ORGANIC AND BIOLOGICAL CHEMISTRY

Stereochemistry of Asymmetric Silicon.   I.   Relative and Absolute Configurations of Optically Active α-Naphthylphenylmethylsilanes[1]

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Correlations of configuration for seven key compounds containing the α-naphthylphenylmethylsilyl group, R_3Si^*-, are reported.   In turn these lead to elucidation of the stereochemistry of some fourteen reactions of optically active R_3Si^*X compounds.   Absolute configurations, based on X-ray results, are also reported.

It is clear that stereochemical studies of organic reactions have contributed greatly to our knowledge of the mechanisms of substitution of carbon compounds. However, prior to 1958, it was not even known whether substitution reactions at silicon atoms are stereospecific.   Resolutions of three organosilicon compounds, only two of which contained relatively unreactive functional groups bonded to silicon, had been carried out by the pioneer of organosilicon chemistry, F. S. Kipping, but the routes to these optically active compounds were tedious and lengthy, the amounts obtained were small, and the optical rotations were feeble.   Furthermore, these substances had the serious disadvantage of sulfonic acid groups bonded to carbon.[2]   For the purpose of carrying out stereochemical studies of asymmetric silicon in organosilicon molecules, it was desirable to have optically active compounds which do not contain reactive functional groups bonded to carbon because of probable reactions between the functional groups on carbon and silicon.[3]

The condition that organosilicon structures suitable for stereochemical studies should have no reactive functional groups bonded to carbon imposed the requirement that resolution be effected by separation of diastereoisomers in which the silicon atom is directly linked to an optically active group provided by the resolving agent.   This requirement was met by separation of the diastereomeric α-naphthylphenylmethyl-(−) menthoxysilanes, $R_3Si^*(−)OMen$, which were prepared as

$$(\pm)R_3SiOCH_3 + (−) \text{ menthol} \xrightarrow{\text{KOH}_{(s)}} (−)R_3Si^*(−)OMen + (+)R_3Si^*(−)OMen$$
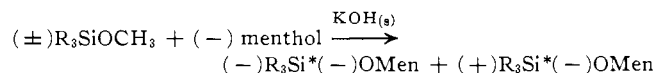
The sirupy mixture of diastereoisomers was dissolved in pentane and cooled to −78°.   The higher-melting less soluble diastereoisomer was obtained in good yield and had m.p. 82–84°, $[\alpha]D$ −53.9° (cyclohexane).   This diastereoisomer is designated $(−)R_3Si^*(−)OMen$, (−)-α-naphthylphenylmethyl-(−)-menthoxysilane.   The lower-melting more soluble diastereoisomer was purified by repeated recrystallization from ethyl alcohol and

(1) For preliminary publications dealing with optically active α-naphthylphenylmethylsilanes, see: L. H. Sommer and C. L. Frye, J. Am. Chem. Soc., **81**, 1013 (1959); L. H. Sommer and C. L. Frye, ibid., **82**, 3796 (1960); L. H. Sommer and C. L. Frye, ibid., **82**, 4118 (1960); L. H. Sommer, C. L. Frye, M. C. Musolf, G. A. Parker, P. G. Rodewald, K. W. Michael, Y. Okaya, and R. Pepinsky, ibid., **83**, 2210 (1961); L. H. Sommer, Angew. Chem. Intern. Ed. Engl. 143 (1962).

(2) F S Kipping and co-workers. J. Chem. Soc., 209 (1917); 2090 (1908); 705 (1910).

(3) Preparation of an optically active organosilicon compound not having a reactive functional group on silicon, p-carboxyphenylmethylethylsilane, has been reported more recently: C. Eaborn and C. Pitt, Chem. Ind. (London). 830 (1958).

had m.p. 56.5–59°, $[\alpha]D$ −47° (cyclohexane).   This diastereoisomer is designated $(+)R_3Si^*(−)OMen$, (+)-α-naphthylphenylmethyl-(−)-menthoxysilane.

Lithium aluminum hydride reduction of the separated diastereoisomers proceeded

$$(−)R_3Si^*(−)OMen + LiAlH_4 \longrightarrow (+)R_3Si^*H$$

$$(+)R_3Si^*(−)OMen + LiAlH_4 \longrightarrow (−)R_3Si^*H$$
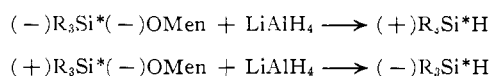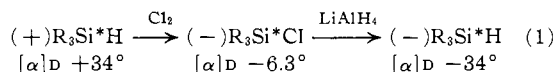
From the optically active α-naphthylphenylmethylsilanes, R_3Si^*H, it has proved possible to prepare many optically active derivatives, R_3Si^*X.
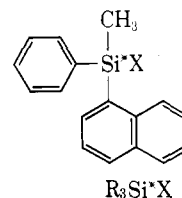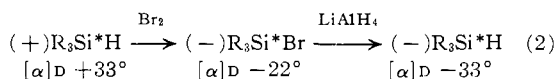

$$R_3Si^*X$$

In order that the stereochemistry of reactions of R_3Si^*X compounds might become known, it was necessary to establish correlations of configurations between different R_3Si^*X compounds.   The discussion which follows deals with the problem of relative configurations for six key R_3Si^*X compounds.   Experimental detail for fourteen stereospecific reactions of these compounds is reported for the first time.
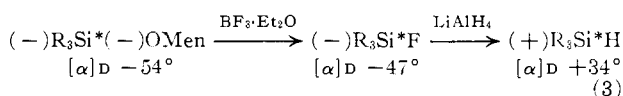
Relative and Absolute Configurations of R_3Si^*X.— Treatment of $(+)R_3Si^*H$ with chlorine in carbon tetrachloride solvent gave $(−)R_3Si^*Cl$, and reduction of the latter with lithium aluminum hydride gave $(−)R_3Si^*H$.   Both reactions proceed with a high degree of stereospecificity and comprised the first example of a Walden cycle involving silicon.

$$(+)R_3Si^*H \xrightarrow{Cl_2} (−)R_3Si^*Cl \xrightarrow{LiAlH_4} (−)R_3Si^*H \quad (1)$$
$$[\alpha]D\ +34° \qquad [\alpha]D\ −6.3° \qquad [\alpha]D\ −34°$$

A similar cycle has also been found for reactions of R_3Si^*H with bromine.

$$(+)R_3Si^*H \xrightarrow{Br_2} (−)R_3Si^*Br \xrightarrow{LiAlH_4} (−)R_3Si^*H \quad (2)$$
$$[\alpha]D\ +33° \qquad [\alpha]D\ −22° \qquad [\alpha]D\ −33°$$

Reduction of R_3Si^*F, obtained by treatment of $(−)R_3Si^*(−)OMen$ with boron trifluoride etherate, furnished R_3Si^*H of high optical purity.

$$(−)R_3Si^*(−)OMen \xrightarrow{BF_3 \cdot Et_2O} (−)R_3Si^*F \xrightarrow{LiAlH_4} (+)R_3Si^*H$$
$$[\alpha]D\ −54° \qquad [\alpha]D\ −47° \qquad [\alpha]D\ +34°$$
$$(3)$$

Hydrolysis and methanolysis of R_3Si*Cl are components of three-step Walden cycles.

$$(+)R_3Si*H \xrightarrow[\text{ether}]{H_2O} (-)R_3Si*OH \xrightarrow{LiAlH_4} (-)R_3Si*H$$
$$[\alpha]_D -20° \qquad [\alpha]_D -33°$$

$$\downarrow Cl_2$$

$$(-)R_3Si*Cl \xrightarrow[\substack{\text{pentane} \\ \text{amine}}]{MeOH} (-)R_3Si*OCH_3 \xrightarrow{LiAlH} (-)R_3Si*H \qquad (4)$$
$$[\alpha]_D -16° \qquad [\alpha]_D -30°$$
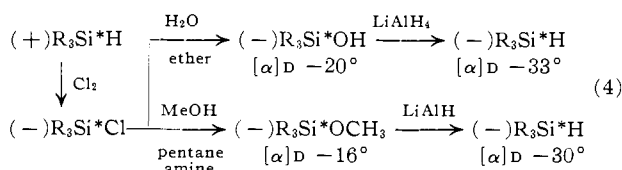
It is clear that the ten displacement reactions of R_3Si*X in sequences 1–4 above are quite stereospecific. However, the above reactions do not, of course, reveal the stereochemical paths which are being followed.

Thus, 63 years after the discovery of the first Walden cycle for carbon,[4] similar cycles were found for silicon and the problem of the Walden cycle, *i.e.*, deciding which reactions in such a cycle are inversions and which are retentions, confronted us. In organic chemistry the problem of the first Walden cycle remained unsolved for at least 40 years.[5] In organosilicon chemistry, the process has been greatly accelerated by the use of modern chemical and physical methods.

One of the most widely used methods for correlating configurations of compounds having closely similar structures is the Fredga method based on differences in phase behavior[6] and this technique seemed ideal for comparison of some key, optically active α-naphthylphenylmethylsilanes: R_3Si*H, R_3Si*F, and R_3SiCl.

The Fredga method as applied by K. Mislow has provided many fruitful results in recent years, and the pertinent case observed in the present work is his "case 2"[7] in which pure optical isomers of two different substances that are isomorphous give solid solutions when they are of the same configuration, and a eutectic when they are of opposite configuration.

In the present work X-ray diffraction[8] provided clear and consistent answers for R_3Si*F, R_3Si*H, and R_3Si*Cl. (1) Solid solutions are formed by $(-)$-R_3Si*F and $(-)R_3Si*H$, by $(-)R_3Si*F$ and $(+)$-R_3Si*Cl, and by $(-)R_3Si*H$ and $(+)R_3Si*Cl$. (2) Eutectic mixtures are formed by $(+)R_3SiF$ and $(-)$-R_3Si*H, by $(+)R_3Si*F$ and $(+)R_3Si*Cl$, and by $(+)$-R_3Si*H and $(+)R_3Si*Cl$.

Optically active R_3Si*H, R_3Si*F, and R_3Si*Cl crystallize individually in the orthorhombic system with space group $P2_12_12_1$; an example of perfect isomorphism is observed. The three mixtures (1) also crystallize in the orthorhombic system and are isomorphous with the pure component compounds; no doubling of the unit cell dimensions or change in the symmetry is observed.

In Table I the crystallographic constants for the pure enantiomers and for the solid solutions (1) are listed.

By comparing the intensities of diffracted X-rays from the mixed crystals with those from the pure

(4) P. Walden, *Ber.*, **28**, 1287, 2766 (1895).

(5) *Cf.* C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, p. 373.

(6) See A. Fredga in "Thé Svedberg," Almqvist and Wikesells, Uppsala, 1944, p. 261; J. Timmermans, *J. chim. phys.*, **49**, 162 (1952). Conclusions drawn on the basis of a *difference* in phase behavior have proved accurate without exception.

(7) K. Mislow and M. Heffler, *J. Am. Chem. Soc.*, **74**, 3668 (1952). For a recent application of "case 2" for determination of the configurational relationships between the pure enantiomers of 3-thioloctanedioic acid and 3-methyloctanedioic acid see K. Mislow and W. C. Meluch, *ibid.*, **78**, 5920 (1956). For other examples see J. Timmermans, ref. 6.

(8) We are indebted to Y. Okaya and R. Pepinsky, Department of Physics, The Pennsylvania State University, for the X-ray results.

component crystals, it is concluded that a random distribution of the component molecules in the crystal is observed for each mixture in (1). A partial list of the two-dimensional reflections used for the criteria is given in Table II.

TABLE I
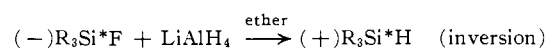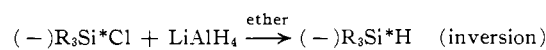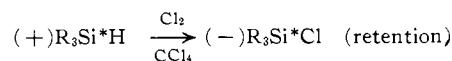
CRYSTALLOGRAPHIC CONSTANTS OF THE PURE AND MIXED CRYSTALS

	a	b	c	Space group
$(-)R_3Si*H$	8.80	20.19	8.00	$P2_12_12_1$
$(-)R_3Si*F$	8.80	19.85	8.00	$P2_12_12_1$
$(+)R_3Si*Cl$	8.84	19.68	8.10	$P2_12_12_1$
$(-)R_3Si*H + (-)R_3Si*F^a$	9.00	20.22	8.15	$P2_12_12_1$
$(-)R_3Si*H + (+)R_3Si*Cl^a$	8.85	20.20	8.20	$P2_12_12_1$
$(-)R_3Si*F + (+)R_3Si*Cl^a$	8.82	19.80	8.40	$P2_12_12_1$

a These data are for equimolar mixtures.

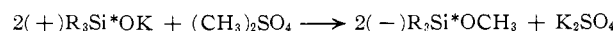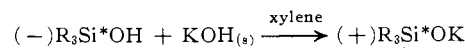### TABLE II

PARTIAL LIST OF REFLECTIONS USED FOR CRITERIA

Reflections	$(-)Si*H$	Mixture	$(-)Si*F$
	For $(-)R_3Si*H + (-)R_3SiF$		
080	Strong	Medium	Weak
600	Strong	Medium	Weak
120	Very weak	Medium	Strong
330	Medium	Weak	Too weak to be obsd.
	$(-)Si*H$		$(+)Si*Cl$
	For $(-)R_3Si*H + (+)R_3Si*Cl$		
0,10,2	Very strong	Medium	Very weak
0,11,2	Very weak	Weak	Medium
	$(-)SiF$		$(+)$-SiCl
	For $(-)SiF + (+)SiCl$		
080	Weak	Medium	Strong
0,10,0	Strong	Medium	Very weak

From the X-ray data it is clear that $(-)R_3Si*H$, $(-)R_3Si*F$, and $(+)R_3Si*Cl$ have the same configuration and that the following reactions proceed by the given stereochemical paths

$$(+)R_3Si*H \xrightarrow[CCl_4]{Cl_2} (-)R_3Si*Cl \quad \text{(retention)}$$

$$(-)R_3Si*Cl + LiAlH_4 \xrightarrow{\text{ether}} (-)R_3Si*H \quad \text{(inversion)}$$

$$(-)R_3Si*F + LiAlH_4 \xrightarrow{\text{ether}} (+)R_3Si*H \quad \text{(inversion)}$$

For elucidation of the stereochemistry of other reactions of optically active α-naphthylphenylmethylsilanes given above, there remains the task of correlation of configuration of R_3Si*H, R_3Si*F, and R_3Si*Cl with R_3Si*Br, R_3Si*OH, and $R_3Si*OCH_3$.

Chemical correlation of configuration for $(-)R_3Si*$-OH and $(-)R_3Si*OCH_3$ was achieved by application of the technique introduced into organic chemistry by Phillips and Kenyon.[9]

$$(-)R_3Si*OH + KOH_{(s)} \xrightarrow{\text{xylene}} (+)R_3Si*OK$$

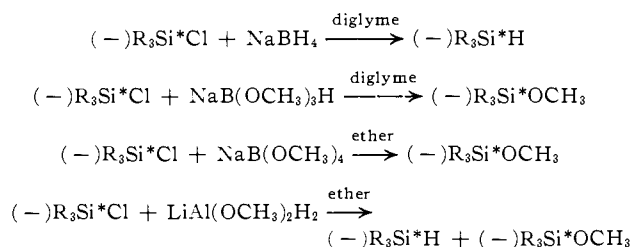$$2(+)R_3Si*OK + (CH_3)_2SO_4 \longrightarrow 2(-)R_3Si*OCH_3 + K_2SO_4$$

The asymmetric center is not affected in the above reactions.

The most direct evidence for correlation of con-

(9) H. Phillips and J. Kenyon, *J. Chem. Soc.*, **123**, 64 (1923); H. Phillips and H. G. Turley, *ibid.*, **127**, 399 (1925), and subsequent papers.

figuration for R_3Si^*H and $R_3Si^*OCH_3$ is provided by the reactions

$$(-)R_3Si^*Cl + NaBH_4 \xrightarrow{\text{diglyme}} (-)R_3Si^*H$$

$$(-)R_3Si^*Cl + NaB(OCH_3)_3H \xrightarrow{\text{diglyme}} (-)R_3Si^*OCH_3$$

$$(-)R_3Si^*Cl + NaB(OCH_3)_4 \xrightarrow{\text{ether}} (-)R_3Si^*OCH_3$$

$$(-)R_3Si^*Cl + LiAl(OCH_3)_2H_2 \xrightarrow{\text{ether}}$$
$$(-)R_3Si^*H + (-)R_3Si^*OCH_3$$

The close similarity of the above reactions justifies the conclusion that $(-)R_3Si^*H$ and $(-)R_3Si^*OCH_3$ have the same configuration and, in view of the other correlations of configuration already given above, this means that $(-)R_3Si^*H$, $(-)R_3Si^*F$, $(+)R_3Si^*Cl$, $(-)R_3Si^*OH$, and $(-)R_3Si^*OCH_3$ all have the same configuration. Also, comparison of the above Walden cycles involving chlorination and bromination of R_3Si^*H leads to the conclusion that $(-)$-R_3Si^*Br and $(-)R_3Si^*Cl$ have the same configuration.

We turn next to another line of evidence which bears on the problem of correlations of configuration. Compared to the α-naphthyl, phenyl, and methyl groups, the -F and -OH groups have smaller polarizabilities and atomic refractions of the atoms directly attached to silicon. Other things being equal, this would lead to assignment of the same configuration to R_3Si^*F and R_3Si^*OH of like sign of rotation, on the basis of Brewster's rules of atomic asymmetry.[10] Furthermore, -F and -OH have considerably smaller steric requirements than α-naphthyl, phenyl, and methyl. Examination of accurately scaled molecular models clearly shows that the hydrogen atom on the naphthalene nucleus in the *peri* position relative to the silicon atom causes considerable "crowding" in its vicinity. Maximum freedom of intramolecular rotation is achieved when the *peri* hydrogen is flanked by the two groups of the remaining three that have the smallest steric requirements. Thus the change from -F to -OH should not significantly alter the free-rotational, conformational distribution. In sum, on the basis of polarizability and steric considerations R_3Si^*F and R_3Si^*OH of like sign rotation should have the same configuration. In fact, the optical rotatory dispersion curves are quite similar for $(-)R_3Si^*F$ and $(-)R_3Si^*OH$. Both are levorotatory from 589 to 340 mμ. In cyclohexane solvent the following data[11] were obtained: $(-)R_3Si^*F$ had $[\alpha]_{589}$ $-33°$, $[\alpha]_{400}$ $-108°$, $[\alpha]_{340}$ $-220°$; $(-)$-R_3Si^*OH had $[\alpha]_{589}$ $-21°$, $[\alpha]_{400}$ $-131°$, $[\alpha]_{337}$ $-314°$. In the same connection it is interesting to note the following data for $(-)R_3Si^*H$ which has the same configuration as $(-)R_3Si^*F$: $(-)R_3Si^*H$ had $[\alpha]_{589}$ $-30°$, $[\alpha]_{400}$ $-100°$, $[\alpha]_{360}$ $-140°$, $[\alpha]_{340}$ $-160°$.

On steric grounds, comparison of rotation for R_3Si^*F with that of R_3Si^*H might seem more appropriate than comparison with R_3Si^*OH. However, on polarizability grounds, the situation for comparison of R_3Si^*F with R_3Si^*H is clouded by a reversal in order for -H and $-C_{alkyl}$ when comparing bond refractions,[12]

(10) J. H. Brewster, *J. Am. Chem. Soc.*, **81**, 5475 (1959).

(11) Optical rotatory dispersion data were obtained with a recently reported apparatus: K. Kirschner, A. J. Sonnesa, D. C. Bhatnagar, and D. May, Abstracts 138th National Meeting of the American Chemical Society, Sept., 1960, p. 14N.

(12) E. L. Warrick, *J. Am. Chem. Soc.*, **68**, 2455 (1946).

$Si-C_{alkyl}$ = 2.52 and $Si-H$ = 3.17; with atomic refractions,[13] C (in CH_2) = 2.51 and H (in CH_2) = 1.028. For -F and -O, bond refractions are: $Si-F$ = 1.50, $Si-O$ = 1.75; atomic refractions are: F = 0.81, -O = 1.52. Thus, bond refractions and atomic refractions both indicate that -F and -O on silicon have smaller polarizabilities than $-C_{alkyl}$. Both bond and atomic refraction data indicate greater polarizability for the terminal atom in C_{aryl} as compared to C_{alkyl}. Thus, correlation of configuration for $(-)R_3Si^*F$ and $(-)R_3Si^*OH$ by optical rotatory dispersion strongly supports the above assignment of the same configuration to $(-)R_3Si^*H$, $(-)R_3Si^*F$, $(+)R_3Si^*Cl$, $(-)R_3Si^*$-OH, and $(-)R_3Si^*OCH_3$.[14]

In an earlier preliminary publication,[15] optical rotatory dispersion data were given for wave lengths down to 315 mμ. The present use of data down to 340 mμ avoids the hazard of possible errors introduced by incursion of high absorbance due to the naphthyl group at lower wave lengths.[16]

In Table III are listed the enantiomers which have been assigned the $(+)R_3Si^*H$ configuration on the basis of evidence presented in this paper.

TABLE III
ENANTIOMERS HAVING THE $(+)R_3Si^*H$ CONFIGURATION

Compound	$[\alpha]_D$, solvent	M.p., °C.
$(+)R_3Si^*H$	$+34°$, pentane	64
$(+)R_3Si^*OH$	$+20°$, ether	Liq.
$(+)R_3Si^*OCH_3$	$+17°$, pentane	64
$(+)R_3Si^*F$	$+47°$, pentane	68
$(-)R_3Si^*Cl$	$-6.3°$, pentane	64
$(-)R_3Si^*Br$	$-22°$, pentane	54
$(-)R_3Si^*OK$	$-75°$, xylene	

In Table IV are given the stereochemical paths for fourteen substitution reactions of R_3Si^*X based on those assignments.

TABLE IV
STEREOSPECIFIC REACTIONS OF R_3Si^*X

Reactant	Reagent	Product	Stereo-chemistry
$(+)R_3Si^*H$	Cl_2	$(-)R_3Si^*Cl$	Retention
$(-)R_3Si^*Cl$	$LiAlH_4$	$(-)R_3Si^*H$	Inversion
$(+)R_3Si^*H$	Br_2	$(-)R_3Si^*Br$	Retention
$(-)R_3Si^*Br$	$LiAlH_4$	$(-)R_3Si^*H$	Inversion
$(-)R_3Si^*Cl$	H_2O	$(-)R_3Si^*OH$	Inversion
$(-)R_3Si^*Cl$	CH_3OH	$(-)R_3Si^*OCH_3$	Inversion
$(-)R_3Si^*F$	$LiAlH_4$	$(+)R_3Si^*H$	Inversion
$(-)R_2Si^*OH$	$LiAlH_4$	$(-)R_3Si^*H$	Retention
$(-)R_3Si^*OCH_3$	$LiAlH_4$	$(-)R_3Si^*H$	Retention
$(-)R_3Si^*Cl$	$NaBH_4$	$(-)R_3Si^*H$	Inversion
$(-)R_3Si^*Cl$	$NaB(OCH_3)_3H$	$(-)R_3Si^*OCH_3$	Inversion
$(-)R_3Si^*Cl$	$NaB(OCH_3)_4$	$(-)R_3Si^*OCH_3$	Inversion
$(-)R_3Si^*Cl$	$LiAl(OCH_3)_2H_2$	$(-)R_3Si^*H$	Inversion
$(-)R_3Si^*Cl$	$LiAl(OCH_3)_2H_2$	$(-)R_3Si^*OCH_3$	Inversion

We turn now to the problem of absolute configuration of optically active R_3Si^*X compounds. A recent report on the application of rigorous X-ray methods to

(13) A. Vogel, *ibid.*, **70**, 1833 (1948).

(14) Investigation of optical rotatory dispersion curves of R_3Si^*X compounds whose relative configurations are known from other data is still in progress. Present data indicate that conclusions concerning relative configuration based on optical rotatory dispersion curves must be drawn with great circumspection and must take into account important contributing factors such as polarizabilities, free-rotational conformation distribution, and others.

(15) L. H. Sommer, *et al.*, *J. Am. Chem. Soc.*, **83**, 2210 (1961).

(16) Private communication from K. Mislow.

the problem[17] shows that the *dextrorotatory* R_3Si*H and R_3Si*F have the configuration

Ph
|
α-Np—Si—Me
|
H

$(+)R_3Si*H$

Ph
|
α-Np—Si—Me
|
F

$(+)R_3Si*F$

These studies confirm the results of application of the Fredga method to the relative configurations of R_3Si*F and R_3Si*H and, in combination with correlations in Table III, provide the absolute configurations of many optically active organosilicon compounds.[18]

Experimental

Racemic α-Naphthylphenylmethylmethoxysilane.—The Grignard reagent was prepared from 6.0 moles of α-bromonaphthalene in a solvent mixture containing ether (400 ml.), benzene (600 ml.), and tetrahydrofuran (200 ml.). It is important to avoid the presence of β-bromonaphthalene in more than trace amounts. Substantial contamination by β-naphthylsilanes causes great difficulty in the subsequent separation of diastereoisomers.

Phenylmethyldimethoxysilane (6.0 moles), supplied by Dow Corning Corp., was added to the Grignard reagent. Stirring overnight at 55° was followed by treatment with cold aqueous ammonium chloride, washing with water, drying over sodium sulfate, and subsequent removal of solvents. Distillation gave 1341 g. (80% yield) of α-naphthylphenylmethylmethoxysilane, b.p. 143–146° (0.15 mm.) and m.p. 62.5–63.5° (after recrystallization from hexane).

Anal. Calcd. for $C_{18}H_{18}SiO$: Si, 10.10; mol. wt., 278. Found: Si, 10.25; mol. wt. (cryoscopically in benzene), 274.

The α-naphthylphenylmethylsilyl group, α-NpPhMeSi–, has characteristic infrared absorption maxima which are found in all of the more than 50 derivatives thus far prepared. Because infrared spectra serve as a valuable aid in the characterization of such derivatives, it is of interest to tabulate the absorption bands of the four substituents in α-naphthylphenylmethylmethoxysilane: CH_3OSi at 3.43, 3.55, 8.40, and 9.20 μ; α-$C_{10}H_7Si$ at 6.30, 6.65, 8.20, 8.70, and 10.15 μ; C_6H_5Si at 7.00, 8.97, and 14.30 μ; and CH_3Si at 7.97 μ.

Diastereomeric α-Naphthylphenylmethyl-($-$)-methoxysilanes. Into a 1-l. distillation flask were placed 278 g. (1.00 mole) of α-naphthylphenylmethylmethoxysilane, 78 g. (0.5 mole) of ($-$)-menthol, 0.093 g. of solid potassium hydroxide, and 175 ml. of toluene. The reaction mixture was maintained at 135–145° for 6 hr. while the methanol–toluene azeotrope (69% methanol, b.p. 63.8°) was distilled through a fractionating column. After removal of the basic catalyst by passing the product through a column of silica gel, fractional distillation gave a 97% yield (195.5 g.) of the diastereomeric α-naphthylphenylmethyl-($-$)-menthoxysilanes as a viscous sirup having b.p. 173–177° (0.07 mm.) and $n^{25}D$ 1.5751. This material had an infrared spectrum virtually identical with that of the crystalline, separated diastereoisomers described below.

Separation of the Diastereoisomers.—The sirupy mixture of diastereoisomers was diluted with twice its own volume of pentane and chilled overnight in a Dry Ice–acetone bath. This gave 116 g. of crude crystals. Recrystallization from pentane gave 90 g. of material, m.p. 82–84°. This material comprised 46% of the original ($-$)-menthoxysilane sirup and had a specific rotation of $[\alpha]D$ $-53.9°$ (c 11.32 in cyclohexane). The infrared spectrum clearly showed the presence of the α-NpPhMeSi– group.

Anal. Calcd. for $C_{27}H_{34}SiO$: Si, 6.97; mol. wt., 402. Found: Si, 7.07; mol. wt. (cryoscopically in benzene), 398.

The ($-$)-menthoxysilane sirup (106 g.) remaining after removal of the less soluble diastereomer was evacuated free of pentane and then taken up in twice its volume of absolute ethanol. Refrigeration for several days gave a deposit of 70 g. of crude crystals, m.p. 50–55°. One of many recrystallizations produced large well-formed crystals, m.p. 56.5–59°, $[\alpha]D$ $-47°$ (c 1.40 in

cyclohexane). It is fairly difficult to free the lower-melting isomer from admixture with the higher-melting diastereomer.

The diastereomeric relationship of the higher- and lower-melting isomers is indicated by their infrared spectra, and by the enantiomeric relationship of the silanes resulting from their reduction with lithium aluminum hydride.

Preparation of ($+$)-α-Naphthylphenylmethylsilane.—A solution of 35 g. (3.7 equiv.) of lithium aluminum hydride in 400 ml. of ether was prepared and then 300 g. (0.745 mole) of ($-$)-α-naphthylphenylmethyl-($-$)-menthoxysilane (m.p. 82–84°) and 400 ml. of di-*n*-butyl ether were added. Diethyl ether was removed by distillation until the reaction temperature reached 80°. Heating at 80–90° was continued for 18 hr. After decomposition of excess metallic hydride with acetone, treatment with crushed ice and concentrated hydrochloric acid was followed by drying over sodium sulfate. Solvents and ($-$)-menthol were removed by distillation up to a head temperature of 151° (1.5 mm.) and a still temperature of 170°. Crystallization of the product gave 178 g. (96% yield) of ($+$)-α-naphthylphenylmethylsilane, m.p. 60–62°. Recrystallization from pentane yielded 169 g. (91% yield) of material, m.p. 61.5–63°, $[\alpha]D$ $+33.4°$ (c 8.00 in cyclohexane). Repeated recrystallization of a portion from hexane raised the melting point to 63.5–64.5°. The specific rotation of this latter material was determined in cyclohexane at three concentrations: $[\alpha]D$ $+33.7°$ (c 4.00), $+34.3°$ (c 10.9), and $+35.0°$ (c 15.6). From this, the above 169 g. are seen to be 98% optically pure (racemic α-naphthylphenylmethylsilane, m.p. 42°, comprises a low-melting eutectic which is separable from active silane by crystallization.) It is assumed that at least half of the silane not recovered (*i.e.*, the theoretical yield of 185 g. less the above 169 g.), or 8 g., was also dextrorotatory. This means that about 174 g. (*i.e.*, 98% of the 169 g. plus the additional 8 g.) of ($+$)-silane was formed and that the reduction is at least 94% stereospecific. The infrared spectrum provided positive proof of structure since it showed an absorption band characteristic of the α-NpPhMeSi– group as well as the strong band at 4.70 μ characteristic of the Si–H group.

Anal. Calcd. for $C_{17}H_{16}Si$: Si, 11.30, H($-$Si), 0.406; mol. wt., 248. Found: Si, 11.4; H($-$Si), by measurement of H_2 volume given with base, 0.415; mol. wt. (cryoscopically in benzene), 244. H($-$Si) refers only to the hydrogen attached to silicon.

Preparation of ($-$)-α-Naphthylphenylmethylsilane.—By a procedure similar to that used for the preparation of the ($+$)-silane, 11.83 g. (0.0295 mole) of ($+$)-α-naphthylphenylmethyl-($-$)-methoxysilane (m.p. 53–56°) was reduced with lithium aluminum hydride and gave 6.25 g. (88% yield) of material, m.p. 56–59°. The infrared spectrum of this material was identical in all respects with that of ($+$)-α-naphthylphenylmethylsilane. Recrystallization from pentane several times furnished 3.03 g. of crystals, m.p. 61.5–62.5°, $[\alpha]D$ -32.8 (c 6.07 in cyclohexane).

Preparation of ($-$)-α-Naphthylphenylmethylchlorosilane.—A solution of 9.92 g. (0.0400 mole) of ($+$)-α-naphthylphenylmethylsilane, $[\alpha]D$ $+33.4°$ (c 8.00 in cyclohexane), 98% optically pure, in 40 ml. of carbon tetrachloride was prepared. While cooling the reaction flask in an ice bath and swirling the contents, chlorine was passed into the solution by means of a fritted-glass, gas-dispersion tube. Reaction was exothermic and so rapid that it was possible to observe a greenish yellow end point when reaction of Si–H was completed. Removal of solvent by heating under reduced pressure was followed by dissolving the product in 25 ml. of pentane. Cooling gave an initial crop of 10.35 g. (91.6% yield) of ($-$)-α-naphthylphenylmethylchlorosilane. Recrystallization from pentane yielded 9.44 g., m.p. 63.5–64°, $[\alpha]D$ $-6.28°$ (c 10.5 in cyclohexane), further recrystallization produced no observable effect upon the properties. Whereas the starting silane absorbs strongly at 4.70 μ (corresponding to Si–H), the infrared spectrum of the chlorosilane shows no maximum at this wave length and shows the characteristic bands for α-NpPhMeSi–.

Anal. Calcd. for $C_{17}H_{15}SiCl$: Si, 9.93; Cl, 12.5; mol. wt., 283. Found: Si, 10.0; Cl, 12.4; mol. wt., 285.

Preparation of ($-$)-α-Naphthylphenylmethylbromosilane.—In a 500-ml. suction flask was placed a solution of 7.58 g. (0.0306 mole) of ($+$)-α-naphthylphenylmethylsilane, $[\alpha]D$ $+33.4°$ (c 8.00 in cyclohexane), in 20 ml. of carbon tetrachloride. A solution of 6.0 g. (0.0375 mole) of bromine in 10 ml. of carbon tetrachloride was added from a buret while cooling the flask in an ice bath and maintaining a blanket of dry nitrogen over the surface of the reaction mixture. Addition of the bromine produced copious evolution of hydrogen bromide. After several minutes the

(17) T. Ashida, R. Pepinsky, and Y. Okaya, Abstracts, International Union of Crystallography Congress, Rome, Italy, Sept., 1963.

(18) Application of Cram's rule of asymmetric induction [D. J. Cram and F. A. Abd Elharez, *J. Am. Chem. Soc.*, **74**, 5828 (1952)] plus some reasonable assumptions as applied to the addition of MeMgBr to $R_3Si*COPh$ have led to the above assignment of absolute configuration for ($+$)R_3Si*H: A. G. Brook and W. W. Limburg, *ibid.*, **85**, 832 (1963).

hydrogen bromide evolution had almost ceased, and the flask was evacuated free of excess bromine, hydrogen bromide, and solvent. The somewhat yellow sirup left as a residue was dissolved in pentane and cooled. This yielded 7.0 g. of crystals, m.p. 35–50°. Recrystallization from pentane yielded 4.1 g. of (−)-α-naphthylphenylmethylbromosilane, m.p. 52–53.5°, [α]D −22.2° (c 9.55 in pentane). The bromosilane is exceedingly sensitive toward atmospheric moisture. The infrared spectrum clearly showed the presence of the α-NpPhMeSi– group.

Anal. Calcd. for C₁₇H₁₅SiBr: Si, 8.59; Br, 24.4. Found: Si, 8.65; Br, 24.1.

Preparation of (−)-α-**Naphthylphenylmethylfluorosilane.**—A solution of 100 g. (0.25 mole) of (−)-α-naphthylphenylmethyl-(−)-menthoxysilane, m.p. 82–84°, in 70 ml. of dry ether was added to 17.8 g. (0.125 mole) of freshly distilled boron trifluoride etherate. The reaction mixture was heated in an oil bath for 5 hr. at 48° and then the solvents were removed under a pressure of 1 mm. while heating the reaction mixture up to a temperature of 90°. The product was dissolved in hexane, and 60 g. of crystals was obtained at a crystallization temperature of −3°, [α]D −40.9°, m.p. 55–68°. This material was then recrystallized once from hexane and twice from pentane giving 33.3 g. of (−)-α-naphthylphenylmethylfluorosilane (0.13 mole), m.p. 67.5–68°, [α]D −46.9° (c 9.12 ether), a yield of 52%. The infrared spectrum clearly showed all of the absorption maxima characteristic of the α-NpPhMeSi– group.

Anal. Calcd. for C₁₇H₁₅SiF: F, 7.13. Found: F, 6.95.

Preparation of (+)-α-**Naphthylphenylmethylsilanol.**—A solution of 30.9 g. of (+)-α-naphthylphenylmethylchlorosilane (prepared from (−)-α-naphthylphenylmethylsilane) in 500 ml. of dry ethyl ether was prepared. The chlorosilane was freshly prepared and was of high optical purity; m.p. 63–64.5°, [α]D +6.4° (c 15.7 in pentane). The ether solution was added, all at once, to 700 ml. of cold tap water in a 2-l. separatory funnel which was immediately stoppered and shaken for 1–2 min. The ether layer was then separated, washed four times with water, and then dried over potassium carbonate. Evaporation of solvent at reduced pressure yielded 28.0 g. (97% yield) of (+)-α-naphthylphenylmethylsilanol, [α]D + 20.5° (c 6.66 in ether) and +27.6° (c 11.2 in benzene). The infrared spectrum of this viscos oil is in complete accord with the assigned structure and shows typical Si–OH absorption at 2.80 and 3.05 μ in addition to the usual α-NpPhMeSi– bands.

Anal. Calcd. for C₁₇H₁₆SiO: Si, 10.61. Found: Si, 10.65.

Preparation of (+)-α-**Naphthylphenylmethylmethoxysilane.**—A solution of 12.4 g. (0.050 mole) of (−)-α-naphthylphenylmethylsilane (98% optically pure) in 40 ml. of carbon tetrachloride was chlorinated in the usual manner. At the appearance of excess chlorine, the solution was immediately diluted with 100 ml. of pentane and added to a well-swirled 1-l. separatory funnel containing 10.0 ml. (0.25 mole) of methanol, 20 ml. (0.2 mole) of cyclohexylamine, and 30 ml. of pentane. The reaction mixture was swirled for a moment and then washed five times with cold water, dried over sodium sulfate, and evacuated free of solvents. A solution of the residue in 40 ml. of pentane yielded crystalline (+)-α-naphthylphenylmethylmethoxysilane, 12.4 g., an 89% yield based on the (−)-silane employed. Recrystallization from pentane gave 11.2 g. of material, m.p. 64.5–65°, [α]D +16.5°; the infrared spectrum of this material was identical with that of the racemic α-naphthylphenylmethylmethoxysilane.

Lithium Aluminum Hydride Reductions. (1) (−)-α-**Naphthylphenylmethylchlorosilane.**—A solution of 1.78 g. (0.0063 mole) of (−)-α-naphthylphenylmethylchlorosilane, [α]D −5.93° (c 10.7 in pentane), in 20 ml. of pentane was added to a solution of 1.0 g. (0.105 equiv.) of lithium aluminum hydride in 100 ml. of ethyl ether. The reduction was exothermic and rapid. After swirling for a moment, the reaction product was slowly added to 30 ml. of concentrated hydrochloric acid, 500 ml. of cold water, and 50 ml. of ether in a 1-l. separatory funnel. The aqueous phase was separated and extracted with 50 ml. of pentane followed by washing of the combined organic layers with water, drying over sodium sulfate, and removal of solvents. This gave 1.49 g. (95.5% yield) of (−)-α-naphthylphenylmethylsilane, [α]D −35.3° (c 9.0 in pentane); the infrared spectrum of this material was identical with that of the silanes prepared by lithium aluminum hydride reduction of menthoxysilane.

(2) (−)-α-**Naphthylphenylmethylbromosilane.**—By a procedure similar to that used for the chlorosilane, 1.29 g. (0.0039 mole) of (−)-α-naphthylphenylmethylbromosilane, [α]D −22.2° (c 9.55 in pentane), was reduced with lithium aluminum hydride

and gave 0.79 g. (80% yield) of (−)-α-naphthylphenylmethylsilane, [α]D −32.7° (c 5.85 in pentane), having the expected infrared spectrum.

(3) (−)-α-**Naphthylphenylmethylfluorosilane.**—Reduction of 1.00 g. of (−)-α-naphthylphenylmethylfluorosilane, [α]D −45.3° (ether), was performed with a solution of 1.0 g. of lithium aluminum hydride in 50 ml. of ether. After heating at reflux temperature for 1 hr., the reaction product was isolated by a procedure similar to that described previously. There was obtained an 82% yield of (+)-α-naphthylphenylmethylsilane, [α]D +33.8° (pentane). The infrared spectrum served to characterize the product.

(4) (−)-α-**Naphthylphenylmethylmethoxysilane.**—A solution of 1.22 g. (0.00439 mole) of (−)-α-naphthylphenylmethylmethoxysilane, m.p. 64–65° and [α]D −15.9° (c 8.30 in pentane), in 15 ml. of pentane was added to a 250-ml. flask containing 2.0 g. (0.21 equiv.) of lithium aluminum hydride in 60 ml. of ether. After standing 16 hr. at room temperature the reduction product was treated as in (1) above and gave 1.1 g. (100% yield) of crude (−)-α-naphthylphenylmethylsilane. Chromatography over silica gel yielded 0.74 g. (68% yield) of material, [α]D −30.0° (c 4.00 in pentane); the infrared spectrum of this material gave clear confirmation of the expected structure.

(5) (−)-α-**Naphthylphenylmethylsilanol.**—A solution of 1.6 g. (0.00566 mole) of (−)-α-naphthylphenylmethylsilanol, [α]D −16.5° (c 5.46 in ether), in 30 ml. of di-n-butyl ether was added to 1.0 g. (0.105 equiv.) of lithium aluminum hydride in 30 ml. of ethyl ether. The flask contents were then maintained at 90° for 30 min. followed by removal of ethyl ether and heating at 140–145° for 1 hr. A 72% yield (1.01 g.) of (−)-α-naphthylphenylmethylsilane was obtained by treating this reduction product as in previous examples and chromatographing over silica gel; [α]D −27.2° (c 2.97 in pentane). The infrared spectrum confirmed the assigned structure of the product. Reduction of the silanol proceeded with a high degree of stereospecificity; i.e., the optical purity of the silanol was about 80.3%, assuming a value of [α]D −20.5° (ether) for the optically pure silanol (see above), and the optical purity of the resultant silane was 74.3%. This indicates that 92.5% of the optical activity was conserved, and that the reduction was at least 96% stereospecific.

Reaction of (−)R₃Si*Cl **with Sodium Borohydride.**—Reduction of (−)-α-naphthylphenylmethylchlorosilane (1.02 g., 0.0036 mole) with 2 g. (0.052 mole) of sodium borohydride in diglyme at room temperature for 1–2 min. gave, after work-up, 0.8 g. of (−)-α-naphthylphenylmethylsilane, [α]D −15° (c 3.7 in pentane). It is likely that the apparent lack of complete stereospecificity is due to racemization of R₃Si*Cl by formed chloride salt prior to reduction. The α-naphthylphenylmethylsilane was identified by infrared spectrum, Si–H maximum at 4.70 μ.

Reaction of (−)R₃Si*Cl **with Sodium Trimethoxyborohydride.**—Reaction of (−)-α-naphthylphenylmethylchlorosilane, 1.15 g., with 2.3 g. of sodium trimethoxyborohydride in diglyme solvent gave 0.86 g. of (−)-α-naphthylphenylmethylmethoxysilane contaminated with a very small amount of R₃Si*H, as shown by its infrared spectrum. The product had [α]D −12.5° (pentane). Except for a very small Si–H maximum, the infrared spectrum was identical with that of authentic methoxysilane; Si–OCH₃ maxima at 3.43, 3.55, 8.40, and 9.20 μ.

Reaction of (−)R₃Si*Cl **with Sodium Tetramethoxyborohydride.**—Reaction of (−)-α-naphthylphenylmethylchlorosilane, 0.70 g., [α]D −6.1°, with 0.70 g. of sodium tetramethoxyborohydride in 25 ml. of dry ether gave 0.67 g., 97% yield, of (−)-α-naphthylphenylmethylmethoxysilane after 2 hr. at room temperature. The product had an infrared spectrum identical with authentic methoxysilane and had [α]D −17.6° (c 4.1 in pentane).

Reaction of (−)R₃Si*Cl **with Lithium Dimethoxyaluminum Hydride.**—Reaction of (−)-α-naphthylphenylmethylchlorosilane, 0.60 g., [α]D −6.1°, with excess lithium dimethoxyaluminum hydride (prepared from the hydride and methanol) for 10 min. gave 0.52 g. of product shown to be ca. 60% R₃Si*H and 40% R₃Si*OCH₃ by an infrared spectrum. The rotation of the mixture was [α]D −22°.

The same quantities of reactants and extension of the reaction time from 10 min. to 44 hr. gave 0.54 g. of product shown to be pure R₃Si*H having [α]D −34°. This experiment proves that the methoxysilane formed after 10 min. is levorotatory and optically pure, since (−)R₃Si*OCH₃ is reduced to (−)R₃Si*H.

Reaction of (+)R₃Si*OH **with KOH₍ₛ₎.**—Powdered potassium hydroxide (70 g., 1.25 moles) was added to a 500-ml. bottle containing 20 g. (0.076 mole) of (−)R₃Si*OH, [α]D −26° (c 23.0 in xylene), diluted to 228 ml. with dry xylene. The bottle was

stoppered 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$_3$Si*OK by titration of an aliquot with standard acid and measurement of rotation of (+)R$_3$Si*OK gave [α]D +75° (c 10.5 in xylene). No change in specific rotation was noted 4 days later.

Reaction of (+)R$_3$Si*OK with Dimethyl Sulfate.—To a 125-ml. flask was added 10.0 ml. (3.49 mmoles) of a xylene solution of (+)R$_3$Si*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$_3$Si*OCH$_3$, [α]D −16° (c. 4.30 in pentane), m.p. 62.5–64°. The infrared spectrum of this material completely confirmed the structure.

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

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

The stereochemistry of displacement of alkoxy and siloxy leaving groups from asymmetric silicon in optically active compounds containing the α-naphthylphenylmethylsilyl group, α-NpPhMeSi*–, has been studied. Retention of configuration was found for reduction to R$_3$Si*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$_N$i–Si is proposed for such mechanisms.
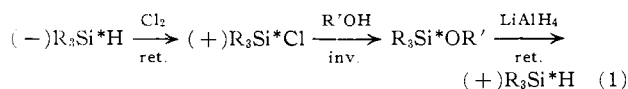
A previous paper in this series on the stereochemistry of asymmetric silicon has demonstrated a high degree of stereospecificity for a number of reactions of R$_3$Si*X in which R$_3$Si*– is the α-naphthylphenylmethylsilyl group, α-NpPhMeSi–, and has dealt with the problems of relative and absolute configurations for a number of key compounds.[1]

These previous studies have made it possible to determine the stereochemistry of a very large number of reactions of R$_3$Si*X in which the leaving X and the attacking reagent are varied over a wide range.

In this paper are reported reactions of R$_3$Si*OR′ in which R′ is CH$_3$, cyclo-C$_6$H$_{11}$, t-C$_4$H$_9$, (−)-menthyl, and R$_3$Si* for optically active (as contrasted with meso) R$_3$Si*OSi*R$_3$. The reactions reported herein comprise reduction of R$_3$Si*OR′ to R$_3$Si*H with lithium aluminum hydride and with t-butylmagnesium chloride (Grignard reduction), and cleavage of the Si*–O bond with KOH$_{(s)}$.

Reduction Reactions.—The R$_3$Si*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,[1] reactions of R$_3$Si*Cl were found to proceed with predominant inversion of configuration with diverse nucleophilic reagents, including lithium aluminum hydride. In contrast, reductions of R$_3$Si*OCH$_3$ and R$_3$Si*OH with lithium aluminum hydride were found to proceed with retention of configuration. These reductions comprised one step in the Walden cycle[1]

$$(-)R_3Si^*H \xrightarrow[\text{ret.}]{Cl_2} (+)R_3Si^*Cl \xrightarrow[\text{inv.}]{R'OH} R_3Si^*OR' \xrightarrow[\text{ret.}]{LiAlH_4}$$
$$(+)R_3Si^*H \quad (1)$$

(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$_3$Si*H to (+)-R$_3$Si*H, was found to obtain in the present work when R′ = cyclo-C$_6$H$_{11}$ or (−)-menthyl. Furthermore, when R′ is t-C$_4$H$_9$ or R$_3$Si* the same cycle was found for reaction of (+)R$_3$Si*Cl with t-C$_4$H$_9$OK in t-butyl alcohol and for reaction of (+)R$_3$Si*Cl with (−)R$_3$Si*OK in xylene. In view of the fact that these six cycles, involving formation and reduction of R$_3$Si*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$_3$Si*OR′ from R$_3$Si*Cl (see ref. 1 for inversion of configuration for R$_3$SiCl with a wide variety of reagents) and retention of configuration in the reduction of R$_3$Si*OR′ to R$_3$Si*H. On this basis, the enantiomers listed in Table I have the (+)R$_3$Si*H configuration and, furthermore, possess the absolute configuration[1]
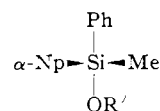
$$\begin{array}{c} Ph \\ | \\ \alpha\text{-Np} \blacktriangleright \!\! Si \!\! \blacktriangleleft Me \\ | \\ OR' \end{array}$$

TABLE I

ENANTIOMERS HAVING THE (+)R$_3$Si*H CONFIGURATION

Compound[a]	[α]D, solvent	M.p., °C.
(+)R$_3$Si*OH	+20°, ether	Liq.
(−)R$_3$Si*OK	−75°, xylene	
(+)R$_3$Si*OCH$_3$	+17, pentane	64
(−)R$_3$Si*O-cyclo-C$_6$H$_{11}$	− 8.0°, pentane	Liq.
(−)R$_3$Si*O(−)Men	−59°, cyclohexane	84
(−)R$_3$Si*O-t-C$_4$H$_9$	−28°, pentane	Liq.
(+)R$_3$Si*OSi*R$_3$	+9.9°, hexane	89

[a] (+)R$_3$Si*OH, (−)R$_3$Si*OK, and (+)R$_3$Si*OCH$_3$ were assigned the (+)R$_3$Si*H configuration in a previous paper[1]; that both silicon atoms in (+)R$_3$Si*OSi*R$_3$ have the (+)R$_3$Si*H configuration follows rigorously from its synthesis from (−)R$_3$Si*OK and (+)R$_3$Si*Cl; see below.

Treatment of (+)R$_3$SiOCH$_3$ with t-butylmagnesium chloride gave (+)R$_3$Si*H in 96% yield. Thus, Grignard reduction proceeds with retention of configuration. The reduction was about 90% stereospecific. Grignard reduction of (−)R$_3$Si*O-cyclo-C$_6$H$_{11}$ with t-