

stopped and shaken vigorously for several minutes; enough heat was evolved to raise the temperature some 10–20°. Upon standing for an hour, the solid material settled, leaving a clear, pale yellow supernatant liquid. Determination of the concentration of  $R_3Si^*OK$  by titration of an aliquot with standard acid and measurement of rotation of  $(+)_R_3Si^*OK$  gave  $[\alpha]_D +75^\circ$  (c 10.5 in xylene). No change in specific rotation was noted 4 days later.

**Reaction of  $(+)_R_3Si^*OK$  with Dimethyl Sulfate.**—To a 125-ml. flask was added 10.0 ml. (3.49 mmoles) of a xylene solution of  $(+)_R_3Si^*OK$ . To this was added 2.0 ml. (0.021 mole) of freshly distilled dimethyl sulfate and the flask was stoppered and shaken.

The reaction appeared to be immediate, forming a flocculent precipitate, and was decidedly exothermic. The reaction mixture was then diluted with 100 ml. of hexane and washed with an excess of potassium carbonate solution. After washing with water, drying, and removal of solvents, the residue was crystallized from pentane. Recrystallization from pentane yielded 0.75 g. (77% yield) of  $(-)_R_3Si^*OCH_3$ ,  $[\alpha]_D -16^\circ$  (c. 4.30 in pentane), m.p. 62.5–64°. The infrared spectrum of this material completely confirmed the structure.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE PENNSYLVANIA STATE UNIVERSITY, UNIVERSITY PARK, PA.]

## Stereochemistry of Asymmetric Silicon. II. Alkoxy and Siloxy Leaving Groups

BY L. H. SOMMER, C. L. FRYE, AND G. A. PARKER

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The stereochemistry of displacement of alkoxy and siloxy leaving groups from asymmetric silicon in optically active compounds containing the  $\alpha$ -naphthylphenylmethylsilyl group,  $\alpha$ -NpPhMeSi<sup>-</sup>, has been studied. Retention of configuration was found for reduction to  $R_3Si^*H$  with lithium aluminum hydride and *t*-butylmagnesium chloride. Reactions with powdered  $KOH_{(s)}$ , using a xylene solvent, also gave retention of configuration. Quasicyclic transition states are postulated for these retention reactions with strong nucleophiles in nonpolar solvents, and the symbol S<sub>ni</sub>-Si is proposed for such mechanisms.

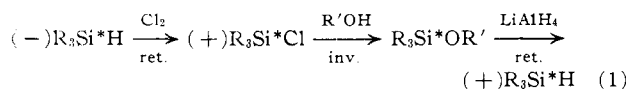
A previous paper in this series on the stereochemistry of asymmetric silicon has demonstrated a high degree of stereospecificity for a number of reactions of  $R_3Si^*X$  in which  $R_3Si^*$  is the  $\alpha$ -naphthylphenylmethylsilyl group,  $\alpha$ -NpPhMeSi<sup>-</sup>, and has dealt with the problems of relative and absolute configurations for a number of key compounds.<sup>1</sup>

These previous studies have made it possible to determine the stereochemistry of a very large number of reactions of  $R_3Si^*X$  in which the leaving X and the attacking reagent are varied over a wide range.

In this paper are reported reactions of  $R_3Si^*OR'$  in which  $R'$  is  $CH_3$ , cyclo- $C_6H_{11}$ , *t*- $C_4H_9$ ,  $(-)$ -menthyl, and  $R_3Si^*$  for optically active (as contrasted with *meso*)  $R_3Si^*OSi^*R_3$ . The reactions reported herein comprise reduction of  $R_3Si^*OR'$  to  $R_3Si^*H$  with lithium aluminum hydride and with *t*-butylmagnesium chloride (Grignard reduction), and cleavage of the Si<sup>\*</sup>-O bond with  $KOH_{(s)}$ .

**Reduction Reactions.**—The  $R_3Si^*OR'$  compounds dealt with in the present paper have leaving groups which may be classed as "poor" on the basis that their conjugate acids have  $pK_a$  larger than *ca.* 10. All five leaving groups undergo displacements at relatively slow rates with reagents generally classed as nucleophilic, compared to the faster rates of "good" leaving groups such as  $-Cl$  or  $-Br$ .

In a previous paper,<sup>1</sup> reactions of  $R_3Si^*Cl$  were found to proceed with predominant *inversion* of configuration with diverse nucleophilic reagents, including lithium aluminum hydride. In contrast, reductions of  $R_3Si^*OCH_3$  and  $R_3Si^*OH$  with lithium aluminum hydride were found to proceed with *retention* of configuration. These reductions comprised one step in the Walden cycle<sup>1</sup>



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

The same cycle, conversion of  $(-)_R_3Si^*H$  to  $(+)_R_3Si^*H$ , was found to obtain in the present work when  $R' = \text{cyclo-}C_6H_{11}$  or  $(-)$ -menthyl. Furthermore, when  $R'$  is *t*- $C_4H_9$  or  $R_3Si^*$  the same cycle was found for reaction of  $(+)_R_3Si^*Cl$  with *t*- $C_4H_9OK$  in *t*-butyl alcohol and for reaction of  $(+)_R_3Si^*Cl$  with  $(-)_R_3Si^*OK$  in xylene. In view of the fact that these six cycles, involving formation and reduction of  $R_3Si^*OR'$ , all proceed to the over-all result given in (1), it seems clear that all six involve *inversion* of configuration in the formation of  $R_3Si^*OR'$  from  $R_3Si^*Cl$  (see ref. 1 for *inversion* of configuration for  $R_3SiCl$  with a wide variety of reagents) and *retention* of configuration in the reduction of  $R_3Si^*OR'$  to  $R_3Si^*H$ . On this basis, the enantiomers listed in Table I have the  $(+)_R_3Si^*H$  configuration and, furthermore, possess the absolute configuration<sup>1</sup>

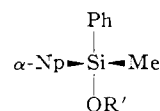


TABLE I

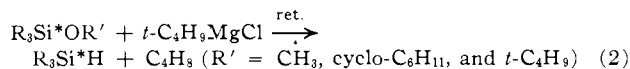
ENANTIOMERS HAVING THE  $(+)_R_3Si^*H$  CONFIGURATION

Compound <sup>a</sup>	$[\alpha]_D$ , solvent	M.p., °C.
$(+)_R_3Si^*OH$	+20°, ether	Liq.
$(-)_R_3Si^*OK$	-75°, xylene	
$(+)_R_3Si^*OCH_3$	+17, pentane	64
$(-)_R_3Si^*O\text{-cyclo-}C_6H_{11}$	- 8.0°, pentane	Liq.
$(-)_R_3Si^*O(-)\text{Men}$	-59°, cyclohexane	84
$(-)_R_3Si^*O\text{-}t\text{-}C_4H_9$	-28°, pentane	Liq.
$(+)_R_3Si^*OSi^*R_3$	+9.9°, hexane	89

<sup>a</sup>  $(+)_R_3Si^*OH$ ,  $(-)_R_3Si^*OK$ , and  $(+)_R_3Si^*OCH_3$  were assigned the  $(+)_R_3Si^*H$  configuration in a previous paper<sup>1</sup>; that both silicon atoms in  $(+)_R_3Si^*OSi^*R_3$  have the  $(+)_R_3Si^*H$  configuration follows rigorously from its synthesis from  $(-)_R_3Si^*OK$  and  $(+)_R_3Si^*Cl$ ; see below.

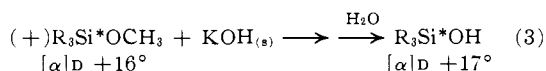
Treatment of  $(+)_R_3Si^*OCH_3$  with *t*-butylmagnesium chloride gave  $(+)_R_3Si^*H$  in 96% yield. Thus, Grignard reduction proceeds with *retention* of configuration. The reduction was about 90% stereospecific. Grignard reduction of  $(-)_R_3Si^*O\text{-cyclo-}C_6H_{11}$  with *t*-

butylmagnesium chloride gave (+)R<sub>3</sub>Si\*H and, similarly, (-)R<sub>3</sub>Si\*O-*t*-C<sub>4</sub>H<sub>9</sub> gave (+)R<sub>3</sub>Si\*H. Thus, all three R<sub>3</sub>Si\*OR' compounds give Grignard reduction products of predominantly *retained* configuration. This is a reasonable result in terms of the probable quasicyclic nature of the rate-controlling transition states for Grignard reductions in general. In turn, this result provides further support for the correlations of configuration in Table I.

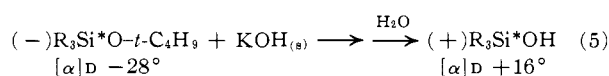


**Reactions with KOH<sub>(s)</sub>.**—We turn now to a consideration of some reactions of Si\*-OR' with another base which provides displacement of -OR by -OH or -O-K<sup>+</sup>. The base is solid potassium hydroxide, KOH<sub>(s)</sub>, containing about 12% water, an exceedingly reactive reagent toward Si-O bonds.<sup>2</sup>

Treatment of R<sub>3</sub>Si\*OCH<sub>3</sub> with excess powdered KOH<sub>(s)</sub>, using a xylene solvent, gave a 90% yield of R<sub>3</sub>Si\*OK after 45 min. at 95°. Treatment of the potassium silanolate with water (which does not affect the asymmetric center) gave R<sub>3</sub>Si\*OH.

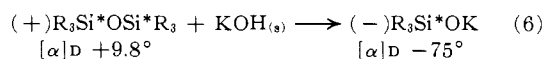


Thus, the predominant stereochemistry is *retention* of configuration and the stereospecificity is about 90%. Similar results were obtained for the cyclohexoxysilane, after a reaction time of 90 min., and with the *t*-butoxysilane after 10 hr.



It should perhaps be pointed out that retention reactions 3, 4, and 5 involve displacement of -OR from asymmetric silicon. Displacement of alkoxy groups from silicon with bases is well known.<sup>3</sup> Furthermore, in the present work treatment of (±)R<sub>3</sub>Si-O(-)Men with KOH<sub>(s)</sub> gave optically pure (-)-menthol, thus showing that KOH<sub>(s)</sub> gives displacement at Si in R<sub>3</sub>Si\*OR'.

The reaction of optically active disiloxane, (+)-R<sub>3</sub>Si\*OSi\*R<sub>3</sub>, with KOH<sub>(s)</sub> is very interesting from the standpoint of stereochemistry. It was carried out using xylene solvent, a temperature of 95°, and excess powdered KOH<sub>(s)</sub>. Assuming a quantitative conversion to R<sub>3</sub>Si\*OK, the specific rotation was found to be [α]<sub>D</sub> -75°.



The stereospecificity is about 95%. Hydrolysis of the silanolate from 6 gave (+)R<sub>3</sub>Si\*OH having [α]<sub>D</sub> +16°.

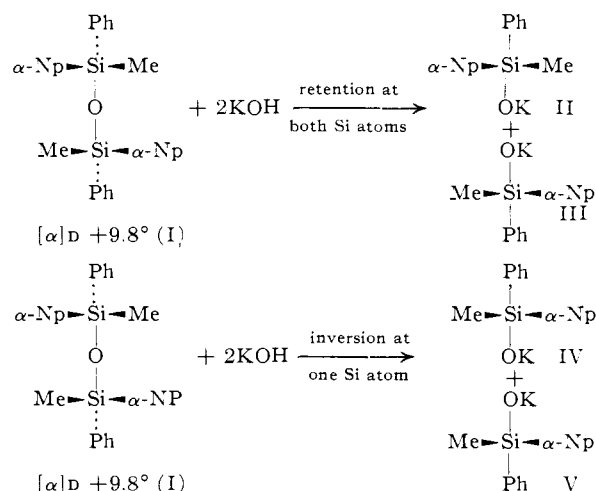
Reaction 6 is an unusual case in stereochemistry.<sup>4</sup> The formation of silanolate of high optical purity proves that the stereochemical course is retention of configuration. This is made clear by consideration of

(2) Cf. D. T. Hurd, R. C. Osthoff, and M. L. Corrin, *J. Am. Chem. Soc.* **76**, 249 (1962).

(3) C. Eaborn, "Organosilicon Compounds," Butterworths, London, 1960, Chapters 8 and 9.

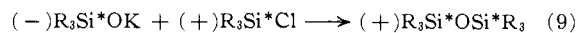
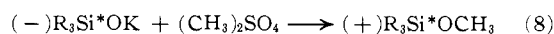
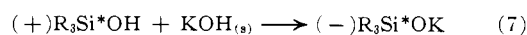
(4) For a preliminary report see L. H. Sommer and C. L. Frye, *J. Am. Chem. Soc.*, **82**, 3769 (1960).

the reaction with the aid of Fisher projection formulas which also give the correct absolute configurations.<sup>1</sup>



The formation of R<sub>3</sub>Si\*OK of high optical purity is itself convincing evidence of retention of configuration in the special case of 6. Rotation of structure III, 180° in the plane of the paper, gives II. Thus, these are identical structures, whereas IV and V are of opposite configuration. A third possibility, inversion at both silicon atoms, which seems unlikely on simple chemical grounds (*i.e.*, rupture of only one Si-O bond is needed to make 2R<sub>3</sub>Si\*OK species, and active R<sub>3</sub>Si\*OK is not racemized by excess KOH), is ruled out by the fact that (+)R<sub>3</sub>Si\*OSi\*R<sub>3</sub> and (-)R<sub>3</sub>Si\*OK have the same configuration at all three silicon atoms (see below).

**Chemical Correlations of Configuration with R<sub>3</sub>Si\*-OK.**—In a previous paper,<sup>1</sup> (-)R<sub>3</sub>Si\*OK and (+)-R<sub>3</sub>Si\*OCH<sub>3</sub> were assigned the same configuration as (+)R<sub>3</sub>Si\*OH based on reactions 7 and 8. Reaction 9 confirms the assignment of the same configuration to the four silicon atoms in (+)R<sub>3</sub>Si\*OH, (-)R<sub>3</sub>Si\*OK, and (+)R<sub>3</sub>Si\*OSi\*R<sub>3</sub>.



Reactions 7, 8, and 9 do not affect the asymmetric center.

**Mechanism Implications.**—Important factors responsible for the *retention* stereochemistry of the above reactions of R<sub>3</sub>Si\*OR' with strong nucleophiles are probably: (1) R'O is a poor leaving group (pK<sub>a</sub> of R'OH is greater than *ca.* 10) and is therefore relatively difficult to displace from silicon as a negative ion. R'O is generally not displaced from saturated carbon centers with bases, except for special cases of ring-strained epoxides. (2) The unshared electron pairs on oxygen in R'O are probably quite available for donation to the electrophilic part of the attacking reagent, especially if nucleophilic attack on silicon is proceeding simultaneously. The latter must significantly decrease dative d<sub>π</sub>p<sub>π</sub> bonding from oxygen to silicon. (3) The combination of relatively high basicity of R'O (compared to, say, Cl or Br) toward the silicon centers and toward the electrophilic part of the attacking reagent results in a situation quite favorable for quasicyclic mechanisms proceeding with retention of

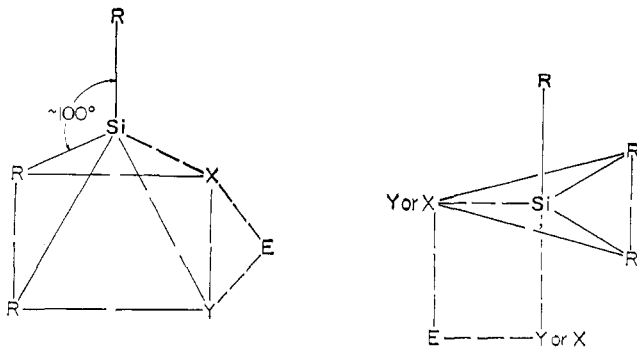


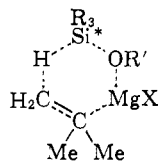
Fig. 1.—Representation of  $S_{Ni}$ -Si transition states, having over-all tetragonal pyramidal and trigonal bipyramidal geometries. Both representations postulate a near pyramidal arrangement of the R groups and Si, and "bonds" to X and Y that are long and weak (dashed lines) compared to the R-Si bonds.

configuration in the relatively nonpolar, aprotic solvents used in the present work.

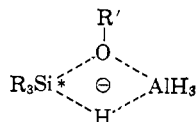
The important role of a nonpolar solvent of poor ion-solvating power in promoting retention reactions of  $R_3Si^*OR'$  is strongly indicated by a recent paper which reports that the rate of methoxy-methoxy exchange, using tritium-labeled  $R_3Si^*OCH_3$ , was found to be one-half the rate of racemization. This was true for use of methanol as the solvent-reactant, regardless of whether an acidic or basic catalyst was used.<sup>5</sup> Thus, in a methanol solvent, in sharp contrast to the results in nonpolar solvents,  $R_3Si^*OCH_3$  reacts with inversion of configuration.

In a comprehensive discussion,<sup>6</sup> quasicyclic mechanisms giving retention of configuration at asymmetric silicon have been termed  $S_{Ni}$ -Si in recognition of some important differences between mechanism  $S_{Ni}$  for carbon and  $S_{Ni}$ -Si for silicon. *Operation of mechanism  $S_{Ni}$ -Si in nonpolar solvents of poor ion-solvating power provides the minimization of charge separation favored by such solvents, and also provides the needed electrophilic assistance (by providing "pull" on X) for removal of poor leaving groups.*<sup>6</sup>

The  $S_{Ni}$ -Si mechanism is the most common polar mechanism for organosilicon reactions proceeding with retention of configuration.<sup>6</sup> Examples of the operation of  $S_{Ni}$ -Si in the present work are provided by the Grignard reductions of  $R_3Si^*OR'$ , for which the rate-controlling transition state may be formulated as<sup>7</sup>



Similarly, the reduction of  $R_3Si^*OR'$  with lithium aluminum hydride, proceeding with retention of configuration, may be formulated as

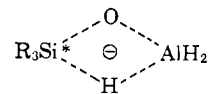


(5) R. Baker, R. W. Bott, C. Eaborn, and P. W. Jones, *J. Organometal. Chem.*, **1**, 37 (1963).

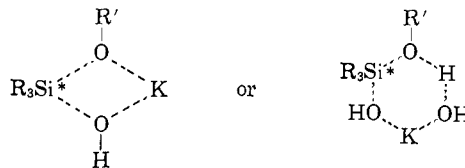
(6) L. H. Sommer, "Stereochemistry, Mechanisms and Silicon," McGraw-Hill Book Co., Inc., New York, N. Y., in press.

(7) Evidence that a  $\beta$ -hydrogen is involved in Grignard reduction of  $\equiv Si-Cl$  has been presented; see M. C. Harvey, W. H. Nebergall, and J. S. Peake, *J. Am. Chem. Soc.*, **79**, 2762 (1957).

For the special case in which  $R' = H$ , reduction with retention of configuration probably involves



The retention reactions of  $KOH_{(s)}$  with  $R_3Si^*OR'$  in xylene may involve



The latter formulation takes into account the presence of ca. 12% water in the reagent and the possibility that the  $H_2O$  coordinated to  $K^+$  ion may function as the electrophilic reagent in a xylene solvent.

It is interesting to note that the assumption of a "pyramidal" arrangement of the three R groups with respect to the silicon atom in  $S_{Ni}$ -Si transition states does not require prohibitive R-R nonbonded repulsions. It has been proposed<sup>6</sup> that the structures shown in Fig. 1 are reasonable representations of  $S_{Ni}$ -Si transition states, and simple calculation shows that the R-R distance for two R groups bonded to tetrahedral carbon (2.52 Å.) is smaller than the R-R distance for two R groups which make a  $100^\circ$  angle with Si (2.98 Å.), or even a  $90^\circ$  angle with Si (2.74 Å.). These values are for the distance between the terminal carbon atoms in different R groups, and they show that the nonbonded R-R repulsions in the tetragonal pyramidal and trigonal bipyramidal structures in Fig. 1 are not at all prohibitive. Thus, although participation of the  $3d$ -orbitals of silicon may lower the free energy of  $S_{Ni}$ -Si transition states for reactions with strong nucleophiles, the large size of silicon (covalent radius 1.17 Å.) makes such retention reactions possible and common.

**Summary of Stereochemistry.**—In Table II are collected, for convenient reference, the stereochemical paths of reactions of  $R_3Si^*OR'$ .

TABLE II  
STEREOCHEMISTRY OF REACTIONS OF  $\alpha$ -NpPhMeSi $^*OR'$

Reactant	Reagent	Product	Stereospecificity <sup>a</sup>
(+) $R_3Si^*OH$	$LiAlH_4$	(+) $R_3Si^*H$	96% retention
(+) $R_3Si^*OCH_3$	$LiAlH_4$	(+) $R_3Si^*H$	97% retention
(+) $R_3Si^*OCH_3$	$t-BuMgCl$	(+) $R_3Si^*H$	94% retention
(-) $R_3Si^*O-cyclo-C_6H_{11}$	$LiAlH_4$	(+) $R_3Si^*H$	95% retention
(-) $R_3Si^*O-cyclo-C_6H_{11}$	$t-BuMgCl$	(+) $R_3Si^*H$	76% retention
(-) $R_3Si^*O-t-C_4H_9$	$LiAlH_4$	(+) $R_3Si^*H$	91% retention
(-) $R_3Si^*O-t-C_4H_9$	$t-BuMgCl$	(+) $R_3Si^*H$	80% retention
(+) $R_3Si^*OSi^*R_3$	$LiAlH_4$	(+) $R_3Si^*H$	86% retention
(-) $R_3Si^*O(-)Men$	$LiAlH_4$	(+) $R_3Si^*H$	94% retention
(+) $R_3Si^*OCH_3$	$KOH_{(s)}$	(+) $R_3Si^*OH^b$	91% retention
(-) $R_3Si^*O-cyclo-C_6H_{11}$	$KOH_{(s)}$	(+) $R_3Si^*OH^b$	100% retention
(-) $R_3Si^*O-t-C_4H_9$	$KOH_{(s)}$	(+) $R_3Si^*OH^b$	90% retention
(+) $R_3Si^*OSi^*R_2$	$KOH_{(s)}$	(+) $R_3Si^*OH^b$	95% retention

<sup>a</sup> A stereospecificity of, say, 90% means that the product was 80% optically pure (20% racemic), if optically pure reactant was used. If the latter was not optically pure, then the stereospecificity value is adjusted accordingly. <sup>b</sup> For the  $KOH_{(s)}$  reactions, the (+) $R_3Si^*OH$  results from hydrolysis of (-) $R_3Si^*OK$ .

### Experimental

**Conversion of (+) $R_3Si^*Cl$  to  $R_3Si^*OR'$ .** (-)- $\alpha$ -Naphthylphenylmethylcyclohexoxysilane, (-) $R_3Si^*O-cyclo-C_6H_{11}$ .—A solution of 7.23 g. (0.0256 mole) of (+) $R_3Si^*Cl$ ,  $[\alpha]_D +6.10^\circ$ , was treated with excess cyclohexanol (0.0770 mole) and 10 ml.

(0.072 mole) of diisopropylamine in 150 ml. of pentane for 25 min. at room temperature. After washing with water followed by treatment with anhydrous potassium carbonate, fractional distillation gave 30% yield of  $R_3Si^*O$ -cyclo- $C_6H_{11}$ ,  $[\alpha]_D - 8.0^\circ$  ( $c$  7.5 in pentane), b.p.  $150^\circ$  (0.10 mm.),  $n_D^{25} 1.5976$ . The infrared spectrum was consistent with the assigned structure and had the following bands characteristic of the Si- $OC_6H_{11}$  group: 3.45, 3.53, 6.91, 7.30, 9.30, 10.05, 11.55, 12.10, and 14.65  $\mu$ .

*Anal.* Calcd. for  $C_{23}H_{36}SiO$ : Si, 8.11. Found: Si, 8.23.

(-)- $\alpha$ -Naphthylphenylmethyl-*t*-butoxysilane,  $(-)-R_3Si^*O-t-C_4H_9$ .—A solution of  $(+)-R_3Si^*Cl$  (0.056 mole) in 25 ml. of xylene and 25 ml. of hexane was treated with potassium *t*-butoxide (0.065 mole) in 50 ml. of *t*-butyl alcohol. After heating at  $62^\circ$  for 2–3 min., addition of 200 ml. of pentane, washing with water, and then drying, fractional distillation gave  $R_3Si^*O-t-C_4H_9$ ,  $[\alpha]_D - 28.1^\circ$  ( $c$  5.39 in pentane), b.p.  $133^\circ$  (0.10 mm.),  $n_D^{25} 1.5845$ . The infrared spectrum was consistent with the assigned structure and had the following bands characteristic of the SiOC(CH<sub>3</sub>)<sub>3</sub> moiety: 3.39, 7.21, 7.34, 8.09, 8.44, 9.60, and 9.80  $\mu$ .

*Anal.* Calcd. for  $C_{21}H_{24}SiO$ : Si, 8.75. Found: Si, 8.84.

(+)-1,3-Di- $\alpha$ -naphthyl-1,3-diphenyl-1,3-dimethyldisiloxane,  $(+)-R_3Si^*OSi^*R_3$ .—A solution of 1.08 g. (3.82 mmoles) of  $(+)-R_3Si^*Cl$  in 10 ml. of xylene was added to a solution of  $(-)-R_3Si^*OK$  (3.82 mmoles) in 11.1 ml. of xylene. A precipitate of KCl formed immediately and heat was evolved. Addition of 20 ml. of pentane, washing with water, drying, and removal of solvents followed by crystallization from isopropyl alcohol gave 1.2 g. of crystalline  $R_3Si^*OSi^*R_3$ , m.p.  $89^\circ$ ,  $[\alpha]_D + 9.9^\circ$  ( $c$  8.1 in hexane), which had the characteristic Si–O–Si band at 9.55  $\mu$  in the infrared.

*Anal.* Calcd. for  $C_{34}H_{30}Si_2O$ : Si, 11.00. Found: Si, 11.10.

(-)- $\alpha$ -Naphthylphenylmethyl-(-)-menthoxysilane,  $(-)-R_3Si^*O(-)Men$ , and Its Reduction.—Treatment of  $(+)-R_3Si^*Cl$  with (-)-menthol according to the procedure described above for  $R_3Si^*O$ -cyclo- $C_6H_{11}$  gave  $(-)-R_3Si^*O(-)Men$  which was difficult to free from admixture with excess (-)-menthol. The impure product was reduced with lithium aluminum hydride, according to the procedure described below for reduction of  $(-)-R_3Si^*O$ -cyclo- $C_6H_{11}$ , and gave  $(+)-R_3Si^*H$  having  $[\alpha]_D + 33^\circ$ . Since the synthesis of  $(+)-R_3Si^*H$  involves reduction of  $(-)-R_3Si^*O(-)Men$ ,<sup>1</sup> it is certain that the latter is the diastereoisomer formed from treatment of  $(+)-R_3Si^*Cl$  with (-)-menthol.

Conversions of  $R_3Si^*OR'$  to  $(+)-R_3Si^*H$ . Reduction of  $(+)-R_3Si^*OCH_3$ .—Reduction of the methoxysilane to  $(+)-R_3Si^*H$  with lithium aluminum hydride has been reported.<sup>1</sup>

Grignard reduction was carried out by addition of  $(+)-R_3Si^*OCH_3$  (3.6 mmoles) to excess *t*-butylmagnesium chloride (0.1 mole) in ether, followed by distillation of the ether and heating at  $92^\circ$  for 12 hr. After hydrolysis with acid, drying, and removal of solvents, the product was purified by chromatography over silica gel. Elution with 10% benzene-pentane gave an 86% yield of  $(+)-R_3Si^*H$ ,  $[\alpha]_D + 30^\circ$ , identified by infrared spectrum.<sup>1</sup> During the reduction, isobutylene was evolved and identified by conversion to the dibromo derivative.

Reduction of  $(-)-R_3Si^*O$ -cyclo- $C_6H_{11}$ .—Reduction of the cyclohexoxysilane (1.76 mmoles) with excess lithium aluminum hydride (0.21 equiv.) was carried out in a solvent which consisted of 30 ml. of ethyl ether and 30 ml. of di-*n*-butyl ether at the start. Heating and removal of diethyl ether during 2 hr. was followed

by a reaction temperature of  $110$ – $140^\circ$  during 3 hr. After hydrolysis, drying, and removal of solvents, there was obtained a dextrorotatory oil which upon chromatography over silica gel furnished 0.30 g. (68% yield) of  $(+)-R_3Si^*H$ ,  $[\alpha]_D + 31^\circ$ .

Grignard reduction of  $(-)-R_3Si^*O$ -cyclo- $C_6H_{11}$  was carried out as described for  $(+)-R_3Si^*OCH_3$ , except that heating was carried out for 28 hr. Even after this period of time, the  $(+)-R_3Si^*H$  product,  $[\alpha]_D + 18^\circ$ , was contaminated with about 10–20% of the starting material, as indicated by an infrared spectrum.

Reduction of  $(-)-R_3Si^*O-t-C_4H_9$ .—The reduction with lithium aluminum hydride was carried out as described for the cyclohexoxysilane except that the reaction mixture was heated for 3 days at  $95$ – $100^\circ$ . An infrared spectrum of the crude product showed that only a small amount of reduction had taken place. By a combination of fractional distillation and chromatography over silica gel, there was finally obtained 0.94 g. (4.5% yield) of  $(+)-R_3Si^*H$ ,  $[\alpha]_D + 28^\circ$ ; an infrared spectrum confirmed the structure.

Like the lithium aluminum hydride reduction, Grignard reduction of the *t*-butoxysilane proved to be a very slow reaction. After heating of the reactants for 5 days, the isolated  $R_3Si^*H$  had  $[\alpha]_D + 20^\circ$ ; its structure was confirmed by an infrared spectrum.

Reduction of  $(+)-R_3Si^*OSi^*R_3$ .—The lithium aluminum hydride reduction was carried out by the procedure described above for the *t*-butoxysilane, except that the reactants were heated for 3 days at  $110^\circ$  and then at  $143^\circ$  for 8 hr. There was obtained a 42% yield of  $(+)-R_3Si^*H$ ,  $[\alpha]_D + 24^\circ$ .

Reactions of  $R_3Si^*OR'$  with KOH<sub>(s)</sub>. Reaction of  $(+)-R_3Si^*OCH_3$ .—To a 50-ml. flask were added 6 g. (0.1 mole) of powdered potassium hydroxide, 10 ml. of xylene, and 0.45 g. (1.62 mmoles) of  $(+)-R_3Si^*OCH_3$ ,  $[\alpha]_D + 15.6^\circ$  ( $c$  9.65 in pentane). The flask, protected from atmospheric moisture, was heated for 45 min. on the steam bath before measuring the specific rotation of the supernatant liquid,  $[\alpha] - 68^\circ$  ( $c$  4.7 in xylene). Hydrolysis yielded 0.38 g. (88% yield) of  $(+)-R_3Si^*OH$ ,  $[\alpha]_D + 16.4^\circ$  ( $c$  2.25 in ether); an infrared spectrum of this material was identical with that of authentic silanol.<sup>1</sup>

Reaction of  $(-)-R_3Si^*O$ -cyclo- $C_6H_{11}$ .—The procedure used for  $R_3Si^*OCH_3$  was followed except that the reactants were heated for 90 min. Hydrolysis gave a 90% yield of  $(-)-R_3Si^*OH$  having  $[\alpha]_D + 20^\circ$  ( $c$  3.2 in ether).

Reaction of  $(-)-R_3Si^*O-t-C_4H_9$ .—The usual procedure and a heating period of 10 hr. gave, after hydrolysis, an 85% yield of  $(+)-R_3Si^*OH$  having  $[\alpha]_D + 16^\circ$  ( $c$  3.2 in ether).

Reaction of  $(+)-R_3Si^*OSi^*R_3$ .—To a 50-ml. flask were added 4 g. (0.07 mole) of powdered potassium hydroxide, 10 ml. of xylene, and 0.82 g. (1.60 mmoles) of  $(+)-R_3Si^*OSi^*R_3$ ,  $[\alpha]_D + 8.5^\circ$  ( $c$  5.02, pentane). The flask was heated for 1 hr. on the steam bath. The supernatant liquid was transferred to a polarimeter tube. Assuming a quantitative conversion to the silanolate, the specific rotation of  $R_3Si^*OK$  was  $[\alpha]_D - 64^\circ$  ( $c$  4.53 in xylene). Hydrolysis yielded 0.80 g. of  $(+)-R_3Si^*OH$ ,  $[\alpha]_D + 16.2^\circ$  ( $c$  1.35 in ether), whose identification was confirmed by an infrared spectrum.

Reaction of  $(\pm)R_3SiO(-)Men$ .—By the usual procedure, involving a xylene solvent and heating for 24 hr. on the steam bath, there was obtained an 86% yield of optically pure  $(-)-menthol$ .

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