The product formed from 2-phenylethanol and (−)R_3Si^*H was identical in every respect with the product of the styrene oxide cleavage. The product formed from 1-phenylethanol (IX), $[\alpha]_D$ +10.1 (*c* 6, cyclohexane), had the characteristic nmr spectrum of a 1:1 mixture of the diasteriomeric α-naphthylphenylmethyl-1-phenylethoxysilane[25] and was resolvable into (+)-α-naphthylphenylmethyl-(+)-1-phenylethoxysilane, $[\alpha]_D$ +49.2° (*c* 3.2, cyclohexane), mp 85°, (lit.[25] $[\alpha]_D$ +47.2°), and (+)-α-naphthylphenylmethyl-(−)-1-phenylethoxysilane, $[\alpha]_D$ −8.0° (*c* 3.0, cyclohexane), viscous oil. No attempt was made to resolve completely the (+, −) diasteriomer. Resolution was carried out by fractional crystallization from a 1:1 pentane–hexane solution.

Methanolysis of (+)R_3Si^*H Using an Exploded Wire Catalyst.[16] A reaction chamber was constructed from two vacuum desiccator bottoms sealed together with a rubber "O" ring. Large electrodes were implanted into the top section of the chamber and an outlet for connection to a vacuum line was built into the side of the vessel. Pure palladium wire 70 mg, No. 30 (California Fine Wire) was connected across the electrodes and was outgassed at red heat electrically with a chamber pressure of 10^{-4} mm for 12 hr. The wire was allowed to cool and pure argon, 650 mm, was then admitted to the system, and the chamber was closed off and removed from the vacuum line. The wire was exploded electrically[16,26] creating a dense black aerosol of palladium metal which settled to the bottom of the vessel after 2 hr. Argon was then admitted to the system until a chamber pressure of 800 mm was reached. A solution of 1.35 g of (+)R_3Si^*H, $[\alpha]_D$ +34.2 (*c* 2.1, pentane), in 14 ml of dry heptane was syringed into the vessel while an overpressure of argon was maintained. The mixture was magnetically stirred for 1 min and then 1.0 ml of dry methanol was injected into the reaction chamber. Bubbling started immediately and continued for 8 hr during which time the chamber pressure was relieved periodically. The reaction mixture was then filtered free of catalyst and solvent evaporated leaving white, crystalline (−)-α-naphthylphenylmethylmethoxysilane, 1.28 g (85% yield), $[\alpha]_D$ −17.1 (*c* 2.42, pentane).

Palladium(II) Chloride Catalyzed Reactions. a. Optically active (−)R_3Si^*H, $[\alpha]_D$ −35° (*c* 2.1, pentane), 0.54 g, was dissolved in 5.4 ml of dry pentane. A suspension of palladium(II) chloride, 6 mg, in 0.33 ml of methanol was syringed into the solution of silane. Rapid gas evolution occurred accompanied by precipitation of metallic palladium. Reaction was over in 3 min and the mixture was filtered free of palladium. Evaporation of pentane at reduced pressure yielded racemic α-naphthylphenylmethylmethoxysilane, 0.55 g (93% yield).

b. A saturated solution of palladium(II) chloride in methanol was prepared by stirring $PdCl_2 \cdot 2H_2O$, 20 mg, with 1 cc of methanol for 30 min and allowing the undissolved powder to settle on standing. Triethylamine, 20 μl, was added and 0.3 ml of the clear yellow supernate syringed into a stirred solution of 0.63 g of (−)R_3Si^*H in 6.3 ml of pentane. The solution remained homogeneous for 25 sec then palladium metal began to precipitate and hydrogen was evolved. Bubbling continued for 6.5 hr after which the reaction mixture was filtered and solvent removed. A total of 0.68 g (99% yield) of white, crystalline $R_3Si^*OCH_3$, $[\alpha]_D$ +16° (*c* 3.1, pentane), was isolated. The palladium metal, 0.4 mg, which was recovered from the reaction mixture was shown to be an active catalyst for the methanolysis of R_3Si^*H.

Reaction of Palladium(II) Chloride with R_3Si^*H. $PdCl_2$ powder (0.88 g, 0.05 mole) was added to a solution of (−)R_3Si^*H, $[\alpha]_D$ −35° (2.24 g, 0.09 mole), in 25 cc of dry pentane. The reaction mixture was stirred under dry nitrogen. Vigorous bubbling occurred and the red solid $PdCl_2$ was converted to the black metal. Bubbling ceased after 30 min and the reaction mixture was filtered and solvent evaporated at reduced pressure yielding white, crystalline α-NpPhMeSi*Cl, mp 62–64°, $[\alpha]_D$ −5.8° (*c* 10, cyclohexane).

Acknowledgments. We are extremely grateful to Dr. C. P. Nash and Mr. R. L. Musselman for the use of exploded wire equipment and for aid in the manipulation of the apparatus. Without their able assistance this experiment could not have been carried out.

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[25] A. G. Brook, C. M. Warner, and W. W. Limburg, *Can. J. Chem.*, **45**, 1231 (1967).

[26] The condenser bank used employed 28.4 μF at a voltage of 10 kV in a circuit having an inductance of 0.3 μH.

Stereochemistry of Asymmetric Silicon. XVII. Synthesis, Resolution, and Stereochemistry of the 1,2,2,2-Tetraphenyl-1-methyldisilane System[1-3]

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Abstract: An entirely new route to optically active functionally substituted organosilicon compounds has been developed, by which the 1,2,2,2-tetraphenyl-1-methyldisilane system has been synthesized and resolved. Whereas previously studied systems PhMeRSi*X (R = α-naphthyl, neopentyl, benzhydryl, or ethyl) have nonreacting groups bonded to asymmetric silicon *via* carbon atoms exclusively, the new system has a nonreacting group bonded to asymmetric silicon *via* a metalloid–metalloid linkage. Thus far, replacement of an organic R group in PhMeRSi*X by Ph_3Si has not resulted in a reversal of functional group stereochemistry, according to chemical evidence. This extends the validity of earlier stereochemical generalizations for R_3Si^*X, and reinforces their nondependence on the nature of the nonreacting groups.

The α-naphthyl systems (*i.e.*, the α-naphthylphenylmethylsilane system, α-NpPhMeSi*X) has afforded a practical route to other systems, where R equals benzhydryl, neopentyl, or ethyl, by the following method[4] (reactions 1–3). Conservation of optical activity has been shown to be very high in the above conversions,

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[1] For the preceding paper in this series, see L. H. Sommer and J. E. Lyons, *J. Am. Chem. Soc.*, **91**, 7061 (1969).

[2] For a preliminary communication, see L. H. Sommer and K. T. Rosborough, *ibid.*, **89**, 1756 (1967).

[3] We are pleased to acknowledge vital support of this work by the National Science Foundation.

[4] L. H. Sommer, K. W. Michael, and W. D. Korte, *J. Am. Chem. Soc.*, **89**, 868 (1967).

$$\alpha\text{-NpPhMeSi*Cl} + \text{RLi} \longrightarrow \alpha\text{-NpPhMeSi*R} \quad (1)$$

$$\alpha\text{-NpPhMeSi*R} + \text{Br}_2 \longrightarrow \text{PhMeRSi*Br} \quad (2)$$

$$\text{PhMeRSi*Br} + \text{LiAlH}_4 \longrightarrow \text{PhMeRSi*H} \quad (3)$$

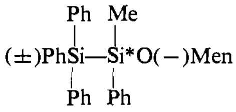
and yields are reasonable. The success of the conversion is dependent upon the R–Si bond being much less labile than the (α-Np)–Si bond (with respect to bromine cleavage), and upon the PhMeRSi*Br being optically stable under the reaction conditions.

By means similar to reaction 1, *non*functionally substituted optically active disilanes have been synthesized,[5,6] in reaction 4 (R = α-naphthyl or neopentyl).

$$\text{RPhMeSi*Cl} + \text{MePh}_2\text{SiLi} \longrightarrow \text{RPhMeSi*Si(Me)(Ph)}_2 + \text{LiCl} \quad (4)$$

Stereochemistry of the lithium cleavage of the silicon–silicon bond (where R = neopentyl) has been reported.[5] Reaction with Br_2 or BrCl gave nearly indiscriminate cleavage of the silicon–silicon bond and silicon–aryl bonds.[6] Thus, functionally substituted disilanes cannot be prepared by bromine cleavage of the (α-Np)–Si bond, although this procedure is successful in preparing the neopentyl, benzhydryl, and ethyl systems (*vide supra*). At present, there appears to be no practical route to optically active functionally substituted disilanes from previously known resolved systems.

In accord with this conclusion, the synthesis and resolution of a completely new system, (±)-1,2,2,2-tetraphenyl-1-methyl-1-(−)-menthoxydisilanes (I and II) was undertaken. The triphenylsilyl group, Ph_3Si, was chosen because (a) it provides a nonreacting (under proper conditions) group bonded to asymmetric silicon *via* an atom other than carbon, (b) the Ph_3Si group possesses crystallinity conferring properties (fractional crystallization is the most potent technique for resolving substantial quantities of optically pure stereoisomers), and (c) starting material triphenylchlorosilane, Ph_3SiCl, is commercially available. The phenyl and methyl groups were chosen because they are common to the more important previously known optically active monosilane systems, and therefore provide a valuable crossover relationship. Also a number of phenylmethylsilanes bearing two functional groups are commerically available or may be synthesized with a minimum of steps *via* known procedures. The (−)-menthoxy group, O(−)Men, is a logical choice since (−)-menthol was readily available in the laboratory for use as a resolving agent, and (−)-menthol had previously proved its effectiveness in the resolution of the α-NpPhMeSi*X system.[7]



$$(\pm)\mathrm{Ph}\underset{\mathrm{Ph}}{\overset{\mathrm{Ph}}{\mathrm{Si}}}—\underset{\mathrm{Ph}}{\overset{\mathrm{Me}}{\mathrm{Si}}}{}^{*}\mathrm{O}(-)\mathrm{Men}$$

I, II

The racemic disilane system (*i.e.*, the 1,2,2,2-tetraphenyl-1-methyldisilane system) was synthesized in good yield as follows.

$$\begin{tikzcd} \text{Ph}_3\text{SiCl} + \text{Li} \arrow[r, "\text{THF}"] & 0.5(\text{Ph}_3\text{Si})_2 + \text{LiCl} \arrow[d, "\text{THF}", "\text{Li}"'] \\ & \text{Ph}_3\text{SiLi} + \text{LiCl} \end{tikzcd} \quad (5)$$

$$\text{Ph}_3\text{SiLi} + (\pm)\text{PhMeSi*HCl} \xrightarrow{\text{THF}} (\pm)\text{Ph}_3\text{SiSi*H(Ph)(Me)} + \text{LiCl} \quad (6)$$

Triphenylsilyllithium, Ph_3SiLi, was prepared (5) in essentially quantitative yield by the action of lithium (high sodium content, ~2%) upon Ph_3SiCl in anhydrous tetrahydrofuran, THF, using the modified procedure of Gilman and coworkers.[8]

Phenylmethylchlorosilane, (±)PhMeSi*HCl was allowed to react with Ph_3SiLi (6), and racemic 1,2,2,2-tetraphenyl-1-methyldisilane, (±)Ph_3SiSi*H(Ph) (Me), mp 68–69°, was obtained.

Of primary concern at this point was to determine whether the new system, racemic Ph_3SiSi*X(Ph) (Me), could undergo displacement reactions at asymmetric silicon without suffering cleavage of the silicon–silicon bond. It was found that (±)Ph_3SiSi*H(Ph)(Me) could be chlorinated to form (±)Ph_3SiSi*Cl(Ph)(Me), which in turn could undergo facile hydrolysis or methanolysis. All of these reactions proceeded in high yield and without significant cleavage of the silicon–silicon bond. (Detailed discussion of these and other reactions is deferred until later.)

Effort was now devoted toward the preparation of diastereomeric derivatives of the new system. However, attempts to attach the (−)-menthoxy group (to asymmetric silicon of the new system) by procedures which worked well with the α-NpPhMeSi*X system or by other techniques failed without exception.[9] In order to attach a bulky resolving agent, such as the (−)-menthoxy group, to a system which is itself crowded, a considerable steric hindrance barrier must be overcome. However, the reaction conditions necessary to overcome this barrier also produced cleavage of the silicon–silicon bond.

At this point in the study, the principle of synthetic sequence was hypothesized, *i.e.*, that the resolving agent need not be the last group to be introduced to the asymmetric center. Practical application of this principle, however, required the development of an entirely new route to the system.

It was found that phenylmethyldichlorosilane, $PhMeSiCl_2$, was capable of undergoing *partial* alcoholysis by (−)-menthol in pentane (reaction 7), to give diastereomeric phenylmethyl-(−)-menthoxychlorosilanes, (±)-PhMeSi*O(−)Men(Cl), in good yield.[10] The HCl generated was removed in large part by a stream of nitrogen gas.

$$\text{PhMeSiCl}_2 + (-)\text{MenOH} \longrightarrow (\pm)\text{PhMeSi*O}(-)\text{Men(Cl)} \quad (7)$$

These diastereomeric chloromenthoxysilanes, bp 110° (0.1 Torr) are clear, colorless, freely flowing liquids with an acrid odor, stable under a dry, inert atmosphere. Although diastereomeric, and hence in theory resolvable, these bifunctional silanes are decidedly noncrys-

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[5] L. H. Sommer and R. Mason, *J. Am. Chem. Soc.*, **87**, 1619 (1965).

[6] R. Mason, Ph.D. Thesis, The Pennsylvania State University, 1966.

[7] L. H. Sommer, "Stereochemistry, Mechanism, and Silicon," McGraw-Hill Book Co., Inc., New York, N. Y., 1965.

[8] H. Gilman and H. J. S. Winkler, "Organometallic Chemistry," H. Zeiss, Ed., Reinhold Publishing Corp., New York, N. Y., 1960, Chapter 6.

[9] K. T. Rosborough, Ph.D. Thesis, The University of California at Davis, 1967.

[10] For a discussion of the partial alcoholysis of polyhalosilanes, see C. Eaborn, "Organosilicon Compounds," Butterworth and Co., Ltd., London, 1960, p 288.

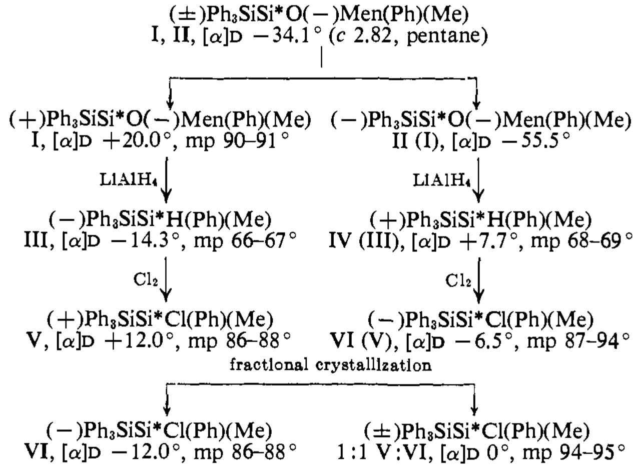
talline and no practical method has been found to separate them. When allowed to couple with $\mathrm{Ph_3SiLi}$ in THF, $(\pm)\mathrm{PhMeSi^*O(-)Men(Cl)}$ gives a high yield of $(\pm)$-1,2,2,2-tetraphenyl-1-methyl-1-$(-)$-menthoxydisilanes (I and II), bp 200° (0.2 Torr), reaction 8.

$$\mathrm{Ph_3SiLi} + (\pm)\mathrm{PhMeSi^*O(-)Men(Cl)} \xrightarrow{\mathrm{THF}} \underset{\text{I, II}}{(\pm)\mathrm{Ph_3SiSi^*O(-)Men(Ph)(Me)}} \tag{8}$$

Resolution of the syrupy mixture of diastereomers I and II was achieved *via* fractional crystallization from pentane and then hexane. The first resolution was achieved with some difficulty at −70°; however, once seed crystals of the higher melting diastereomer I, (+)-1,2,2,2-tetraphenyl-1-methyl-1-(−)-menthoxydisilane, mp 90–91°, $[\alpha]_{\mathrm{D}}$ +20.0° (*c* 2.0, pentane), were available, resolution could readily be achieved at −15°, or even slowly at room temperature. The other diastereomer II (containing some I) was obtained in lesser optical purity $[\alpha]_{\mathrm{D}}$ −55.5° (*c* 1.0, pentane) and has thus far resisted efforts at crystallization.

In the manner outlined in Scheme I, the diastereomeric relationship of I and II and the enantiomeric relationship of their derivatives have been clearly established. Where phase behavior permitted, recrystallization to constant melting point and rotation was taken as indication of optical purity. Thus identical melting points, infrared spectra, and equal but opposite in sign rotations of V and VI prove their enantiomeric relationship. Reactions and phase behavior pertinent to Scheme I are discussed later.

Scheme I. Resolution of 1,2,2,2-Tetraphenyl-1-methyldisilane System



All solid enantiomeric pairs of the α-naphthyl system α-$\mathrm{NpPhMeSi^*X}$, which have been examined in detail[11] appear to form racemic mixtures (X = H, Cl, F, and probably Br and OMe also). As a consequence of the solubility properties of racemic mixtures, optically pure derivatives of the α-naphthyl system are easily separable from partially racemic material.[12] The optically pure materials tends to crystallize out while the racemic material remains in solution.

Table I. Phase Behavior of $\mathrm{Ph_3SiSi^*X(Ph)(Me)}$ Derivatives

Derivative X	Mp, °C Optically pure	Mp, °C Racemic	Change[a]	Assignment[b]
H	66–67	68–69	Small	S.S
Cl	86–88	94–95[c]	Depression	R.C.
Br	63–66	80–83	Depression	R.C.
OH	85–87[d]	114–115	Depression	R.C.
OMe	74–76	73–74	Small	S.S.
OBz[e]		103–104		
α-Np		149–151[f]		
neo-$\mathrm{C_5H_{11}}$		Glassy		

[a] This refers to the change in melting point when a small amount of a pure enantiomeric component was added to the racemic material. [b] In the assignment of phase behavior, S.S. is solid solution; R.C., racemic compound. [c] Mixture melting point with $\mathrm{Ph_3SiCl}$ (lit. mp 97°, see ref 10, p 189) was depressed, 68–80°. [d] Mixture melting point with optically pure parent chlorodisilane was depressed, 66–80°. [e] OBz is the benzoxy group. [f] Mixture melting point with $\mathrm{Ph_3SiOH}$ (lit. mp, 150.5–151.5°, see ref 10, p 277) was depressed, 125–145°.

The phase behavior of derivatives of the disilane system, $\mathrm{Ph_3SiSi^*X(Ph)(Me)}$, is summarized in Table I. In contrast to the α-naphthyl system, which thus far has exhibited only racemic mixtures, the disilane system forms both solid solutions and racemic compounds. The 1,2,2,2-tetraphenyl-1-methyldisilanes, III and IV (see also Scheme I), being enantiomeric components of a solid solution, differ in melting points (hence, relative solubilities) only slightly in the racemic and optically active forms; therefore, fractional crystallization is futile. However, the 1,2,2,2-tetraphenyl-1-methyl-1-chlorodisilanes, V and VI, being enantiomeric components of a racemic compound, display in the optically active and racemic modifications different crystalline forms which may be separated mechanically by tweezers. However, starting with 100% racemic $\mathrm{Ph_3SiSi^*Cl(Ph)(Me)}$, crystals of the optically active form have not been obtained.

The (−)- and (+)-disilanols, IX and X, and the (+)- and (−)-bromodisilanes, VII and VIII, may be treated similarly to the above to obtain essentially optically pure enantiomers.

With the bromodisilanes, however, the process is difficult because of their sensitivity to racemization and hydrolysis, especially when in solution. The (−)- and (+)-methoxydisilanes, XI and XII, being enantiomeric components of a solid solution, do not lend themselves to the above treatment.

In general disilanes $\mathrm{Ph_3SiSi^*X(Ph)(Me)}$ undergo many displacement reactions (9) similar to those which have been reported[4,7,13–15] for monosilanes RPhMe-Si*X (where R = α-naphthyl, neopentyl, benzhydryl, or ethyl), thus allowing valuable comparisons to be made. Exceptions occur, however, in the cases of reagents or reaction conditions which are capable of cleaving the silicon–silicon bond in addition to displacing the leaving group X from asymmetric silicon (10).

The $\mathrm{LiAlH_4}$ reduction of I (see Scheme I) is surprisingly facile, requiring at most 20 hr of gentle reflux in ethyl ether (36°) to give III in 95% yield. Reduction of II to IV is equally facile. In contrast, the $\mathrm{LiAlH_4}$ reduction of (−)-α-$\mathrm{NpPhMeSi^*O(-)Men}$ to (+)-α-$\mathrm{NpPhMeSi^*H}$ in 90–96% yield requires 18 hr of heating

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(11) C. L. Frye, Ph.D. Thesis, The Pennsylvania State University, 1960.

(12) Reference 7, p 42.

(13) L. H. Sommer, G. A. Parker, N. C. Lloyd, C. L. Frye, and K. W. Michael, *J. Am. Chem. Soc.*, **89**, 857 (1967).

(14) L. H. Sommer, C. L. Frye, and G. A. Parker, *ibid.*, **86**, 3276 (1964).

(15) L. H. Sommer, C. L. Frye, G. A. Parker, and K. W. Michael, *ibid.*, **86**, 3271 (1964).

to 80–90° in a mixture of ethyl ether and di-*n*-butyl ether.[7,11,15] At lower temperatures the reduction of (−)-α-NpPhMeSi*O(−)Men is incomplete.[16] The mechanistic significance of this acceleration of rate will be discussed later.

The addition of chlorine to carbon tetrachloride solutions of III afforded nearly quantitative yields of (+)-$Ph_3SiSi^*Cl(Ph)(Me)$, IV, $[\alpha]_D$ +12.0° (ether), mp 86–88° (see Scheme I). The substitution of the H of the disilane is clearly favored over the cleavage of the silicon–silicon bond by chlorine.[17] The newly introduced negative substituent then protects the silicon–silicon bond against further attack by chlorine. Thus V or its enantiomer VI are recovered unreacted, with essentially no loss in optical activity, even after several hours' exposure to a multifold excess of chlorine in CCl_4 at room temperature.[18] When treated with $LiAlH_4$, the (+)-chlorodisilane V yielded (+)$Ph_3SiSi^*H(Ph)(Me)$, the optical purity of which attested to excellent stereospecificity of displacement in both the halogenation and the reduction. From the enantiomeric relationship of the reduction product to the starting disilane, it is obvious that one of the reactions has proceeded with at least 95% predominant inversion and the other with at least 95% predominant retention of configuration. For the method of calculation see ref 1.

The following sequence of reactions (9) constitutes the first Walden cycle to be observed for substitutions at asymmetric silicon in a disilane.

$$\begin{tikzcd}
\underset{\text{III}}{(-)Ph_3SiSi^*H(Ph)(Me)} \arrow[r, "Cl_2"] & \underset{\text{V}}{(+)Ph_3SiSi^*Cl(Ph)(Me)} \arrow[d, "LiAlH_4"] \\
\underset{\text{VI}}{(-)Ph_3SiSi^*Cl(Ph)(Me)} \arrow[u, "LiAlH_4"] & \underset{\text{IV}}{(+)Ph_3SiSi^*H(Ph)(Me)} \arrow[l, "Cl_2"']
\end{tikzcd} \qquad (9)$$

An assignment[19] of retention for halogenation and inversion for reduction is internally consistent and is in complete harmony with previous stereochemical principles[4,7,13–15] which have been found to apply to monosilanes RPhMeSi*X where R = α-naphthyl, benzhydryl, neopentyl, or ethyl. The chemical evidence strongly suggests that the chlorination of the disilane proceeds with retention of configuration *via* the (SNi–SEi)–Si mechanism.[20]

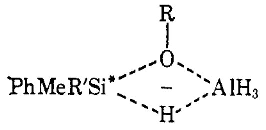
The stereochemistry of chlorination of III or IV is 95% predominant retention, which compares favorably with very clean retention for the above monosilanes.

The (SNi–SEi)–Si mechanism is also probably the predominant mechanism for the bromination of disilanes III and IV. The predominant stereochemistry here, however, is lowered to 73% retention, which compares poorly with very clean retention for bromination of monosilanes. Furthermore, some cleavage of the silicon–silicon bond is observed, although substitution of the H is still favored (in CCl_4 solution, and where local over-concentration of Br_2 is avoided). Nevertheless, VIII is recovered unreacted and without significant loss in optical activity when exposed to an excess of Br_2 in CCl_4 for several hours at room termperature. At the moment, the reasons for diminished stereospecificity in bromination are not clear.

The hydrolysis, methanolysis, and lithium aluminum hydride reduction of chloro- and bromomonosilanes PhMeRSi*X, where R = α-naphthyl, neopentyl, benzhydryl (also ethyl in the case of $LiAlH_4$ reduction), all proceed with highly stereospecific inversion of configuration and have been assigned the SN2–Si mechanism.[4,13] On the basis of similar highly stereospecific inversions under similar reaction conditions, for the chlorodisilanes V and VI, it seems entirely reasonable to assign the SN2–Si mechanism to their hydrolysis, methanolysis, and lithium aluminum hydride reduction. On the other hand, the predominant stereochemistries of these same reactions for the bromodisilanes VII and VIII are lowered into the range 70–74% inversion. It appears likely that the predominant mechanism is still SN2–Si, but a competing mechanism may be operative. Because of its greater size and polarizability it is possible that bromine relative to chlorine may be more capable of interacting with the nonasymmetric silicon center and that such interaction may lead to reaction mechanisms other than SN2–Si.

Analogous to the lithium aluminum hydride reductions of the methoxydisilane and the hydroxydisilane (both OMe and OH are poor leaving groups) which proceed with predominant retention of configuration, the reduction of the menthoxydisilanes I and II (OMen is also a poor leaving group) is thought to proceed with retention.

The SNi–Si mechanism is the most common mechanism for organosilicon reactions proceeding with retention of configuration.[7,14] Analogous to the reduction of monosilanes,[14] the lithium aluminum hydride reduction of $Ph_3SiSi^*OR(Ph)(Me)$, proceeding with retention of configuration, may be formulated as follows, where R′ = Ph_3Si.



Inspection of space-filling models shows clearly that the steric requirement of the triphenylsilyl, Ph_3Si, group is much greater than that of the α-naphthyl group (the proximity of the *peri* hydrogen to the asymmetric silicon center notwithstanding). This may explain why the reduction of $Ph_3SiSi^*O(-)Men(Ph)(Me)$ is much more facile than that of α-NpPhMeSi*O(−)Men. In the above formulation, where R′ = Ph_3Si, relief of steric strain as the bulky menthoxy group departs would be expected to be greater than for the case of R′ = α-Np.

No such accelerating effect has been observed in the reduction of the methoxydisilane, as compared with methoxymonosilanes. All of the optically active methoxysilanes known are reduced with comparative ease by lithium aluminum hydride. Continuing, for the time, to base the argument upon steric grounds, this may be explained by the small size of the methoxy group compared with the bulky menthoxy group. Thus for the methoxy group in the above formulation (R = Me) significant steric compression may not occur.

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(16) C. L. Frye, private communication.

(17) A similar observation has been made in the halogenation of simpler disilanes; see U. Stollberg, *Ber.*, **96**, 2798 (1963).

(18) Under similar conditions optically active α-NpPhMeSi*Cl undergoes chlorination of the α-Np group (without racemization of the asymmetric silicon center).[11]

(19) Determination of the absolute configuration of III or IV by X-ray methods is made very difficult, and has not been done, due to the presence of four molecules per unit cell, two molecules comprising one asymmetric unit.

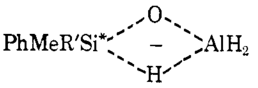
(20) Reference 7, p 109.

Table II. Summary of Stereochemistry for Optically Active $Ph_3SiSi^*X(Ph)(Me)$

Reactant	Reagent	Solvent	Product	Predominant stereochemistry[a]	Reference to parallel monosilane work
(−)H	Cl_2	CCl_4	(+)Cl	95% ret	
(−)H	Br_2	CCl_4	(+)Br	73% ret	15
(+)Cl	H_2O	Et_2O	(−)OH	87% inv	15
(+)Cl	$MeOH/Et_3N$	Pentane	(−)OMe	90% inv	15
(+)Cl	$LiAlH_4$	Et_2O	(+)H	95% inv	15
(+)Br	H_2O	Et_2O	(−)OMe	74% inv	15
(+)Br	$MeOH/Et_3N$	Pentane	(−)OH	70% inv	13
(+)Br	$LiAlH_4$	Et_2O	(+)H	73% inv	13
(−)OH	$LiAlH_4$	Et_2O	(+)H	87% ret	15
(−)OMe	$LiAlH_4$	Et_2O	(+)H	90% ret	15
(−)Cl	α-NpLi	Et_2O	(±)-α-Np	100% rac	4
(−)Cl	neo-$C_5H_{11}Li$	Et_2O	(±)-neo-C_5H_{11}	100% rac	4
(−)Cl	$C_6H_{11}NH_3^+OBz^{-b}$	$CHCl_3$	(±)OBz	100% rac	13
(−)Cl	$C_6H_{11}NH_3^+F^{-b}$	$CHCl_3$	(±)F	100% rac	13
(−)Cl	$C_6H_5NH_3^+OAc^{-b}$	$CHCl_3$	(±)OAc[c]	100% rac	13

[a] A predominant stereochemistry of, *e.g.*, 90% inversion means that the product was composed of 90% inverted and 10% retained material and had an optical purity of 80%. For an explicit definition, see L. H. Sommer, J. D. Citron, and G. A. Parker, *J. Am. Chem. Soc.*, **91**, 4729 (1969). [b] C_6H_{11} is cyclohexyl. [c] (±)OH was a major by-product.

However, the above steric argument may fail to explain why optically active hydroxydisilanes ($R' = Ph_3Si$) are reduced by lithium aluminum hydride much more readily than the optically active monosilanols (R' = α-naphthyl, neopentyl, and benzhydryl).[21] For the special case where R = H, reduction with retention probably involves[14]



$$PhMeR'Si^{*}\langle{}^{O}_{H}\rangle AlH_2$$

Here there is no bulky alkoxy group whose departure might provide release of steric strain, and hence display a sensitivity to the size of R′.

An alternative possibility (perhaps acting in combination with a steric effect) is that an electronic effect of the Ph_3Si group (possibly resulting from d_π–d_π interaction between the adjacent Si atoms) facilitates formation of quasi-cyclic negatively charged formulations such as the above, and thereby lowers the energy barrier to reaction.

Whereas optically active chloromonosilanes $PhMeRSi^*Cl$ readily couple with a variety of organolithium reagents $R'Li$ to give optically active $PhMeRSi^*R'$ (reaction 10),[22] *e.g.*, R = α-Np, R′ = neoC_5H_{11}, or

$$RPhMeSi^*Cl + R'Li \longrightarrow RPhMeSi^*R' + LiCl \qquad (10)$$

vice versa, optically active chlorodisilanes V or VI ($R = Ph_3Si$) react slowly (R' = α-Np or neo-C_5H_{11}) and yield essentially racemic hexaorganodisilanes.

Apparently the rate of racemization of the chlorodisilane in ether in the presence of lithium chloride is much faster than the coupling of the chlorodisilane with R′Li. Less attractive alternatives are that the hexaorganodisilane products racemize,[23] or that the coupling reactions are nonstereospecific. The rapid racemization of $Ph_3SiSi^*Cl(Ph)(Me)$ in the presence of cyclohexylammonium salts (*vide infra*) has also been observed under conditions in which chloromonosilanes $RPhMeSi^*Cl$ (R = α-naphthyl, neopentyl, or benzhydryl) racemize much more slowly, if at all. It has been shown that chloromonosilanes can react with cyclohexylammonium salts with predominant inversion of configuration by an SN2-Si mechanism,[24] and it has been proposed that racemization by an SN1-Si mechanism takes place when the anionic component of the salt is less basic and less nucleophilic (for asymmetric silicon) than chlorine.[25,26]

We are presently undertaking the study of the racemization mechanism of halodisilanes by kinetic techniques, including chloride–radiochloride exchange, analogous to extensive studies of halomonosilanes.[25,27–31] Most of the dynamic stereochemistry of the disilane system is summarized in Table II. Despite certain differences in rates, thus far stereospecific replacement of an organic R group in $PhMeRSi^*X$ by Ph_3Si has not resulted in a reversal of functional group stereochemistry, according to the chemical evidence (although the tendency to obtain racemic products is certainly more marked with the disilane system due to factors not yet clear).

Table II extends the validity of earlier stereochemical generalizations[7] and their nondependence on the nature of the nonreacting groups.

Confirmation of Stereochemical Assignments. Stereochemistry Crossover for the Disilane Fluoride.[32] The foregoing stereochemical assignments of predominant stereochemical path were based primarily on two factors: (a) assignments consistent with past work hold

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(21) The reduction of disilanol IX is complete (92% yield) using excess $LiAlH_4$ in refluxing ethyl ether (pot temperature 36°) after 23 hr. In contrast, the reduction of monosilanols $RPhMeSi^*OH$ calls for excess $LiAlH_4$ in a mixture of di-*n*-butyl ether and ethyl ether, at over 100°.[4,15]

(22) L. H. Sommer, W. D. Korte, and P. G. Rodewald, *J. Am. Chem. Soc.*, **89**, 862 (1967).

(23) Other studies indicate that hexaorganodisilanes are optically stable under reaction conditions similar to 11.[6] See reaction 4.

(24) Reference 7, Chapter 4.

(25) L. H. Sommer, F. O. Stark, and K. W. Michael, *J. Am. Chem. Soc.*, **86**, 5683 (1964).

(26) Reference 7, p 178.

(27) G. A. Parker, Ph.D. Thesis, The Pennsylvania State University, 1963.

(28) L. H. Sommer, G. A. Parker, and C. L. Frye, *J. Am. Chem. Soc.*, **86**, 3280 (1964).

(29) F. O. Stark, Ph.D. Thesis, The Pennsylvania State University, 1962.

(30) K. W. Michael, Ph.D. Thesis, The Pennsylvania State University, 1963.

(31) D. L. Bauman, Ph.D. Thesis, The University of California at Davis, 1967.

(32) Work recently performed in this laboratory by Jerome McLick.

for *all* of the reactions in Table II and give over-all internal consistency; (b) the SN2-Si stereochemistry rule of inversion of configuration for good leaving groups. Nevertheless, a third criterion was desirable, is presented in this paper, and confirms again the general conclusion that replacement of organic R on Si* by $\mathrm{Ph_3Si}$ has basically left stereochemistry unchanged. The criterion used here is stereochemistry crossover (change from inversion to retention or *vice versa*) for the reduction of the fluorosilane with change in the reducing agent.

The optically active fluorosilane was prepared from I and $\mathrm{BF_3}$ in pentane, a reaction known to proceed with inversion of configuration with other alkoxysilanes.[33]

$$\underset{[\alpha]\mathrm{D}\ +19.9^\circ}{(+)\mathrm{Ph_3SiSi^*O(-)Men(Ph)(Me)}} \xrightarrow[\text{inversion}]{\mathrm{BF_3\cdot pentane}} \underset{[\alpha]\mathrm{D}\ -8.6^\circ}{(-)\mathrm{Ph_3SiSi^*F(Ph)(Me)}} \quad (11)$$

The product from (11) was reduced with lithium aluminum hydride, a reaction known to proceed with *inversion* of configuration with other fluorosilanes.[4]

$$\underset{[\alpha]\mathrm{D}\ -8.6^\circ}{(-)\mathrm{Ph_3SiSi^*F(Ph)(Me)}} \xrightarrow[\text{inversion}]{\mathrm{LiAlH_4}} \underset{[\alpha]\mathrm{D}\ -14.2^\circ}{(-)\mathrm{Ph_3SiSi^*H(Ph)(Me)}} \quad (12)$$

The formulation of (12) as proceeding with *inversion* is enormously strengthened by the demonstration, in this work, of stereochemistry crossover to *retention* of configuration with diisobutylaluminum hydride in hexane solvent, a reagent which has been shown to give *retention* of configuration with α-NpPhMeSi*F.[34] Since

$$\underset{[\alpha]\mathrm{D}\ -8.6^\circ}{(-)\mathrm{Ph_3SiSi^*F(Ph)(Me)}} \xrightarrow[\text{hexane}]{i\text{-}\mathrm{Bu_2AlH}} \underset{[\alpha]\mathrm{D}\ +12.4^\circ}{(+)\mathrm{Ph_3SiSi^*H(Ph)(Me)}} \quad (13)$$

(12) and (13) obviously pursue opposite stereochemical paths the choice (in view of precedent based on previous work) of *inversion* for (12) and retention for (13) is clear and firm. Thus, with reactions 11, 12, and 13 we have demonstrated a consistency with earlier work which is certainly beyond the limits of reasonable coincidence. We feel that (11), (12), and (13) help greatly to anchor our stereochemical assignments. For the latter purpose, physical methods, specifically ORD and CD curves, have been used, but they require extremely cautious interpretation because of complexities which will be dealt with in a future paper.

Experimental Section[35]

Preparation of Triphenylsilyllithium. A modified procedure of Gilman[8] was used. A 1000-ml Grignard flask with a stop-cocked bottom outlet was employed with a mechanical stirrer, condenser, nitrogen inlet, and a pressure-equalizing addition funnel. In the flask was placed 100 ml of dry tetrahydrofuran (THF), *freshly* distilled from $\mathrm{LiAlH_4}$, and, under nitrogen, 150 cm (approximately 6.0 g, 0.86 g-atom) of hexane-rinsed lithium wire (high sodium content, ~2%) was cut into 1-cm pieces and added to the flask. Triphenylchlorosilane, 95.0 g (0.322 mole) in 200 ml of THF, was added dropwise, with stirring, to the flask at such a rate that the reaction mixture became only slightly warm. During the course of the addition, a white precipitate of hexaphenyldisilane formed which later dissolved with reaction. Total time of addition was 4 hr. Rapid stirring was continued overnight, giving a dark black-brown solution free of solid, with the exception of unreacted excess lithium. Titration of a hydrolyzed 1.00-ml aliquot indicated an essentially quantitative yield of triphenylsilyllithium, and the 1.07 *N* solution was then used immediately.

Preparation of Racemic 1,2,2,2-Tetraphenyl-1-methyldisilane. A 1000-ml, three-necked flask was fitted with the Grignard flask (described in the previous experiment) containing 320 ml of a 1.07 *N* solution (0.322 mole) of triphenylsilyllithium in THF, a magnetic stirrer, a condenser, a nitrogen inlet, an ice bath, and thermometer. The reaction flask and the Grignard flask were connected with a length of rubber tubing to allow equalization of nitrogen pressure. In the reaction flask was placed 52.82 g (0.338 mole) of phenylmethylchlorosilane dissolved in 100 ml of dry THF. Dropwise addition of the lithium reagent solution was commenced with stirring. Each drop of the black-brown lithium reagent solution was rapidly decolorized as it came into contact with the chlorosilane solution. With a flask temperature of 10–20°, total time of addition was 2 hr. The reaction mixture was worked up by shaking with 300 ml of pentane, 250 ml of cool distilled water, and 20 ml of concentrated hydrochloric acid in a 1-l. separatory funnel. The organic layer was then washed with five portions of water until neutral, dried over anhydrous sodium sulfate, and then stripped of solvent, yielding a sticky pale yellow solid. Distillation on the spinning band gave 90.0 g (79.0%) of a clear, colorless viscous liquid, bp 180–190° (~0.2 Torr), which was taken as racemic 1,2,2,2-tetraphenyl-1-methyldisilane. After recrystallization from hexane, this material melted at 68–69°. The infrared spectrum of the product was essentially identical with that of subsequently isolated authentic (–)-1,2,2,2-tetraphenyl-1-methyldisilane.

Preparation of Diastereomeric Phenylmethyl-(–)-menthoxychlorosilanes. A 1-l. suction flask was fitted with a two-hole rubber stopper, a 500-ml pressure-equalizing addition funnel, a magnetic stirrer, and a 4-mm diameter glass tube (for the inlet of nitrogen) which reached nearly to the bottom of the flask. In the flask was placed a solution of 142.7 g (0.746 mole) of phenylmethyldichlorosilane dissolved in 250 ml of purified pentane. The solution was saturated with nitrogen *via* gentle bubbling through the inlet tube. In the addition funnel was placed 117.0 g (0.746 mole) of (–)-menthol dissolved in 250 ml of pentane, and this solution was added dropwise to the chlorosilane solution with vigorous stirring and flushing with nitrogen (to remove hydrogen chloride as it formed). During the total addition time of 15 min, the reaction mixture was kept below room temperature by the evaporation of pentane solvent. Nitrogen flushing was continued for several minutes, and then residual hydrogen chloride and solvent were removed by an aspirator overnight. The crude product was then subjected to a vacuum of less than 1 Torr for 1 day. There remained 232 g (100%) of a clear, pale yellow, freely flowing liquid with a biting odor. Distillation on the spinning band gave a small forerun of phenylmethyldichlorosilane, and a large middle cut of 191.8 g (82.6%) of diastereomeric phenylmethyl-(–)-menthoxychlorosilanes, bp 110° (0.1 Torr), [α]D –53.2° (*c* 8.54, pentane), a clear, colorless, freely flowing liquid with an acrid odor. A final cut weighing 30.0 g was a clear, colorless, odorless liquid, which on the basis of its infrared spectrum appeared to be phenylmethyldi-(–)-menthoxysilane. Major identifying infrared absorption bands of the desired product are as follows (cm^{-1}): $\mathrm{C_{10}H_{19}O}$–Si—2950, 2900, 1450, 1370, 1175, 1080, 1070, 1050, 1000, 950, and 875; $\mathrm{C_6H_5}$–Si—3060, 3050, 1430, 1140, and 700; $\mathrm{CH_3}$–Si—1250.

Anal. Calcd for $\mathrm{C_{17}H_{27}OClSi}$: C, 65.66; H, 8.75; Cl, 11.40. Found: C, 65.84; H, 8.68; Cl, 11.66.

Preparation of Diastereomeric 1,2,2,2-Tetraphenyl-1-methyl-1-(–)-menthoxydisilanes. 1. Preparation of the Syrupy Mixture of Diastereomers. A 1000-ml, three-necked, round-bottomed flask was fitted as for the preparation of racemic 1,2,2,2-tetraphenyl-1-methyldisilane, except that the Grignard flask contained 350 ml (0.187 mole) of a freshly prepared 0.535 *N* solution of triphenylsilyllithium in THF. In the reaction flask was placed 58.2 g (0.187 mole) of diastereomeric phenylmethyl-(–)-menthoxychlorosilanes dissolved in 100 ml of dry THF. In an atmosphere of nitrogen, the lithium reagent solution was added dropwise with stirring to the chlorosilane solution. The lithium reagent solution was rapidly decolorized as it mixed with the chlorosilane solution. The exothermic reaction was cooled by an ice–water bath. Total addition time was 2 hr. At this point, the reaction mixture was cloudy tan

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(33) See Table II, footnote *a*.

(34) Recent work of L. H. Sommer and J. McLick in this laboratory, to be published.

(35) Analyses by the Analytical Laboratory, University of California at Berkeley, and Galbraith Laboratories. Melting points are uncorrected. (a) "Handbook of Chemistry and Physics," 35th ed, C. D. Hodgman, R. C. Weast, and C. W. Wallace, Ed., Chemical Rubber Publishing Co., Cleveland, Ohio, 1953.

in appearance, and it was worked up using pentane and dilute hydrochloric acid, then washed to neutrality, and dried over sodium sulfate. Removal of solvent from the dry organic solution by aspirator and vacuum pump left a pale yellow viscous liquid weighing 95.0 g, representing a crude yield of 95%. Distillation on the spinning band gave 73.4 g (73.4%) of a clear, colorless, extremely viscous syrupy liquid, bp 195–200° (0.2 Torr), [α]D −34.1° (*c* 2.82, pentane), taken as diastereomeric 1,2,2,2-tetraphenyl-1-methyl-1-(−)-menthoxydisilane. The infrared spectrum of this product was virtually identical with that of the subsequently isolated authentic (+)-1,2,2,2-tetraphenyl-1-methyl-1-(−)-menthoxydisilane.

2. Isolation of (+)-1,2,2,2-Tetraphenyl-1-methyl-1-(−)-menthoxydisilane from the Syrupy Mixture of Diastereomers. Of the above syrupy mixture of diastereomers, 73.3 g was dissolved in 120 ml of purified pentane. The first crystals were obtained with difficulty at −70° using a Dry Ice–acetone bath. However, once a few seed crystals were available, fractional crystallization occurred readily at −15° or even slowly at room temperature. This particular batch deposited at −15° 29.1 g of crude crystals, mp 81–88°, [α]D +9.0° (*c* 1.0 pentane). Recrystallization from hexane raised these values to unchanging maxima of mp 90–91° and [α]D +20.0° (*c* 2.0, pentane). This sharply melting crystalline material was taken as pure (+)-1,2,2,2-tetraphenyl-1-methyl-1-(−)-menthoxydisilane.

Anal. Calcd for $C_{35}H_{42}OSi_2$: C, 78.59; H, 7.92. Found: C, 78.51; H, 7.81.

The infrared spectrum of this compound had absorption bands characteristic of $C_{10}H_{19}O$–Si, C_6H_5–Si, and CH_3–Si (*vide supra*).

Removal of solvent from the mother liquor remaining after filtration of the first crop of crude (+)-1,2,2,2-tetraphenyl-1-methyl-1-(−)-menthoxydisilane left in lesser optical purity (−)-1,2,2,2-tetraphenyl-1-methyl-1-(−)-menthoxydisilane, [α]D −55.5° (*c* 1.0, pentane), a clear, colorless, viscous liquid which has resisted, thus far, efforts toward crystallization. The infrared spectrum of this material was virtually identical with that of authentic (+)-1,2,2,2-tetraphenyl-1-methyl-1-(−)-menthoxydisilane.

Preparation of (−)- and (+)-1,2,2,2-Tetraphenyl-1-methyldisilane. To a 500-ml flask containing a mixture of 4.0 g (0.105 mole) of lithium aluminum hydride in 75 ml of dry ethyl ether was added rapidly 17.55 g (0.0328 mole) of (+)-1,2,2,2-tetraphenyl-1-methyl-1-(−)-menthoxydisilane, mp 90–91°, [α]D +20.0° (pentane), dissolved in 100 ml of dry ethyl ether. The reaction mixture was heated to gentle reflux (pot temperature 36°) with stirring for 24 hr. After cooling and addition of 100 ml of hexane, excess hydride was destroyed by addition of acetone with stirring, followed by work-up with cold dilute HCl, and subsequent washing to neutrality. After drying with sodium sulfate, the solvent was stripped off and there remained about 15.9 g of white crystals smelling strongly of menthol. Vacuum sublimation (70–75° at ~1 Torr for 24 hr) removed most of the (−)-menthol, mp 42–43° (lit.[35a] 42.5°). The remainder of the menthol was removed by chromatography over an 18 in. × 0.5 in. column of silica gel. The column was first washed with 50 ml of eluent (1:1 pentane-benzene by volume), then the crude product dissolved in 50 ml of eluent was loaded onto the column, followed by six successive 50-ml portions of eluent. From the first four cuts, totalling about 200 ml, 11.90 g (95.0%) of a white solid, mp 66–70°, [α]D −14.3° (*c* 4.2, pentane), was obtained after removal of solvent under reduced pressure, and was pure (+)-1,2,2,2-tetraphenyl-1-methyldisilane. The specific rotation and melting point of this material were unaffected by recrystallization from hexane.

Anal. Calcd for $C_{25}H_{24}Si_2$: C, 78.88; H, 6.36. Found: C, 78.62; H, 6.25.

Since this compound may be regarded as the "parent compound" of the system, the major infrared absorption bands are detailed below (cm^{-1}): C_6H_5–Si—3070, 3050, 1430, 1110, 700; CH_3–Si: 1250 and Si–H, 2100.

In the same manner as described above, (−)-1,2,2,2-tetraphenyl-1-methyl-1-(−)-menthoxydisilane was reduced to give in 96% yield (+)-1,2,2,2-tetraphenyl-1-methyldisilane, mp 68–69°, [α]D +7.7° (*c* 4.0, pentane). The lower magnitude of rotation of this product reflects the lower diastereomeric purity of the parent compound. The melting point and specific rotation of this material were unaffected by recrystallization from hexane. The infrared spectrum of this material was essentially identical with that of enantiomeric authentic (−)-1,2,2,2-tetraphenyl-1-methyldisilane.

When small amounts of either enantiomer were added to racemic 1,2,2,2-tetraphenyl-1-methyldisilane, mp 68–69°, the melting point range was depressed less than 1 deg.

Halogenation of 1,2,2,2-Tetraphenyl-1-methyldisilanes. 1. Chlorination. A polarimeter tube of 30-ml volume and 2.50-dm path length was fitted with a gas inlet tube at one end and vented through a calcium chloride drying tube at the other end. To the polarimeter tube was added a solution of 1.006 g (2.64 mmoles) of (−)-1,2,2,2-tetraphenyl-1-methyldisilane, mp 66–67°, [α]D −14.3° (pentane), in purified carbon tetrachloride, made up to a volume of 25.0 ml. The compound had [α]D −12.6° in CCl_4. Dry chlorine gas was then passed through the tube, with an occasional pause to take a reading. The observed rotation changed from negative to positive and climbed to a constant positive value, at which time there was appearance of a faint yellowish color (indicative of excess chlorine) at the end of the mildly exothermic reaction. The rotation of the chlorodisilane was then determined, [α]D +8.4° (*c* 4.4, CCl_4), assuming a quantitative yield. Normally, the product was isolated at this point by quantitatively transferring the solution to a 125-ml suction flask and removing volatiles at reduced pressure, affording after crystallization from hexane pure (+)-1,2,2,2-tetraphenyl-1-methyl-1-chlorodisilane (1.05 g, 95% yield). However, in one experiment a multifold excess of chlorine gas was passed through the polarimeter tube and the intensely yellow solution was allowed to stand for several hours at room temperature. There was no change in observed rotation. The chlorodisilane product was isolated as before and its melting point and infrared spectrum were found to be essentially identical with that of the authentic material. Later preparations of optically active chlorodisilane were carried out in a suction flask fitted with a gas inlet tube and vented through a calcium chloride drying tube and gave consistent results. Authentic (+)-1,2,2,2-tetraphenyl-1-methyl-1-chlorodisilane has mp 86–88°, [α]D +12.0° (*c* 4.1, ether), [α]D +13.2° (*c* 4.0, hexane). These values were unchanged by recrystallization.

Anal. Calcd for $C_{25}H_{23}ClSi_2$: C, 72.34; H, 5.58; Cl, 8.54. Found: C, 72.38; H, 5.43; Cl, 8.67.

The chlorination of (+)-1,2,2,2-tetraphenyl-1-methyldisilane, mp 68–69°, [α]D +7.7° (*c* 4.0, pentane), was carried out by similar procedures to give crude (−)-1,2,2,2-tetraphenyl-1-methyl-1-chlorodisilane, mp ~87–94°, [α]D −6.5° (*c* 4.0, ether). Fractional crystallization (see Scheme I) of this material from hot hexane solution first deposited small dense clumps of needle-like crystals (arbitrarily called the α form) and then more slowly on top of these clumps, crystals with well-formed faces (β form). Each crystalline aggregate (α form and β form) was only a few millimeters in diameter, but with tweezers and sufficient patience the α form and the β form can be picked apart in sufficient quantity to take melting points and rotations. From the first separation, the α form had mp 93–95°, [α]D −2.1° (*c* 3.3, pentane), and the β form had mp 89–93°, [α]D −9.3° (*c* 3.2, pentane). Repeated fractional crystallization and mechanical separation eventually gave essentially complete separation of (−)-1,2,2,2-tetraphenyl-1-methyl-1-chlorodisilane, mp 86–88°, [α]D −12.0° (*c* 4.0, ether), from racemic or (±)-1,2,2,2-tetraphenyl-1-methyl-1-chlorodisilanes, mp 94–95°, [α]D 0°.

The racemic material and the (−) enantiomer have infrared spectra essentially identical with that of the authentic (+)-1,2,2,2-tetraphenyl-1-methyl-1-chlorodisilane. Absence of starting material is shown by transparency at 2100 cm^{-1}. Lack of hydrolysis is shown by transparency at 3100–3600 and 1050 cm^{-1}. The Si–Cl absorption band occurs at 520 cm^{-1} in related chloromonosilanes. The chlorodisilane has an absorption at 555 cm^{-1} which may be Si–Cl or C_6H_5–Si.

2. Bromination. To the polarimeter tube fitted for gaseous reagents (previously described) was added a solution (25.0 ml) of (−)-1,2,2,2-tetraphenyl-1-methyldisilane (1.1755 g, 3.08 mmoles), mp 66–67°, [α]D −14.3° (*c* 4.0, pentane), in purified carbon tetrachloride. Bromine vapor (use of Br_2/CCl_4 solution cleaves Si–Si) was slowly swept into the solution from a 125-ml suction flask fitted with a nitrogen inlet tube and a glass outlet tube connected by a very short piece of rubber tubing to the gas inlet tube of the polarimeter tube. The ensuing mildly exothermic reaction caused rapid depletion of the bromine color. The observed rotation gradually changed from negative to positive and a constant positive value was reached when the red-orange color of the bromine no longer faded, indicating the presence of an excess of bromine. The product was isolated at this point by quantitatively transferring the contents of the polarimeter tube into a 125-ml suction flask and removing volatiles under reduced pressures. The crude product weighed 1.327 g (94.0% yield). Crystallization from pentane at −20° aided by a minute seed of the (+)-chlorodisilane gave (+)-1,2,2,2-tetraphenyl-1-methyl-1-bromodisilane, [α]D +9.8° (*c* 4.0, ether), mp 63–66°, separable from a lesser amount of the racemic bromodisilane, mp 80–83°. Another experiment, similar to that described above for chlorination, indicated that the product was not affected by the presence of excess bromine for several hours.

Slow addition of bromine vapor was required to avoid local over concentrations of Br_2 and consequent cleavage of the Si–Si bond.

The infrared spectrum of the product had an absorption band at 420 cm^{-1} which may be Si–Br (however, C_6H_5–Si in this system may also appear in this region). This band is very close to that of 425 cm^{-1}, reported for Si–Br in related monosilanes. Absence of starting material was shown by transparency at 2100 cm^{-1}. Lack of hydrolysis was shown by transparency at 3100–3600 and 1050 cm^{-1}.

Anal. Calcd for $C_{25}H_{23}BrSi_2$: C, 65.34; H, 5.04; Br, 17.39 Found: C, 65.55; H, 4.92; Br, 17.28.

Hydrolysis of 1,2,2,2-Tetraphenyl-1-methyl-1-halodisilanes. 1. 1,2,2,2-Tetraphenyl-1-methyl-1-chlorodisilanes. In a 250-ml separatory funnel was placed 50 ml of cool distilled water. To this was added all at once 3.10 g (7.48 mmoles) of (+)-1,2,2,2-tetraphenyl-1-methyl-1-chlorodisilane, mp 86–88°, $[\alpha]_D$ +12.0° (*c* 4.0, ether), dissolved in 75 ml of ethyl ether. After thorough shaking for about 2 min, the acidic aqueous layer was drained off and the organic layer was washed with five 25-ml portions of cool distilled water. The washes continued to be weakly acidic, so 50 ml of purified hexane was added. The organic layer was washed with three additional 25-ml portions of water, and the final wash was neutral to pH paper. The clear, colorless organic liquid was dried over anhydrous potassium carbonate overnight. The solution was filtered and solvent removed under reduced pressure, leaving a crude crystalline product weighing 2.88 g (97.5%), mp 83–86°, with a slight opacity persisting in the melt up to about 95–100°, $[\alpha]_D$ −9.8° (*c* 4.2, ether). The crude product was dissolved in 35 ml of ether and filtered through quantitative paper. The ether solution failed to deposit crystals even at −70°, so 50 ml of purified hexane was added and the ether was boiled off. The hexane solution was allowed to cool to room temperature, whereupon it deposited white crystals taken as (−)-1,2,2,2-tetraphenyl-1-methyldisilanol, mp 85–87°, $[\alpha]_D$ −9.8° (*c* 4.2, ether). The mixture melting point with the optically pure parent (+)-chlorodisilane was depressed, 68–80°. The product was characterized by O–H absorption bands in the infrared spectrum at 3670, 3580, and 3430 cm^{-1}. Absence of Si–O–Si was indicated by transparency at 1050 cm^{-1}.

Anal. Calcd for $C_{25}H_{24}OSi_2$: C, 75.70; H, 6.10. Found: C, 75.51; H, 6.14.

2. 1,2,2,2-Tetraphenyl-1-methyl-1-bromodisilanes. A solution of 1.247 g (2.70 mmoles) of (−)-1,2,2,2-tetraphenyl-1-methyl-1-bromodisilane, $[\alpha]_D$ −4.5° (*c* 5.0, ether), was prepared in 45 ml of ether, and the solution was added all at once to 75 ml of cool distilled water in a 250-ml separatory funnel, and shaken thoroughly for 1–2 min. The acidic aqueous layer was drained off and the organic layer was washed with 25 ml of cool distilled water. The organic layer was diluted with 20 ml of purified hexane and washed with an additional three 25-ml portions of cool distilled water. The last water wash was neutral to pH paper. The organic solution was dried over anhydrous sodium sulfate overnight, filtered, and volatiles were removed under reduced pressure. There remained a pale yellow viscous liquid weighing 1.019 g (93.5% yield), $[\alpha]_D$ +2.9° (*c* 4.08, ether), which was taken as (+)-1,2,2,2-tetraphenyl-1-methyldisilanol. The infrared spectrum confirmed the structure. To the above ether solution (for the polarimeter) was added 20 ml of purified hexane and the ether was boiled off on the steam bath. Overnight at room temperature the hexane solution deposited white crystals, mp 100–113°, hydroxydisilane of low optical purity. A small amount of material was also identified as triphenylsilanol on the basis of its melting point range.

Methanolysis of 1,2,2,2-Tetraphenyl-1-methyl-1-halodisilanes. 1. 1,2,2,2-Tetraphenyl-1-methyl-1-chlorodisilanes. (+)-1,2,2,2-Tetraphenyl-1-methyl-1-chlorodisilane (1.664 g, 4.01 mmoles) was dissolved with heating in 50 ml of purified pentane. This pentane solution was added all at once to a solution of 2.0 ml (50 mmoles) of purified methanol and 2.0 ml (14 mmoles) of purified triethylamine in 25 ml of purified pentane in a 125-ml erlenmeyer flask with swirling. A copious white precipitate appeared almost immediately. The reaction mixture was swirled for 2 min and then washed with 50 ml of cool distilled water in a 250-ml separatory funnel. The moderately basic aqueous layer was drained off, and the organic layer was washed with 50 ml of dilute hydrochloric acid, followed by three 25-ml portions of distilled water. The final water wash was neutral to pH paper. The clear colorless organic solution was dried with anhydrous sodium sulfate and then the solvent was removed under reduced pressure. There remained 1.549 g (94.2%) of pale yellowish white crude crystals, mp 74–76°, $[\alpha]_D$ −26.3° (*c* 4.2, pentane). Crystallization from hexane gave white crystals, mp 74–76°, $[\alpha]_D$ −27.0° (*c* 4.0, pentane). These values were unchanged by recrystallization. The product, (−)-1,2,2,2-tetraphenyl-1-methyl-1-methoxydisilane, was characterized by infrared absorption at 2950, 2930, 2820, 1180, and 1070 cm^{-1}, attributed to the CH_3–O–Si moiety.

Anal. Calcd for $C_{26}H_{26}OSi_2$: C, 76.04; H, 6.38. Found: C, 75.38; H, 6.38.

2. 1,2,2,2-Tetraphenyl-1-methyl-1-bromodisilanes. A solution containing 3.47 mmoles of (−)-1,2,2,2-tetraphenyl-1-methyl-1-bromodisilane, $[\alpha]_D$ −4.7° (*c* 6.4, pentane), in 25 ml of pentane was added all at once to a solution of 1.0 ml (25 mmoles) of methanol and 1.0 ml (7 mmoles) of triethylamine in 50 ml of purified pentane, with swirling. A copious white precipitate promptly appeared. The reaction mixture was worked up exactly as in the preceding preparation of the methoxydisilane. The crude product was a pale yellow viscous liquid weighing 1.271 g (89.7%), $[\alpha]_D$ +6.9° (*c* 5.1, pentane). Crystallization from pentane of the crude product gave white crystals of the correct melting range and infrared spectrum for (+)-1,2,2,2-tetraphenyl-1-methyl-1-methoxydisilane.

Lithium Aluminum Hydride Reductions of 1,2,2,2-Tetraphenyl-1-methyldisilane Derivatives. 1. 1,2,2,2-Tetraphenyl-1-methyl-1-chlorodisilane. In the 500-ml flask was placed 1.0 g (26 mmoles) of lithium aluminum hydride and 100 ml of dry ethyl ether, and to the hydride solution–slurry was added rapidly a solution of 2.100 g (5.06 mmoles) of (+)-1,2,2,2-tetraphenyl-1-methyl-1-chlorodisilane, mp 86–88°, $[\alpha]_D$ +12.0° (*c* 4.2, ether), dissolved in 75 ml of dry ether. The reaction mixture was stirred for 0.5 hr at room temperature. Then 50 ml of purified hexane were added to the reaction mixture, and excess hydride was destroyed by the *cautious* addition of acetone with stirring. The reaction mixture was then worked up by pouring it into a 1-l. separatory funnel containing 25 ml of concentrated hydrochloric acid, 250 ml of distilled water, and 100 ml of purified pentane. After thorough shaking, the acidic aqueous layer was drained off and the organic layer was washed with three 50-ml portions of cool distilled water. The final wash was neutral to pH paper. The clear, colorless organic solution was dried over anhydrous sodium sulfate overnight, filtered, and solvent removed under reduced pressure. The product was a colorless slightly viscous liquid (which rapidly solidified after scratching with a spatula), weighing 1.830 g (95.0%), mp 65–67°, $[\alpha]_D$ +12.9° (*c* 4.2, pentane). Crystallization from pentane raised the melting point to 67–68°, but without appreciably affecting the specific rotation. The infrared spectrum was consistent with the structure of (+)-1,2,2,2-tetraphenyl-1-methyldisilane.

2. 1,2,2,2-Tetraphenyl-1-methyl-1-bromodisilane. A mixture of 0.5 g (13 mmoles) of lithium aluminum hydride in 50 ml of ethyl ether was prepared and to this was added, all at once, 1.054 g (2.29 mmoles) of (+)-1,2,2,2-tetraphenyl-1-methyl-1-bromodisilane, $[\alpha]_D$ +9.8° (*c* 4.0, ether), dissolved in 50 ml of ether. The reaction mixture was stirred for 0.5 hr, diluted with 50 ml of purified hexane, and excess hydride was destroyed by the *cautious* addition of acetone. The reaction mixture was worked up by the procedure of the previous experiment, yielding a pale yellow, slightly cloudy, slightly viscous liquid weighing 0.825 g (94.5%), $[\alpha]_D$ +6.5° (*c* 3.3, pentane). Crystallization from pentane gave white crystals of the correct melting range and infrared spectrum for (+)-1,2,2,2-tetraphenyl-1-methyldisilane.

3. 1,2,2,2-Tetraphenyl-1-methyl-1-methoxydisilane. In a 100-ml flask with a thermometer was placed 0.4 g (10 mmoles) of lithium aluminum hydride and 25 ml of dry ethyl ether, and then to this mixture was added 0.741 g (1.80 mmoles) of (+)-1,2,2,2-tetraphenyl-1-methyl-1-methoxydisilane, $[\alpha]_D$ +19.5° (*c* 3.0, ether), $[\alpha]_D$ +19.4° (*c* 3.1, pentane), dissolved in 35 ml of dry ether. The reaction mixture was heated to gentle reflux (pot temperature 36°) with stirring for 25 hr. After addition of 10 ml of hexane and decomposition of excess hydride with acetone, the reaction mixture was worked up in the usual manner with cold aqueous HCl. The product was slightly cloudy, slightly viscous liquid (which rapidly turned into a white crystalline solid upon scratching) weighing 0.660 g (99.0%), $[\alpha]_D$ −9.1° (*c* 2.1, pentane), mp 64–66°. Crystallization from pentane gave white crystals of mp 67–68°, but the specific rotation was essentially unaffected. The infrared spectrum confirmed the structure of (−)-1,2,2,2-tetraphenyl-1-methyldisilane.

4. 1,2,2,2-Tetraphenyl-1-methyldisilanol. A mixture of 0.4 g (10 mmoles) of lithium aluminum hydride and 25 ml of dry ethyl ether was prepared in a 100-ml flask. To this was added *cautiously* (hydrogen gas is evolved) a solution of 1.040 g (2.62 mmoles) of (−)-1,2,2,2-tetraphenyl-1-methyldisilanol, mp 85–87°, $[\alpha]_D$ −9.8° (*c* 4.2, ether), in 35 ml of dry ether. The reaction mixture was heated to gentle reflux (pot temperature 36°) with stirring for 23 hr, after which time excess hydride was decomposed by acetone addition, and the mixture was worked up in the usual manner with cold aqueous HCl. The product was a slightly cloudy, slightly viscous liquid (which gradually solidified) weighing 0.920 g (92.3%), [α]D +10.5 (*c* 3.6, pentane). Crystallization from pentane gave white crystals of the correct melting range and infrared spectrum for (+)-1,2,2,2-tetraphenyl-1-methyldisilane.

Reactions of 1,2,2,2-Tetraphenyl-1-methyl-1-chlorodisilane with Organolithium Reagents. 1. Neopentyllithium. A solution of 9.984 g (24.0 mmoles) of (−)-1,2,2,2-tetraphenyl-1-methyl-1-chlorodisilane, [α]D −7.5° (*c* 4.0, ether), in 75 ml of dry ether under a nitrogen atmosphere was chilled to 0° in a 500-ml flask with an ice-water bath. To the chlorodisilane solution was added rapidly by syringe with stirring 50 ml (40 mmoles) of a 0.80 *N* solution of neopentyllithium[36] in ether (also chilled to 0–10°). The mixture assumed the straw-yellow color of the lithium reagent. After stirring for 0.5 hr, a small aliquot of the reaction mixture was removed and hydrolyzed. The racemic disilanol, identified by its melting range of 114–155°, was the only product isolated. Stirring of the reaction mixture was continued for 12 hr while allowing it to warm slowly to room temperature. At this point there was a visible white precipitate (presumably lithium chloride) and the yellow color was partially discharged. The reaction mixture was worked up by washing with cold aqueous HCl and then with neutral water. The product was a clear, very pale yellow, extremely viscous liquid weighing 10.70 g (99.0%), [α]D 0° (*c* 4.0, hexane, benzene, or ether), within experimental error, which resisted efforts toward crystallization. The infrared spectrum contained the usual C_6H_5–Si and CH_3–Si peaks, and absorptions attributed to the neo-C_5H_{11}–Si moiety at 2950, 2860, 1475, 1365, 1235, and 1160 cm^{-1}. A trace of the disilanol was indicated by weak absorption at 3660 cm^{-1}. Because of its optically inactive nature, the product was not subjected to further analysis. However, the infrared spectrum and the mode of synthesis leave but little doubt that the correct structure of the product is (±)-1,2,2,2-tetraphenyl-1-methyl-1-neopentyldisilane.

2. α-Naphthyllithium. In a 500-ml flask was placed a solution of 9.50 g (23.0 mmoles) of (−)-1,2,2,2-tetraphenyl-1-methyl-1-chlorodisilane, [α]D −7.5° (*c* 4.0, ether), in 75 ml of dry ether, and the flask and contents were chilled to 0° in an ice-water bath. To the chlorodisilane solution was added rapidly by syringe 90 ml (27 mmoles) of a 0.3 *N* solution of α-naphthyllithium[37] with stirring. The cloudy yellow color of the lithium reagent solution persisted, even after stirring the reaction mixture for 0.5 hr. Stirring was continued for 12 hr while the reaction mixture slowly warmed to room temperature. The reaction mixture was worked up by washing with cold aqueous acid and then water. The crude product was a pale yellow solid with the odor of naphthalene, weighing 12.0 g (103% yield). The solid was relatively insoluble in pentane or hexane, but moderately soluble in benzene, in which the specific rotation was essentially zero within experimental error. Extraction of the crude solid in a Soxhlet extractor with pentane removed the naphthalene in less than 1 hr, as evidenced by the lack of odor of the powdery white solid remaining in the thimble of the extractor. Further extraction of this solid with hexane for a day gave white clumps of crystals in the pot, which when removed and allowed to dry had mp 149–151°. The mixture melting point with triphenylsilanol (mp 150.5–151.5°) was depressed, 125–145°. The infrared spectrum contained the usual C_6H_5–Si and CH_3–Si absorption as well as absorptions attributed to the α-$C_{10}H_7$–Si moiety at 1590, 1510, 1220, 1145, and 980 cm^{-1}. The product was (±)-1,2,2,2-tetraphenyl-1-methyl-1-α-naphthyldisilane.

Anal. Calcd for $C_{35}H_{30}Si_2$: C, 82.95; H, 5.97. Found: C, 82.70; H, 5.91.

Reactions of 1,2,2,2-Tetraphenyl-1-methyl-1-chlorodisilanes with Cyclohexylammonium Salts. 1. Cyclohexylammonium Benzoate. In a 2.5-dm polarimeter tube was placed a solution (20.0 ml) of 1.667 g (4.00 mmoles) of (−)-1,2,2,2-tetraphenyl-1-methyl-1-chlorodisilane in purified chloroform. The observed rotation (at the sodium D line) was −1.43° and did not change upon standing for 0.5 hr. To the solution was added a solution–suspension of cyclohexylammonium benzoate[29] (0.872 g, 3.94 mmoles) in 5.0 ml of purified chloroform. The cyclohexylammonium salt dissolved promptly with reaction. As soon as the field cleared (less than 1 min) the observed rotation was found to be essentially zero. The reaction mixture was quenched in 200 ml of purified pentane and the precipitated amine salts were removed by filtration on quantitative paper. Removal of solvent from the filtrate solution left in near theoretical yield a white crystalline solid. Crystallization from hexane gave white crystalline clumps, mp 103–104°. The infrared spectrum showed the usual C_6H_5–Si and CH_3–Si absorptions as well as absorptions characteristic of the $C_6H_5CO_2$–Si moiety at 1700, 1580, 1450, 1310, 1275, 1175, 1095, 1065, and 845 cm^{-1}. Despite the fact that the product appeared racemic, it was reduced by lithium aluminum hydride by the procedure of Parker[27] as a check. The product was 100% racemic 1,2,2,2-tetraphenyl-1-methyldisilane. Inverse addition, *i.e.*, the addition of the chlorodisilane solution to the benzoate solution, also gave racemic product. Use of a deficiency of cyclohexylammonium benzoate led to incomplete reaction and to complete racemization.

Anal. Calcd for $C_{32}H_{28}O_2Si_2$: C, 76.75; H, 5.64. Found: C, 76.50; H, 5.63.

2. Cyclohexylammonium Acetate. In a 2.5-dm polarimeter tube was placed a solution (25.0 ml) of 2.010 g (4.82 mmoles) of (−)-1,2,2,2-tetraphenyl-1-methyl-1-chlorodisilane, [α]D −6.5° (*c* 4.0, ether), in purified chloroform, αD −1.15°, [α]D −5.8° (*c* 8.0, $CHCl_3$). To the polarimeter solution was added all at once 0.9137 g (120% of theory) of finely crystalline cyclohexylammonium acetate,[29] which dissolved rapidly. As soon as the field cleared (about 1 min), the rotation was observed to be essentially zero within experimental error. The reaction mixture was quenched in 200 ml of purified pentane and the fluffy white precipitate which formed was filtered using quantitative paper. Removal of solvent from the filtrate under vacuum left a slightly cloudy, nearly colorless, viscous liquid which had the odor of acetic acid, and which upon standing formed a few white crystals. The infrared spectra of both the liquid and the solid showed the C_6H_5–Si and CH_3–Si peaks of the parent system. However, only the liquid showed characteristic CH_3CO_2–Si adsorption bands at 1725, 1250, and 1020 cm^{-1}. The solid was apparently the hydroxydisilane. Chromatography of the crude product over a short column of silica gel with 50/50 (v/v) benzene/pentane improved the acetoxydisilane/disilanol ratio only slightly.

3. Cyclohexylammonium Fluoride. In a 2.5-dm polarimeter tube was placed a solution (20.0 ml) of 1.172 g (2.82 mmoles) of (−)-1,2,2,2-tetraphenyl-1-methyl-1-chlorodisilane in purified chloroform. The observed rotation was −0.50°. To the polarimeter solution was added all at once a solution–slurry of 0.336 g (2.82 mmoles) of cyclohexylammonium fluoride[27] in chloroform. Dissolution was rapid and complete. As soon as the field cleared (about 1 min) the observed rotation was zero within experimental error. The reaction mixture was quenched in 200 ml of purified pentane and the copious white precipitate which formed was removed by filtration using quantitative paper. Removal of solvent left a slightly cloudy viscous liquid with an acrid odor. The crude product was taken up in 25 ml of purified pentane and filtered to remove a faint cloudiness. The observed rotation was zero in pentane. Removal of solvent under vacuum left a clear, colorless viscous liquid weighing 1.027 g (84.0%). The faint but biting odor persisted. The product was characterized by a strong absorption band at 840 cm^{-1} (this band is absent in the parent chlorodisilane) attributed to the Si–F moiety, in addition to the usual C_6H_5–Si and CH_3–Si absorptions of the parent system. Absence of hydroxydisilane was shown by transparency in the region 3700–3200 cm^{-1}. The above procedure and variations such as inverse addition and the use of an excess or deficiency of the fluoride salt invariably led to essentially racemic 1,2,2,2-tetraphenyl-1-methyl-1-fluorodisilane.

Preparation of (−)-1,2,2,2-Tetraphenyl-1-methyl-1-fluorodisilane. A solution of 2.70 g (5.05 mmoles) of (+)-1,2,2,-tetraphenyl-1-methyl-1-(−)-menthoxydisilane, mp 90–91°, [α]D +19.9° (*c* 2.0, pentane), in 50 ml of pentane was prepared in a 250-ml filter flask fitted with a gas inlet tube and a $CaCl_2$ outlet tube. Boron trifluoride gas was bubbled into the pentane solution at a moderately slow rate for 60 min. The clear, colorless solution was then poured into a separatory funnel containing crushed ice, 50 ml of 10% HCl, and 25 ml of pentane. The mixture was agitated well, separated, and the organic layer washed with three portions of water until neutral. After drying with sodium sulfate, the mixture was stripped of solvent, and the residue, which had a strong odor of menthol, was chromatographed on a 18 in. × 0.5 in. silica gel column with elution by 150 ml of pentane–benzene (50:50 v/v). Evaporation of the eluent at reduced pressure yielded a residue (1.92 g) which was placed under vacuum (1 Torr) at room temperature for 12 hr during which time it solidified, mp 68–72°, [α]D −7.9° (*c* 4.0, pentane).

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[37] H. Gilman and C. G. Brannen, *J. Am. Chem. Soc.*, 73, 4640 (1951).

Recrystallization from pentane gave 1.32 g (66% yield) of needles, mp 73.5–75°, [α]D −8.6° (*c* 2.0, in pentane), which were identified as pure (−)-1,2,2,2-tetraphenyl-1-methyl-1-fluorodisilane. The infrared spectrum in CCl_4 displayed all of the adsorption bands characteristic of the $Ph_3SiSi(Ph)(Me)$ system, plus a strong band at 840 cm^{-1} attributed to the Si–F stretching vibration.[38] The melting point and optical rotation of the compound were unaffected by subsequent recrystallizations.

Anal. Calcd for $C_{25}H_{23}Si_2F$: C, 75.33; H, 5.82. Found: C, 75.26; H, 5.75.

Reductions of (−)-1,2,2,2-Tetraphenyl-1-methyl-1-fluorodisilane. 1. $LiAlH_4$. To a mixture of 0.38 g (10 mmoles) of $LiAlH_4$ in 15 ml of ethyl ether was added a solution of 0.500 g (1.26 mmoles) of (−)-1,2,2,2-tetraphenyl-1-methyl-1-fluorodisilane, [α]D −8.6° (*c* 2.0, pentane), in 8 ml of ether. The mixture was refluxed for 60 min after which time acetone and moist ether were added to decompose excess hydride. The mixture was then worked up by shaking it with ice cold dilute HCl and pentane in a separatory funnel, and then washing the resultant organic layer with portions of cold water until neutral. After drying with sodium sulfate, the clear, colorless solution was stripped of solvent leaving 0.473 g (99% yield) of solid (−)-1,2,2,2-tetraphenyl-1-methyldisilane, [α]D −14.2° (*c* 1.89, pentane), identified by its infrared spectrum which was identical with that of authentic disilane.

2. Diisobutylaluminum Hydride. To a magnetically stirred solution of 0.600 g (1.5 mmoles) of (−)-1,2,2,2-tetraphenyl-1-methyl-1-fluorodisilane, [α]D −8.6° (*c* 2.0, pentane), in 10 ml of purified *n*-hexane under a nitrogen atmosphere was added 0.56 ml (3.0 mmoles) of neat liquid *i*-Bu_2Al-H (Texas Alkyls Co.) by syringe. The clear, colorless solution was stirred for 90 min at room temperature and then worked up by slowly syringing it into a separatory funnel containing crushed ice, 10 ml of 10% HCl, and 30 ml of pentane. The mixture was cautiously, and then more vigorously, agitated, giving rise to a white suspension in the organic layer. This suspension was removed by washing the organic layer with a second portion of 10% HCl. The organic layer was then washed with three portions of water until neutral, dried with sodium sulfate, and stripped of solvent leaving 0.518 g (91% yield) of (+)-1,2,2,2-tetraphenyl-1-methyldisilane, [α]D +12.4° (*c* 2.07, pentane), which solidified on standing. The product was clearly identified by its infrared spectrum which was identical with that of authentic disilane.

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Stereochemistry of Asymmetric Silicon. XVIII. Hydrogen–Halogen Exchange of R_3Si^*H with Trityl Halides[1,2]

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Abstract: For the reaction of optically active R_3Si^*H with trityl halides, Ph_3CX, the hydrogen–halogen exchange reaction does *not* proceed with predominant retention of configuration for X = Cl or Br in $CHCl_3$ solvent. A *new* mechanism for these reactions is proposed on the basis of the stereochemical results.

It has been known for some time that organosilicon hydrides undergo hydrogen–halogen exchange with various alkyl halides in the presence of Lewis acid

$$R_3SiH + R'X \xrightarrow{AlCl_3} R_3SiX + R'H$$

catalysts.[3] Later, it was found that heating a silicon hydride with an appropriate active halogen compound was sufficient to bring about the exchange process.[4,5] More recently, in a somewhat more extensive study, Corey and West found that triphenylmethyl halides and silicon hydrides undergo hydrogen–halogen exchange at room temperature when dissolved in an appropriate solvent.[6] The exchange was operative at room temperature in only those solvents which are known to bring about dissociation of triarylmethyl halides into ion pairs. The rate of exchange was found qualitatively to increase in the series chloride, bromide, and iodide, and the addition of anhydrous hydrogen chloride produced a marked rate enhancement.

The facts were consistent with a mechanism in which electrophilic attack on the silicon–hydrogen bond by a triphenylmethyl cation was important. An attractive activated complex featured four-center association of the two reacting molecules and involved both electrophilic hydride abstraction and nucleophilic attack by the halide ion. If this were correct, the geometry about silicon could approximate either a trigonal bipyramid with leaving and entering groups occupying apical and equatorial positions, or a tetragonal pyramid with both leaving and entering groups basal and in a *cis* relationship. Support was given to this mechanistic picture when it was reported[7] that optically active α-naphthylphenylmethylsilane, R_3Si^*H, reacted with triphenylmethyl chloride in refluxing benzene to give chlorosilane which was 95% optically pure and whose sign of rotation corresponded to predominant retention of absolute configuration.

In this paper, we wish to report the results of some stereochemical studies in which it was found that *retention of configuration at silicon is not the sole preferred stereochemical path for the exchange process.*

Results and Discussion

The steric course of the exchange reaction between R_3Si^*H and triphenylmethyl chloride and bromide was determined in benzene, chloroform, and methylene chloride. The results of the study are summarized in Table I.

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[1] We are grateful to the National Science Foundation for vital support of this work.

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