

Recrystallization from pentane gave 1.32 g (66% yield) of needles, mp 73.5–75°,  $[\alpha]_D -8.6^\circ$  ( $c$  2.0, in pentane), which were identified as pure (–)-1,2,2,2-tetraphenyl-1-methyl-1-fluorodisilane. The infrared spectrum in  $\text{CCl}_4$  displayed all of the adsorption bands characteristic of the  $\text{Ph}_3\text{SiSi}(\text{Ph})(\text{Me})$  system, plus a strong band at  $840\text{ cm}^{-1}$  attributed to the Si–F stretching vibration.<sup>38</sup> The melting point and optical rotation of the compound were unaffected by subsequent recrystallizations.

*Anal.* Calcd for  $\text{C}_{25}\text{H}_{23}\text{Si}_2\text{F}$ : 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.  $\text{LiAlH}_4$ .** To a mixture of 0.38 g (10 mmoles) of  $\text{LiAlH}_4$  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,  $[\alpha]_D -8.6^\circ$  ( $c$  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,  $[\alpha]_D -14.2^\circ$  ( $c$  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,  $[\alpha]_D -8.6^\circ$  ( $c$  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 *t*- $\text{Bu}_2\text{Al-H}$  (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,  $[\alpha]_D +12.4^\circ$  ( $c$  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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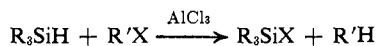
## Stereochemistry of Asymmetric Silicon. XVIII. Hydrogen–Halogen Exchange of $\text{R}_3\text{Si}^*\text{H}$ with Trityl Halides<sup>1,2</sup>

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**Abstract:** For the reaction of optically active  $\text{R}_3\text{Si}^*\text{H}$  with trityl halides,  $\text{Ph}_3\text{CX}$ , the hydrogen–halogen exchange reaction does *not* proceed with predominant retention of configuration for  $\text{X} = \text{Cl}$  or  $\text{Br}$  in  $\text{CHCl}_3$  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



catalysts.<sup>3</sup> Later, it was found that heating a silicon hydride with an appropriate active halogen compound was sufficient to bring about the exchange process.<sup>4,5</sup> 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.<sup>6</sup> 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<sup>7</sup> that optically active  $\alpha$ -naphthylphenylmethylsilane,  $\text{R}_3\text{Si}^*\text{H}$ , 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  $\text{R}_3\text{Si}^*\text{H}$  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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(2) For the preceding paper in this series, see: L. H. Sommer and K. T. Rosborough, *J. Amer. Chem. Soc.*, **91**, 7067 (1969).

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(5) H. Westermarck, *Acta Chem. Scand.*, **8**, 1086 (1954).

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**Table I.** Stereochemistry of the Reaction between  $\alpha$ -NpPhMeSiH and Ph<sub>3</sub>CX

Halide	Solvent	$k_2, M^{-1} \text{ sec}^{-1}$	Stereochemistry, %
Br	CCl <sub>4</sub>	$1.6 \times 10^{-4}$	23, <sup>a</sup> 77 <sup>b</sup>
Cl	CCl <sub>4</sub>	$5.4 \times 10^{-6}$	38, <sup>a</sup> 62 <sup>b</sup>
Br	PhH		11, <sup>c</sup> 89 <sup>b</sup>
Br	H <sub>2</sub> CCl <sub>2</sub>	$5.5 \times 10^{-4}$	100 <sup>b</sup>
Cl	H <sub>2</sub> CCl <sub>2</sub>	$1.3 \times 10^{-4}$	100 <sup>b</sup>

<sup>a</sup> Inversion. <sup>b</sup> Racemization. <sup>c</sup> Retention.

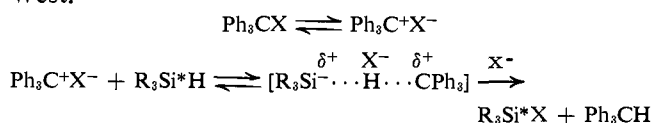
The rotation of the reaction mixture was followed as a function of time. The reaction was assumed to be complete when the Si-H stretching band at  $4.7 \mu$  could no longer be seen in the infrared spectrum of an aliquot of the reaction mixture. The resulting polarimetric data gave a good straight line when plotted as a second-order reaction. In chloroform, the predominant stereochemical course was inversion of configuration while a small net retention of configuration was observed in benzene and complete racemization in methylene chloride.

These stereochemical results were complicated somewhat when it was found that the bromosilane produced was not optically stable under the reaction conditions in chloroform and neither the bromosilane nor the chlorosilane were optically stable under the reaction conditions in methylene chloride. The second-order rate constant ( $8.0 \times 10^{-5} M^{-1} \text{ sec}^{-1}$ ) for the racemization of the bromosilane in the presence of triphenylmethyl bromide in chloroform is only slightly smaller than the second-order rate constant for exchange ( $1.6 \times 10^{-4} M^{-1} \text{ sec}^{-1}$ ). In view of this fact, the stereochemistry of exchange between R<sub>3</sub>Si\*H and triphenylmethyl bromide in chloroform can be only approximate and is likely actually more stereospecific (*i.e.*, >23% inversion) than the data indicate.

The second-order rate constant for the exchange reaction between R<sub>3</sub>Si\*H and triphenylmethyl chloride in methylene chloride ( $1.3 \times 10^{-4} M^{-1} \text{ sec}^{-1}$ ) is nearly six times as large as the second-order rate constant for the racemization of the chlorosilane in the presence of triphenylmethyl chloride in the same solvent ( $2.3 \times 10^{-5} M^{-1} \text{ sec}^{-1}$ ). This indicates that the exchange is indeed completely nonstereospecific in this solvent.

Reactions carried out with a twofold excess of R<sub>3</sub>Si\*H showed the unreacted starting material to be partially racemized (30–50%). This racemization of unreacted R<sub>3</sub>Si\*H was not the result of reversal of the exchange process because optically active silane was found to be completely optically stable in the presence of R<sub>3</sub>Si\*Cl and triphenylmethane in chloroform.

The data are all consistent with a mechanism in which electrophilic attack on the silicon hydride by a triphenylmethyl cation is of primary importance. The triphenylmethyl cation would likely be intimately associated with its counter ion. This mechanistic picture is somewhat similar to the one proposed by Corey and West.<sup>6</sup>



Racemization of the unreacted R<sub>3</sub>Si\*H could easily arise from partial breakage of the Si-H bond, and

rotation of the R<sub>3</sub>Si moiety followed by return of the hydride. Similar pictures have been proposed to rationalize processes in which the rate of racemization exceeds the rate of isotope exchange both for carbanion intermediates<sup>8</sup> and for carbonium ion intermediates.<sup>9</sup>

The observed stereochemistry resulting from such a mechanism should be somewhat solvent dependent. If the dissociating power of the solvent were quite large, the ion-pair framework of the activated complex should be rather loose. In this situation, Si-H bond breakage might be somewhat complete before the Si-X bond begins to form, allowing attack from the front or from the rear of the silicon to occur with about equal probability. This would, of course, lead to racemic products and is observed when methylene chloride is used as the solvent. A solvent such as methylene chloride which has a relatively small dielectric constant (9.08) is not generally considered to possess a particularly high ion solvating power. However, it has been found that partially chlorinated ethanes facilitate the dissociation of triarylmethyl halides much better than would be expected on the basis of their dielectric constants.<sup>10</sup>

If the dissociating power of the solvent were only moderate, the ion-pair framework of the activated complex should be somewhat tighter and Si-X formation might be expected to begin somewhat before the Si-H bond is broken. However, it is possible that the framework could still be loose enough to allow the halide ion to slip preferentially around to the rear of the silicon while the front side is still shielded. This is apparently the situation when chloroform is used as the solvent. Both the dielectric constant (4.81) and the dipole moment (1.02 D) of chloroform are somewhat smaller than those of methylene chloride. It should not then seem surprising that chloroform should possess a somewhat smaller ion solvating power than methylene chloride.

Triphenylmethyl fluoroborate was observed to react with R<sub>3</sub>Si\*H in chloroform to product R<sub>3</sub>Si\*F which was 40% optically pure and whose sign of rotation corresponded to *inversion* of configuration. It is interesting also to note that silver fluoroborate reacts with R<sub>3</sub>Si\*H in ether to give fluorosilane of inverted configuration which is about 90% optically pure.<sup>11</sup> The mechanistic sequence followed by these two reactions is apparently very similar to that just described.

Finally, if the dissociating power of the solvent is quite low, the ion-pair framework at the activated complex should be quite tight and frontside attack would be expected to be the preferred path for attack by halide. In such a situation, the reacting molecules will likely be associated in a quasi four-membered ring. This situation apparently exists when benzene is used as the solvent for the exchange reaction and is common for many nucleophilic displacement reactions at silicon when the leaving group cannot easily accept a negative charge and when the solvent is nonpolar. This type of reaction has been designated by the symbol S<sub>N</sub>i-Si.<sup>12</sup>

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## Experimental Section

Chloroform, methylene chloride, and benzene, all Mallinckrodt analytical reagents, were extracted with several portions of concentrated sulfuric acid and then passed over a column (1 in.  $\times$  36 in.) of silica gel.

The preparation of all optically active silicon compounds together with their configurational relationships has been described in detail elsewhere.<sup>13</sup>

**Triphenylmethyl bromide** was prepared by the action of hydrobromic acid (48%) on a glacial acetic acid solution of triphenylcarbinol following the procedure of Wieland.<sup>14</sup>

**Triphenylmethyl chloride** was prepared by the action of acetyl chloride on a benzene solution of triphenylcarbinol according to the procedure of Bachmann.<sup>15</sup>

**Triphenylmethyl fluoroborate** was prepared by the action of fluoroboric acid on a propionic anhydride solution of triphenylcarbinol according to the procedure of Dauben.<sup>16</sup>

**Exchange Reactions.** The procedures followed for all exchange reactions are identical and only one detailed description will be given. (–)- $R_3Si^*H$  (1.55 g, 6.25 mmol),  $[\alpha]_D -35^\circ$  ( $c$  1.00, in pentane), and triphenylmethyl chloride (3.59 g, 12.5 mmol) were put into a 2.5-dm jacketed polarimeter tube and enough purified chloroform added to make the total volume equal to 25 ml. The jacket of the tube was connected to a circulating constant temperature bath held at  $25.0 \pm 0.05^\circ$ . The rotation was followed as a function of time and an aliquot of the reaction mixture was removed at intervals for an infrared spectrum. The reaction was assumed to be complete when the Si–H stretching band at  $4.7 \mu$  could no longer be detected. Assuming complete conversion to the chlorosilane, a specific rotation of  $[\alpha]_D -2.5^\circ$  was calculated. The sign of rotation corresponds to the product of inverted configuration which is 38% optically pure. The infrared spectrum of the product mixture was completely equivalent with one of a known mixture of  $R_3Si^*Cl$ , triphenylmethyl chloride, and triphenylmethane.

**Reaction of  $R_3Si^*H$  with Triphenylmethyl Fluoroborate.** To a suspension of triphenylmethyl fluoroborate (0.382 g, 1.21 mmol) in purified chloroform (25 ml) was added a solution of (–)- $R_3Si^*H$  (0.300 g, 1.21 mmol),  $[\alpha]_D -35^\circ$  ( $c$  1.00, in pentane) in chloroform

10 ml). As the silane was added, the solid fluoroborate disappeared and a gas assumed to be boron trifluoride was evolved. After allowing the solution to stand for 20 min, the chloroform was removed under reduced pressure. An infrared spectrum of the product mixture was identical with that of an equimolar mixture of  $R_3Si^*F$  and triphenylmethane. The residue (0.606 g, 97% yield) when dissolved in pentane had a specific rotation of  $[\alpha]_D +18.9^\circ$  ( $c$  2.4, in pentane), allowing for the triphenylmethane calculated to be present. This corresponds to material of 42% optical purity and of inverted configuration.

**Racemization of Halosilanes in the Presence of Triphenylmethyl Halides.** The procedure used in all racemization studies will be illustrated by one specific example. (–)- $R_3Si^*Br$  (0.788 g, 2.41 mmol),  $[\alpha]_D -26^\circ$  ( $c$  7.90 in chloroform), and triphenylmethyl bromide were put into a jacketed 2.5-dm polarimeter tube and enough purified chloroform added to make the total volume equal to 10 ml. The jacket of the polarimeter tube was connected to a circulating constant temperature bath held at  $25.0 \pm 0.05^\circ$  and the rotation of the solution followed as a function of time. Any given run followed good pseudo-first-order kinetics; however, variation of the triphenylmethyl bromide concentration showed a first-order dependence of the pseudo-first-order rate constant on the concentration of the latter compound.

**Racemization of  $R_3Si^*H$  during Exchange.** Again, the general procedure used in all experiments of this type will be illustrated by one specific example. (+)- $R_3Si^*H$  (1.55 g, 6.25 mmol),  $[\alpha]_D +35^\circ$  ( $c$  1.00, in pentane), and triphenylmethyl chloride (0.87 g, 3.12 mmol) were dissolved in purified chloroform (25 ml). The resulting solution was allowed to stand for 72 hr. At the end of this time, the solution was diluted with ether (100 ml), washed well with water, converting the chlorosilane to silanol, and then the organic layer was dried over anhydrous sodium sulfate. Volatiles were removed and the residue placed on a column ( $1/2$  in.  $\times$  18 in.) of silica gel. A mixture of 10% benzene in pentane was used as elutant. The  $R_3Si^*H$  moved down the column slightly faster than the triphenylmethane while the  $R_3Si^*OH$  adhered strongly to the silica gel. It was possible to collect 0.34 g (42% of theory) of essentially pure  $R_3Si^*H$ ,  $[\alpha]_D +22^\circ$  ( $c$  1.4, in pentane), in this manner. This rotation corresponds to 37% racemization of the unreacted silane.

**Optical Stability of  $R_3Si^*H$  in the Presence of  $R_3Si^*Cl$  and Triphenylmethane.**  $R_3Si^*H$  (0.52 g, 2.1 mmol),  $[\alpha]_D -35^\circ$  ( $c$  1.00, in pentane),  $R_3Si^*Cl$  (0.57 g, 2.0 mmol), and triphenylmethane (0.58 g, 2.4 mmol), were dissolved in 25 ml of purified chloroform. This solution was allowed to stand for 68 hr and then worked up in a manner identical with that described for the preceding experiment. Chromatography yielded 0.22 g (42% of theory) of pure  $R_3Si^*H$ ,  $[\alpha]_D -34^\circ$  ( $c$  1.00, in pentane).

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