−11.1° (*c* 1.2 in pentane). The infrared spectrum of the product was identical with that of the authentic *p*-methoxybenzylsilane.

Anal. Calcd for $C_{25}H_{24}Si$: C, 81.4; H, 6.57; Si, 7.63. Found: C, 81.5; H, 6.37; Si, 7.43.

Reactions with Allyllithium. Tetraallyltin (7.0 g) was added to 250 ml of 0.2 *N* *n*-butyllithium in pentane solvent.[26] The allyllithium was formed as a solid which was allowed to settle after stirring the reaction mixture for 20 min. The slightly cloudy supernatant liquid was removed by use of nitrogen pressure, and the solid washed twice with 150-ml portions of pentane by stirring the mixture, allowing the solid to settle, and removing the supernatant liquid. The allyllithium was then dissolved in 150 ml of dry ether and the (+)-chlorosilane (5.12 g) was added slowly since the reaction was very exothermic. After a 10-min reaction period, the reaction mixture was hydrolyzed in the usual way except that hydrochloric acid was not used. After fractional distillation, (+)-α-naphthylphenylallylmethylsilane, $[\alpha]_D$ +12.8° (*c* 5.7 in pentane), was obtained as an oil, bp 169–178° (1 mm), in 48% yield (2.51 g). The infrared spectrum showed the bands characteristic of the α-naphthylphenylmethylsilyl group and also bands at 3.48, 3.51, 6.17, 8.40, and 11.5 μ attributed to the allyl group on silicon. The addition of the (−)-fluorosilane to allyllithium, prepared as described above, gave the (+)-allylsilane, with $[\alpha]_D$ +5.5° (*c* 5.5 in pentane).

Anal. Calcd for $C_{20}H_{20}Si$: C, 83.3; H, 6.99; Si, 9.74. Found: C, 83.4; H, 7.51; Si, 9.55.

Reactions with α-Naphthyllithium. Addition of (−)-benzhydrylphenylmethylchlorosilane[8] (4.63 g) to a 0.12 *N* solution of α-naphthyllithium prepared by the halogen–metal interchange of α-bromonaphthalene and *n*-butyllithium gave, after hydrolysis in the usual manner and fractional distillation, a 40% yield (2.30 g) of a product which had an infrared spectrum identical with that of the authentic α-naphthylphenylbenzhydrylmethylsilane, and had $[\alpha]_D$ +7.0° (*c* 7.1 in pentane). From reaction with (−)-benzhydrylphenylmethylfluorosilane[27] (4.83 g) with $[\alpha]_D$ −11.6° (*c* 2.6 in pentane), by a similar procedure, the product was obtained in 66% yield (4.27 g) with $[\alpha]_D$ −17.4° (*c* 5.4 in $CHCl_3$).

Acknowledgment. We thank Dow Corning Corporation for continued generous support.

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[26] D. Seyferth and M. A. Weiner, *J. Org. Chem.*, **26**, 4797 (1961).

[27] Unpublished work from this laboratory.

Stereochemistry of Asymmetric Silicon. VI. Synthesis, Stereochemistry, and Absolute Configurations of New Optically Active Monofunctional Organosilicon Systems[1,2]

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Abstract: Syntheses and stereochemical studies of three new optically active monofunctional organosilicon systems, PhMeRSi*X, in which R = neopentyl, benzhydryl, and ethyl, are reported. Compared to the original system, α-NpPhMeSi*X, it is shown that predominant stereochemistry for the new systems, involving diverse leaving groups, reagents, and solvents, is unchanged. *This demonstrates the validity of earlier stereochemical generalizations for R_3Si^*X and their nondependence on the nature of the nonreacting organic groups.*

Previous stereochemical studies of optically active triorganomonofunctional silicon systems were limited to compounds containing the α-naphthylphenylmethylsilyl group, α-NpPhMeSi*.[4–6] During the course of these studies, which encompassed a wide variety of leaving groups, reagents, and solvents, the following generalizations have been made concerning the stereochemistry of substitution at silicon in acyclic R_3Si^*X. (1) Good leaving groups, X, whose conjugate acids have pK_a less than ~6, usually undergo nucleophilic displacement from R_3Si^*X with inversion of configuration, regardless of the nature of the solvent, and providing only that the attacking reagent furnishes an entering group Y that is more basic than X.[4a] (2) For poor leaving groups, whose conjugate acids have pK_a greater than ~6, the stereochemical path may be inversion or retention of configuration—relatively nonpolar solvents[4f] favor a retention stereochemistry. Since these generalizations were based solely on reactions of α-NpPhMeSi*X, it was important to determine whether their implied nondependence on the nature of the three R groups is valid.

Synthesis. The synthetic route to the new systems utilized an organolithium compound, RLi, for conversion of optically active α-NpPhMeSi*Cl to α-NpPhMeSi*R by an invertive stereochemical path.[1] Stereospecific removal of the α-naphthyl group with bromine, as α-bromonaphthalene, gave PhMeRSi*Br.[7] The bromide was then reduced to PhMeRSi*H by treatment with lithium aluminum hydride. Purification of

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[1] For the preceding paper in this series, see: L. H. Sommer, W. D. Korte, and P. G. Rodewald, *J. Am. Chem. Soc.*, **89**, 862 (1967).

[2] For a preliminary communication, see: L. H. Sommer, K. W. Michael, and W. D. Korte, *J. Am. Chem. Soc.*, **85**, 3712 (1963).

[3] Department of Chemistry, University of California, Davis, Calif.

[4] (a) L. H. Sommer, G. A. Parker, N. C. Lloyd, C. L. Frye, and K. W. Michael, *J. Am. Chem. Soc.*, **89**, 857 (1967); (b) L. H. Sommer and R. Mason, *ibid.*, **87**, 1619 (1965); (c) L. H. Sommer, J. D. Citron, and C. Frye, *ibid.*, **86**, 5684 (1964); (d) L. H. Sommer, F. D. Stark, and K. W. Michael, *ibid.*, **86**, 5683 (1964); (e) L. H. Sommer, G. A. Parker, and C. L. Frye, *ibid.*, **86**, 3280 (1964); (f) L. H. Sommer, C. L. Frye, and G. A. Parker, *ibid.*, **86**, 3276 (1964); (g) L. H. Sommer, C. L. Frye, G. A. Parker, and K. W. Michael, *ibid.*, **86**, 3271 (1964); (h) L. H. Sommer and P. G. Rodewald, *ibid.*, **85**, 3898 (1963). Early preliminary communications published later as articles are not included in this listing.

[5] (a) A. G. Brook and C. M. Warner, *Tetrahedron Letters*, **18**, 815 (1962); (b) A. G. Brook and W. W. Limburg, *J. Am. Chem. Soc.*, **85**, 832 (1963).

[6] (a) C. Eaborn and O. W. Steward, *Proc. Chem. Soc.*, 59 (1963); (b) R. Baker, R. W. Bott, and C. Eaborn, *J. Organometal. Chem.* (Amsterdam), 1, 37 (1963).

[7] The bromine cleavage of α-NpPhMeSi*-C_6H_4-OCH_3-*p* to give α-NpPhMeSi*Br and BrC_6H_4-OCH_3-*p* proceeds with inversion of configuration.[6a]

the new systems, removal of α-bromonaphthalene and small amounts of other organic products, is best accomplished after reduction.

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

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

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

Using the above reaction sequence, three new organosilicon systems, PhMeRSi*X, were derived in which R is neopentyl, benzhydryl, and ethyl.

For all three of these new systems, a four-reaction sequence obtains which results in the conversion of α-NpPhMeSi*R into its enantiomer. Since a high degree of conservation of optical activity is found for these sequences, it follows that the reactions involved are highly stereospecific.

$$\underset{\text{I}}{\alpha\text{-NpPhMeSi*R}} \xrightarrow[\text{inversion}]{\text{Br}_2} \text{PhMeRSi*Br} \xrightarrow[\text{inversion}]{\text{LiAlH}_4}$$
$$\text{PhMeRSi*H} \xrightarrow[\text{retention}]{\text{Cl}_2} \text{PhMeRSi*Cl} \xrightarrow[\text{inversion}]{\alpha\text{-NpLi}} \underset{\text{II}}{\alpha\text{-NpPhMeSi*R}} \quad (4)$$

For R = neopentyl, I had $[\alpha]_D$ +23.2°, whereas II had $[\alpha]_D$ −18.6°. For R = ethyl, I had $[\alpha]_D$ −6.2° whereas II had $[\alpha]_D$ +5.1°. For R = benzhydryl, the cycle was somewhat less stereospecific, perhaps owing to the presence of active hydrogen in this group; I had $[\alpha]_D$ +15.5°, whereas II had $[\alpha]_D$ −7.1°.

Earlier demonstration of an inversion path for silicon in aromatic desilylation with bromine[7] and the finding of inversion of configuration for 24 coupling reactions of RLi with α-NpPhMeSi*Cl,[1] plus the demonstrated parallelism in stereochemistry of displacement of Br and Cl from silicon (both are classed as good leaving groups),[4a] all combine to favor the assigned stereochemical paths in reaction sequence 4. To accord with the experimental finding of net inversion of configuration for sequence 4 for all three of the new systems, an odd number of inversions (one or three) must be involved. Thus, if the stereochemical assignments in (4) are not all correct, this would require that at least two assignments, or all four, be incorrect. These latter alternatives are considered highly improbable and would certainly lead to a lack of internal consistency in the considerable body of stereochemical facts reported below for the new systems, and to a lack of parallelism in comparing the new systems with α-NpPhMeSi*X reactions. Neither of these is observed.

Stereochemistry. The first Walden cycle for silicon involved conversion of α-NpPhMeSi*H to its enantiomer *via* chlorination followed by lithium aluminum hydride reduction. For the new systems, similar Walden cycles were found. For the new system in which R = neopentyl, Si*H, $[\alpha]_D$ +2.5°, gives Si*Cl, $[\alpha]_D$ +7.5°, which upon reduction furnishes Si*H, $[\alpha]_D$ −2.5°. For the new system in which R = benzhydryl, Si*H, $[\alpha]_D$ +7.1°, gives Si*Cl, $[\alpha]_D$ +14.1°, which upon reduction furnishes Si*H, $[\alpha]_D$ −6.4°. For the new system in which R = ethyl, Si*H, $[\alpha]_D$ +2.5°, gives Si*Cl, $[\alpha]_D$ +3.0°, which upon reduction gives Si*H, $[\alpha]_D$ −2.5°. The parallel behavior of the four systems in these cycles leaves little doubt that for the new systems, as for the original system, chlorination proceeds *via* retention and reduction by inversion of configuration.[4g] For R = neopentyl, benzhydryl, or ethyl

$$(+)\text{PhMeRSi*H} \xrightarrow[\text{retention}]{\text{Cl}_2} (+)\text{PhMeRSi*Cl} \xrightarrow[\text{inversion}]{\text{LiAlH}_4} (-)\text{PhMeRSi*H} \quad (5)$$

For R = neopentyl and R = benzhydryl, similar Walden cycles were obtained *via* bromination followed by lithium aluminum hydride reduction. The analogous cycle obtains for the original system.[4a]

$$(+)\text{PhMeRSi*H} \xrightarrow[\text{retention}]{\text{Br}_2} (+)\text{PhMeRSi*Br} \xrightarrow[\text{inversion}]{\text{LiAlH}_4} (-)\text{PhMeRSi*H} \quad (6)$$

For R = ethyl, sensitivity of PhMeRSi*Br to racemization, especially by HBr, prevented the isolation of optically pure bromide and the carrying out of (6). However, lithium aluminum hydride reduction of crude (+)PhMeEtSi*Br, obtained during (4), gave (−)PhMeEtSi*H. It should perhaps be noted that the results in (5) and (6) are consistent with stereochemical assignments made in (4). Thus, (+)PhMeRSi*H, (+)-PhMeRSi*Cl, and (+)PhMeRSi*Br have the same configuration when R = neopentyl, R = benzhydryl, or R = ethyl.[8]

For R = neopentyl, chemical correlation of configuration for (+)PhMeRSi*OH, (−)PhMeRSi*OK, (+)PhMeRSi*OCH$_3$, and (+)PhMeRSi*OOCCH$_3$ was achieved by the important technique introduced into organic chemistry by Phillips and Kenyon[9] and previously used with the original α-NpPhMeSi* system.[4g]

$$(+)\text{PhMeRSi*OH} + \text{KOH(s)} \xrightarrow[\text{retention}]{\text{xylene}} (-)\text{PhMeRSi*OK} \quad (7)$$

$$(-)\text{PhMeRSi*OK} + (\text{CH}_3)_2\text{SO}_4 \xrightarrow[\text{retention}]{} (+)\text{PhMeRSi*OCH}_3 \quad (8)$$

$$(-)\text{PhMeRSi*OK} + \text{CH}_3\text{COCl} \xrightarrow[\text{retention}]{} (+)\text{PhMeRSi*OOCCH}_3 \quad (9)$$

The asymmetric center is not affected in the above reactions.

The simplest and most direct evidence for correlation of configuration for (+)PhMeRSi*H and (+)PhMeRSi*OCH$_3$, where R = neopentyl, is provided by reactions 10 and 11. The conclusion that, for the neopentyl

$$(+)\text{PhMeRSi*Cl} + \text{LiAlH}_4 \xrightarrow[\text{inversion}]{\text{ether}} (-)\text{PhMeRSi*H} \quad (10)$$

$$(+)\text{PhMeRSi*Cl} + \text{LiAl(OCH}_3)_2\text{H}_2 \xrightarrow[\text{inversion}]{\text{ether}} (-)\text{PhMeRSi*H} + (-)\text{PhMeRSi*OCH}_3 \quad (11)$$

series, (−)PhMeRSi*H and (−)PhMeRSi*OCH$_3$ have the same configuration is justified by the close similarity of reactions 10 and 11. In view of other correlations of configuration given above, this means that (+)PhMeRSi*H, (+)PhMeRSi*Cl, (+)PhMeRSi*Br, (+)-PhMeRSi*OH, (+)PhMeRSi*OCH$_3$, (+)PhMeRSi*-

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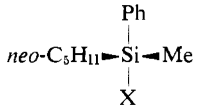
[8] For R = α-Np, it is interesting to note that (+)PhMeRSi*H, (−)PhMeRSi*Cl, and (−)PhMeRSi*Br have the same configuration. Detailed presentation and discussion of optical rotatory dispersion curves for various R$_3$Si*X compounds is deferred to a later paper, but it may be noted here that among compounds of the same configuration the relationships between structure and optical rotation can be quite complex.

[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.

Table I. *neo*-C_5H_{11}PhMeSi*X Compounds Having the Configuration



$$\begin{array}{c} \text{Ph} \\ | \\ \textit{neo}\text{-}C_5H_{11}\blacktriangleright\text{Si}\blacktriangleleft\text{Me} \\ | \\ \text{X} \end{array}$$

Si*X[a]	$[\alpha]_D$, deg, solvent[b]
(*S*)-(+)SiH	+2.5, CCl_4
(*R*)-(+)SiF	+5.0, pentane
(*R*)-(+)SiCl	+7.5, CCl_4
(*R*)-(+)SiBr	+10.1, CCl_4
(*R*)-(+)SiOH	+7.5, pentane
(*R*)-(−)SiOK	−3.8, xylene
(*R*)-(+)$SiOOCCH_3$	+2.2, pentane
(*R*)-(+)$SiOCH_3$	+13.7, pentane
(*R*)-(+)α-Np	+23.2, pentane

[a] Names for these compounds, in the order of listing, are: (*S*)-(+)-phenylneopentylmethylsilane; (*R*)-(+)-phenylneopentylmethylfluorosilane; (*R*)-(+)-phenylneopentylmethylchlorosilane; (*R*)-(+)-phenylneopentylmethylbromosilane; (*R*)-(+)-phenylneopentylmethylsilanol; potassium (*R*)-(+)-phenylneopentylmethylsilanolate; (*R*)-(+)-phenylneopentylmethylacetoxysilane; (*R*)-(+)-phenylneopentylmethylmethoxysilane; (*R*)-(+)-α-naphthylphenylneopentylmethylsilane. [b] Products with the largest specific rotation are assumed to be optically pure. This assumption must be nearly correct in view of high conservation of optical activity in reaction sequence 4 and the stereochemical interrelationships and high stereospecificities given in Table II.

Table II. Summary of Stereochemistry for *neo*-C_5H_{11}PhMeSi*X

No.	R_3Si*X reactant	Reagent	Solvent	Product	Stereospecificity,[a] %	α-NpPhMeSi*X, ref
II-1	(+)SiOH	$LiAlH_4$	Bu_2O	(+)SiH	100 ret	4g
II-2	(+)$SiOCH_3$	$LiAlH_4$	Ether	(+)SiH	100 ret	4g
II-3	(+)$SiOCH_3$	KOH(s)	Xylene	(−)SiOK	100 ret	4f
II-4	(+)$SiOOCCH_3$	$LiAlH_4$	Ether	(−)SiH	100 inv	4e
II-5	(+)$SiOOCCH_3$	KOH(s)	Xylene	(+)SiOK	98 inv	4e
II-6	(+)$SiOOCCH_3$	CH_3OH[b]	Pentane	(−)$SiOCH_3$	91 inv	4e
II-7	(+)SiCl	H_2O	Ether	(−)SiOH	95 inv	4g
II-8	(+)SiCl	CH_3OH[b]	Pentane	(−)$SiOCH_3$	88 inv	4g
II-9	(+)SiCl	$NaB(OCH_3)_4$	Ether	(−)$SiOCH_3$	100 inv	4g
II-10	(+)SiCl	$Hg(OCOCH_3)_2$	Benzene	(−)$SiOOCCH_3$	84 inv	4a
II-11	(+)SiCl	$LiAlH_4$	Ether	(−)SiH	100 inv	4g
II-12	(+)SiCl	$C_6H_{11}NH_3F$[c]	$CHCl_3$	(−)SiF	77 inv	4a
II-13	(+)SiCl	$LiAlH_2(OCH_3)_2$	Ether	(−)SiH (−)$SiOCH_3$	96 inv 80 inv	4g 4g
II-14	(+)SiBr	H_2O	Ether	(−)SiOH	89 inv	4a
II-15	(+)SiBr	CH_3OH[b]	Pentane	(−)$SiOCH_3$	86 inv	4a
II-16	(+)SiBr	$LiAlH_4$	Ether	(−)SiH	100 inv	4g
II-17	(+)SiBr	$C_6H_{11}NH_3Cl$[c]	$CHCl_3$	(−)SiCl	79 inv	4a
II-18	(+)SiBr	$C_6H_{11}NH_3F$[c]	$CHCl_3$	(−)SiF	77 inv	4a
II-19	(+)SiF	$LiAlH_4$	Ether	(−)SiH	100 inv	4g
II-20	(+)SiH	Cl_2	CCl_4	(+)SiCl	100 ret	4g
II-21	(+)SiH	Br_2	CCl_4	(+)SiBr	100 ret	4g
II-22	(+)Si-α-Np	Br_2	Benzene	(−)SiBr	82 inv	None
II-23	(+)SiCl	α-NpLi	Ether	(−)Si-α-Np	82 inv	None

[a] 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. [b] Cyclohexylamine was used as an acid acceptor. [c] C_6H_{11} is cyclohexyl.

OOCCH$_3$, and (−)PhMeRSi*OK, R = neopentyl, all have the same configuration.

For correlation of configuration for (+)PhMeRSi*F with the other compounds in which R = neopentyl, reactions 12 and 13 provide good evidence that the

$$(+)\text{PhMeRSi*Br} \xrightarrow[\text{Inversion}]{C_6H_{11}NH_3Cl} (-)\text{PhMeRSi*Cl} \qquad (12)$$

$$(+)\text{PhMeRSi*Br} \xrightarrow[\text{inversion}]{C_6H_{11}NH_3F} (-)\text{PhMeRSi*F} \qquad (13)$$

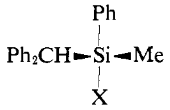
dextrorotatory fluoride has the same configuration as the other dextrorotatory compounds listed above. The similarity in reagents used in (12) and (13), the prior correlations which assign inversion as the path in 12, and the finding of inversion for (12) and (13) with the original system (R = α-Np),[4a] all lead to the conclusion that (+)PhMeRSi*F has the same configuration as the dextrorotatory bromide and the other (+)PhMeRSi*X compounds in which R = neopentyl.

The above configurational correlations, the assignment of an inversion path for cleavage of the α-naphthyl group with bromine in sequence 4, and the absolute configuration of (+)-α-NpPhMeSi*H, shown to be (*R*)-(+)-α-naphthylphenylmethylsilane by the X-ray method,[4g] now permit a listing in Table I of *neo*-C_5H_{11}PhMeSi*X enantiomers having the designated configuration.

In Table II are summarized the stereochemical studies made on the neopentylphenylmethylsilyl system. Included in the table are references to the corresponding studies made with the original α-NpPhMeSi*X system. Although reactions II-1 through II-21 include diverse leaving groups, reagents, and solvents, *predominant stereochemistry for all 21 reactions is unchanged by replacement of α-naphthyl by neopentyl in R_3Si^*X.* Present detailed mechanistic discussion of the stereochemical results in Table II is made unnecessary by previous discussion[4] of the same results obtained with the α-NpPhMeSi*X system.

For the new system containing the benzhydryl group, $Ph_2CHPhMeSi^*X$, sensitivity of the benzhydryl group to cleavage from silicon by basic reagents such as KOH(s) imposed certain limitations on the stereochemical studies which could be carried out with these compounds. Nevertheless, by methods and arguments similar to those used above for the neopentyl

Table III. $Ph_2CHPhMeSi^*X$ Compounds Having the Configuration



$$\mathrm{Ph_2CH}\blacktriangleright\overset{\mathrm{Ph}}{\underset{\mathrm{X}}{\mathrm{Si}}}\blacktriangleleft\mathrm{Me}$$

Si^*X[a]	[α]D, deg, solvent[b]	Mp, °C
(*S*)-(+)SiH	+7.1, CCl_4	57
(*R*)-(+)SiF	+11.6, pentane	81
(*R*)-(+)SiCl	+14.1, pentane	69
(*R*)-(+)SiBr	+16.2, pentane	
(*R*)-(+)SiOH	+17.9, pentane	
(*R*)-(+)$SiOCH_3$	+26.4, pentane	
(*R*)-(+)SiO-cyclo-C_6H_{11}	+25.6, pentane	
(*R*)-(−)$SiOOCCH_3$	−6.5, pentane	
(*R*)-(−)$SiOOCC_6H_5$	−16.4, pentane	
(*R*)-(+)$SiCH_2CH_3$	+11.0, pentane	
(*R*)-(+)Si-α-Np	+17.7, $CHCl_3$	124

[a] Names for these compounds, in the order of listing, are: (*S*)-(+)-benzhydrylphenylmethylsilane; (*R*)-(+)-benzhydrylphenylmethylfluorosilane; (*R*)-(+)-benzhydrylphenylmethylchlorosilane; (*R*)-(+)-benzhydrylphenylmethylbromosilane; (*R*)-(+)-benzhydrylphenylmethylsilanol; (*R*)-(+)-benzhydrylphenylmethylmethoxysilane; (*R*)-(+)-benzhydrylphenylmethylcyclohexoxysilane; (*R*)-(−)-benzhydrylphenylmethylacetoxysilane; (*R*)-(−)-benzhydrylphenylmethylbenzoxysilane; (*R*)-(+)-benzhydrylphenylethylmethylsilane; (*R*)-(+)-benzhydryl-α-naphthylphenylmethylsilane. [b] Products with the largest specific rotations are assumed to be optically pure. This assumption must be nearly correct in view of high conservation of optical activity in reaction sequence 4 and the stereochemical interrelationships and high stereospecificities given in Table IV. In the case of the first three and last compounds in the above table, the products could be crystallized up to optical purity, and in these cases the above assumption was rigorously shown to be correct.

compounds, the relative and absolute configurations of the benzhydryl compounds listed in Table III were obtained and, using these as a basis, the stereochemical results given in Table IV were found for these compounds. Again, comparison with the stereochemistry of the original system shows that *no stereochemical changes result from the replacement of α-naphthyl by benzhydryl.*

A total of 35 reactions in Tables II and IV demonstrate the validity of the generalization that *inversion* of configuration is common for *good leaving groups.* In Table II these are II-4 to II-18 plus II-23. In Table IV these are IV-4 to IV-21 plus IV-27.

Displacement of *poor leaving groups* with *retention* of configuration is shown in Table II by reactions II-1 to II-3, II-20 and II-21, and in Table IV by reactions IV-1 to IV-3, IV-22, and IV-23. Displacement of α-naphthyl (formally a poor leaving group) with *inversion* of configuration is shown by II-22 and IV-26.

Although the pK_a of HF (~3.5) places F in the category of good leaving groups, the high bond energy of Si–F and the capacity of F for coordination with the electrophilic center of an attacking reagent frequently cause R_3Si^*F to react with retention of configuration by an SNi–Si mechanism. Although the stereochemistry of R_3Si^*F is sensitive to the nature of the attacking reagent,[1] it is interesting to note that predominant stereochemistry in reactions II-19, IV-24, and IV-25 is the same as for the corresponding reactions of α-Np-PhMeSi*F.

In view of the above studies, first carried out with the neopentyl and benzhydryl compounds, which achieved the general objective of demonstrating that the stereochemistry of reaction of R_3Si^*X is *not* uniquely determined by the presence of an α-naphthyl, a phenyl, and a methyl group bonded to the asymmetric silicon, only a limited number of studies were made on the ethyl compounds. For EtPhMeSi*X these led to the relative and absolute configurations listed in Table V and to the stereochemical results given in Table VI. The latter show that the predominant stereochemical course of the reactions listed remains unchanged by replacement of α-naphthyl by ethyl.

The next step in a logical development of organosilicon stereochemistry would be the preparation and study of optically active bifunctional organosilicon compounds, RR′Si*XX′, including RR′Si*HX. To date, our cursory efforts in that direction have not yet met with success, but we are now seriously turning our attention to this problem.

Experimental Section

Conversion of α-NpPhMeSi*Cl to α-NpPhMeSi*R. The conversions of α-naphthylphenylmethylchlorosilane to the neopentylsilane, the benzhydrylsilane, and the ethylsilane by coupling with neopentyllithium, benzhydryllithium, and ethyllithium, respectively, have been reported.[1]

Preparation of (+)PhMeRSi*H from α-NpPhMeSi*R. The preparation of (+)-phenylneopentylmethylsilane will be described in detail as being typical of the procedure used. Purified bromine (16.0 g) mixed with benzene (10 ml) was added rapidly to (+)-α-naphthylphenylneopentylmethylsilane (30 g), [α]D +23.2° (*c* 4.5 in pentane), dissolved in benzene (30 ml). The exothermic reaction did not cause immediate depletion of the bromine color, but after standing at ambient temperature for 20 min only a faint orange color remained. The crude bromide was not isolated, but was converted to the silane by addition of the reaction mixture to lithium aluminum hydride (3.80 g) in dry ether (100 ml). After 5 min, the hydride solution was slowly added to concentrated hydrochloric acid (100 ml), ice (400 g), and pentane (50 ml) in a 1-l. separatory funnel. The aqueous phase was discarded and the organic layer washed with water and dried over sodium sulfate. Isolation of the crude silane was accomplished by distillation at atmospheric pressure and collecting the fraction boiling in the range 200–300°. Fractional crystallization from pentane at −78° removed naphthalene from the distillate. Fractional distillation of the remaining liquid gave (+)-phenylneopentylmethylsilane (16.2 g) in 89% yield with bp 220–222°, [α]D +2.5° (*c* 10.0 in CCl_4), [α]D +1.2° (*c* 23.2 in pentane), and n^{24}D 1.4968. The silane had an infrared absorption band at 4.75 μ attributed to the Si–H group. Characteristic infrared absorption maxima of the *neo*-C_5H_{11}-PhMeSi group are found at 3.0, 3.42, 6.82, 7.0, 7.42, 7.98, 8.08, 8.60, 8.95, 9.85, 10.65, 13.8, and 14.2 μ.

Anal. Calcd for $C_{12}H_{20}Si$: C, 75.1; H, 10.4; Si, 14.6. Found: C, 75.1; H, 10.5; Si, 14.4.

Treatment of (+)-α-naphthylphenylbenzhydrylmethylsilane (48.6 g), [α]D +17.7° (*c* 4.5 in $CHCl_3$), with bromine in chloroform solvent for 1 hr gave, after removal of solvent, lithium aluminum hydride reduction, and fractional distillation, 24.6 g of (+)-benzhydrylphenylmethylsilane, bp 140–161° (1 mm). Crystallization from pentane gave a 65% yield (21.7 g) of the (+)-benzhydrylphenylmethylsilane, mp 45–50°, [α]D +5.9° (*c* 19.5 in CCl_4). A fraction recrystallized several times from pentane had mp 56–57° and [α]D +7.1° (*c* 3.5 in CCl_4), [α]D +3.9° (*c* 3.5 in pentane). The silane had an infrared band at 4.75 μ attributed to the Si–H group. Characteristic infrared absorption maxima of the Ph_2-CHPhMeSi group are found at 3.30, 3.32, 3.52, 6.25, 6.70, 6.90, 7.0, 7.98, 8.97, 9.30, 9.68, 13.75, and 14.3 μ.

Anal. Calcd for $C_{20}H_{20}Si$: C, 83.3; H, 6.99; Si, 9.74. Found: C, 83.3; H, 6.64; Si, 9.80.

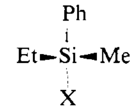
Treatment of (−)-α-naphthylphenylethylmethylsilane (13.7 g), [α]D −6.2° (*c* 7.3 in pentane), with bromine in benzene solvent gave, after reduction and fractional distillation, a 99% yield (7.93 g) of (+)-phenylethylmethylsilane, bp 178–180°, with [α]D +2.53° (*c* 10.1 in CCl_4), [α]D +1.22° (*c* 23.2 in pentane), and n^{28}D 1.5013. The silane had an infrared band at 4.75 μ attributed to the Si–H group. Characteristic infrared absorption maxima of the PhEt-

Table IV. Summary of Stereochemistry for $Ph_2CHPhMeSi^*X$

No.	R_3Si^*X reactant	Reagent	Solvent	Product	Stereo-specificity, %[a]	α-NpPh-MeSi*X, ref
IV-1	(+)SiOH	$LiAlH_4$	Et_2O–Bu_2O	(+)SiH	92 ret	4g
IV-2	(+)$SiOCH_3$	$LiAlH_4$	Ether	(+)SiH	94 ret	4g
IV-3	(+)$SiOC_6H_{11}$[b]	$LiAlH_4$	Et_2O–Bu_2O	(+)SiH	95 ret	4f
IV-4	(−)$SiOOCCH_3$	$LiAlH_4$	Ether	(−)SiH	92 inv	4e
IV-5	(−)$SiOOCCH_3$	CH_3OH[c]	Pentane	(−)$SiOCH_3$	73 inv	4e
IV-6	(−)$SiOOCC_6H_5$	$LiAlH_4$	Ether	(−)SiH	83 inv	4e
IV-7	(−)$SiOOCC_6H_5$	CH_3OH[c]	Pentane	(−)$SiOCH_3$	86 inv	4e
IV-8	(+)SiCl	H_2O	Ether	(−)SiOH	93 inv	4g
IV-9	(+)SiCl	CH_3OH[c]	Pentane	(−)$SiOCH_3$	94 inv	4g
IV-10	(+)SiCl	$NaB(OCH_3)_4$	Ether	(−)$SiOCH_3$	91 inv	4g
IV-11	(+)SiCl	$LiAlH_4$	Ether	(−)SiH	100 inv	4g
IV-12	(+)SiCl	$C_6H_{11}OH$[c]	Pentane	(−)$SiOC_6H_{11}$	98 inv	4f
IV-13	(+)SiCl	CH_3COOK	Benzene	(+)$SiOOCCH_3$	88 inv	4e
IV-14	(+)SiCl	$Hg(OOCCH_3)_2$	Benzene	(+)$SiOOCCH_3$	92 inv	4a
IV-15	(+)SiCl	$C_6H_{11}NH_3O_2CC_6H_5$	$CHCl_3$	(+)$SiOOCC_6H_5$	93 inv	4a
IV-16	(+)SiCl	$C_6H_{11}NH_3F$	$CHCl_3$	(−)SiF	79 inv	4a
IV-17	(+)SiCl	EtLi	Ether	(−)SiEt	100 inv	1
IV-18	(+)SiBr	H_2O	Ether	(−)SiOH	92 inv	4a
IV-19	(+)SiBr	CH_3OH[c]	Pentane	(−)$SiOCH_3$	94 inv	4a
IV-20	(+)SiBr	$LiAlH_4$	Ether	(−)SiH	100 inv	4g
IV-21	(+)SiBr	$C_6H_{11}NH_3F$	$CHCl_3$	(−)SiF	90 inv	4a
IV-22	(+)SiH	Cl_2	CCl_4	(+)SiCl	99 ret	4g
IV-23	(+)SiH	Br_2	CCl_4	(+)SiBr	99 ret	4g
IV-24	(+)SiF	$LiAlH_4$	Ether	(−)SiH	77 inv	4g
IV-25	(+)SiF	EtLi	Ether	(+)SiEt	97 ret	1
IV-26	(+)Si-α-Np	Br_2	Benzene	(−)SiBr	87 inv	None
IV-27	(+)SiCl	α-NpLi	Ether	(−)Si-α-Np	70 inv	None
IV-28	(+)SiF	α-NpLi	Ether	(+)Si-α-Np	98 ret	None

[a] Refer to corresponding footnote in Table II. [b] C_6H_{11} = cyclohexyl. [c] Cyclohexylamine used as acid acceptor.

Table V. EtPhMeSi*X Compounds Having the Configuration



$$\begin{array}{c} Ph \\ | \\ Et\blacktriangleright Si \blacktriangleleft Me \\ \vdots \\ X \end{array}$$

Si*X[a]	[α] D, deg, solvent[b]
(*S*)-(+)-SiH	+2.5, CCl_4
(*R*)-(+)-SiCl	+3.0, CCl_4
(*R*)-(+)-SiBr	+3.4, benzene
(*R*)-(−)-Si-α-Np	−6.2, pentane

[a] Names for these compounds, in the order of listing, are: (*S*)-(+)-phenylethylmethylsilane; (*R*)-(+)-phenylethylmethylchlorosilane; (*R*)-(+)-phenylethylmethylbromosilane; (*R*)-(−)-α-naphthylphenylethylmethylsilane. [b] High conservation of optical activity in sequence 4 makes it probable that the above rotations correspond to high optical purity.

Table VI. Summary of Stereochemistry of EtPhMeSi*X

R_3Si^*X reactant	Reagent	Solvent	Product	Stereo-specificity, %[a]	α-NpPh-MeSi*X, ref
(+)SiH	Cl_2	CCl_4	(+)SiCl	100 ret	4g
(+)SiCl	$LiAlH_4$	Ether	(−)SiH	100 inv	4g
(+)SiBr	$LiAlH_4$	Ether	(−)SiH	100 inv	4g
(+)SiCl	α-NpLi	Ether	(+)Si-α-Np	95 inv	None
(−)Si-α-Np	Br_2	Benzene	(−)SiBr	95 inv	None

[a] Refer to corresponding footnote in Table IV.

MeSi group are found at 3.32, 3.42, 6.88, 7.0, 7.99, 8.95, 9.86, 10.35, 13.8, and 14.3 μ.

Anal. Calcd for $C_9H_{14}Si$: C, 72.0; H, 9.34; Si, 18.7. Found: C, 72.0; H, 9.39; Si, 18.8.

Preparation of (+)PhMeRSi*Cl. The chlorosilanes were prepared by following the procedure reported for the preparation of α-naphthylphenylmethylchlorosilane.[4g]

Chlorination of (+)-phenylneopentylmethylsilane (1.18 g), [α] D +2.5° (*c* 10.0 in CCl_4), in carbon tetrachloride solvent gave, after removal of solvent, 1.37 g (99% yield) of (+)-phenylneopentylmethylchlorosilane with [α]D +7.5° (*c* 12.5 in CCl_4). The infrared spectrum showed no absorption at 4.70 μ and showed the bands characteristic of the phenylneopentylmethylsilyl system.

Anal. Calcd for $C_{12}H_{19}ClSi$: C, 63.8; H, 8.41; Cl, 15.7; Si, 12.4. Found: C, 64.0; H, 8.43; Cl, 15.4; Si, 12.2.

Chlorination of (+)-benzhydrylphenylmethylsilane (7.34 g), [α]D +7.1° (*c* 3.5 in CCl_4), in carbon tetrachloride solvent gave, after removal of solvent, solution in pentane, and cooling, an initial crop of 6.90 g (84% yield) of (+)-benzhydrylphenylmethylchlorosilane. A portion recrystallized several times from pentane had mp 68.0–69.0°, and [α]D +14.1° (*c* 12.4 in pentane). The infrared spectrum showed no absorption at 4.70 μ and showed the bands characteristic of the benzhydrylphenylmethylsilyl system.

Anal. Calcd for $C_{20}H_{19}ClSi$: C, 74.4; H, 5.93; Cl, 11.0; Si, 8.70. Found: C, 74.1; H, 5.93; Cl, 11.2; Si, 8.80.

Chlorination of (+)-phenylethylmethylsilane (1.08 g), [α]D +2.53° (*c* 12.1 in CCl_4), gave 1.32 g (100% yield) of (+)-phenylethylmethylchlorosilane, [α]D +3.0° (*c* 10.0 in CCl_4). The infrared spectrum clearly showed the presence of the phenylethylmethylsilyl group.

Anal. Calcd for $C_9H_{13}ClSi$: C, 58.8; H, 7.07; Cl, 19.0; Si, 15.2. Found: C, 58.7; H, 7.07; Cl, 18.9; Si, 15.4.

Reactions of PhMeRSi*Cl with α-Naphthyllithium. The coupling reaction of (−)-benzhydrylphenylmethylchlorosilane with α-naphthyllithium has been reported.[1] A similar procedure was used for the reactions of the neopentylchlorosilane and the ethylchlorosilane with α-naphthyllithium. Reaction of (+)-phenylneopentylmethylchlorosilane (1.18 g), [α]D +7.5° (*c* 12.5 in CCl_4), with α-naphthyllithium in ether solvent at 0° gave (−)-α-naphthylphenylneopentylmethylsilane (1.05 g) in 64% yield with [α]D −18.6° (*c* 7.0 in pentane). The infrared spectrum was identical with that of the authentic α-naphthylphenylneopentylmethylsilane.

Reaction of (+)-phenylethylmethylchlorosilane (1.22 g), [α]D +3.0° (*c* 13 in CCl_4), with α-naphthyllithium in ether solvent at 0° gave (+)-α-naphthylphenylethylmethylsilane (0.55 g) in 30% yield with [α]D +5.1° (*c* 4.0 in pentane). The infrared spectrum was identical with that of the authentic α-naphthylphenylethylmethylsilane.

Preparation of PhMeRSi*Br. The bromosilanes were prepared by following the procedure reported for preparation of α-naphthylphenylmethylbromosilane.[4g] Treatment of (+)-phenylneopentylmethylsilane (1.03 g), $[\alpha]_D$ +2.5° (*c* 11.8 in CCl_4), with bromine (0.86 g) in carbon tetrachloride solvent gave, after removal of solvent, 1.45 g (99% yield) of (+)-phenylneopentylmethylbromosilane, $[\alpha]_D$ +10.1° (*c* 10.1 in CCl_4). The absence of the infrared band at 4.75 μ indicated complete reaction. The infrared bands characteristic of the phenylneopentylmethylsilyl group were present.

Anal. Calcd for $C_{12}H_{19}BrSi$: C, 53.2; H, 7.01; Br, 29.6; Si, 10.8. Found: C, 53.1; H, 6.98; Br, 29.7; Si, 10.8.

Treatment of (−)-benzhydrylphenylmethylsilane (2.16 g), $[\alpha]_D$ −7.1° (*c* 10.5 in CCl_4), with bromine (1.2 g) gave after removal of solvent 2.61 g (95% yield) of (−)-benzhydrylphenylmethylbromosilane with $[\alpha]_D$ −16.2° (*c* 13.0 in pentane). The infrared bands characteristic of the benzhydrylphenylmethylsilyl group were present.

Anal. Calcd for $C_{20}H_{19}BrSi$: C, 65.4; H, 5.21; Br, 21.8; Si, 7.65. Found: C, 64.4; H, 5.01; Br, 21.7; Si, 7.61.

Preparation of PhMeRSi*OH. The silanols were prepared by following the procedure reported for the preparation of α-naphthylphenylmethylsilanol.[4g] Hydrolysis of (+)-phenylneopentylmethylchlorosilane (0.79 g), $[\alpha]_D$ +4.7° (*c* 12.5 in CCl_4), in ether solvent gave a 95% yield (0.69 g) of (−)-phenylneopentylmethylsilanol, $[\alpha]_D$ −4.3° (*c* 6.8 in pentane). The infrared spectrum showed typical Si–OH absorption at 2.80 and 3.05 μ in addition to the usual phenylneopentylmethylsilyl bands.

Anal. Calcd for $C_{12}H_{20}OSi$: C, 69.3; H, 9.61; Si, 13.5. Found: C, 69.6; H, 9.82; Si, 13.6.

Hydrolysis of (−)-benzhydrylphenylmethylchlorosilane (1.17 g), $[\alpha]_D$ −13.7° (*c* 10.8 in pentane), in ether solvent gave an 88% yield of (+)-benzhydrylphenylmethylsilanol, $[\alpha]_D$ +17.9° (*c* 5.1 in pentane), as a viscous oil. The infrared spectrum shows typical Si–OH absorption at 2.80 and 3.05 μ in addition to the usual benzhydrylphenylmethylsilyl bands.

Anal. Calcd for $C_{20}H_{20}OSi$: C, 78.9; H, 6.62; Si, 9.23. Found: C, 78.4; H, 6.62; Si, 9.49.

Hydrolysis of (+)-phenylneopentylmethylbromosilane (3.22 g), $[\alpha]_D$ +8.4° (*c* 14.9 in CCl_4), in ether solvent gave a 100% yield (2.48 g) of (−)-phenylneopentylmethylsilanol, $[\alpha]_D$ −4.6° (*c* 6.2 in ether), having the expected infrared spectrum.

Hydrolysis of (−)-benzhydrylphenylmethylbromosilane (1.54 g), $[\alpha]_D$ −11.7° (*c* 31.4 in pentane), gave a 93% yield (1.17 g) of (+)-benzhydrylphenylmethylsilanol, $[\alpha]_D$ +10.1° (*c* 5.7 in pentane).

Preparation of PhMeRSi*F. The method used for the preparation of the fluorosilanes was similar to the procedure described in detail for the preparation of α-naphthylphenylmethylfluorosilane.[4a] Reaction of (+)-phenylneopentylmethylchlorosilane (0.62 g), $[\alpha]_D$ +4.7° (*c* 12.5 in CCl_4), with cyclohexylammonium fluoride (0.33 g) in chloroform solvent gave (−)-phenylneopentylmethylfluorosilane (0.53 g) in 93% yield with $[\alpha]_D$ −2.7° (*c* 2.6 in pentane). The infrared spectrum showed all of the bands characteristic of the phenylneopentylmethylsilyl group.

Anal. Calcd for $C_{12}H_{19}FSi$: C, 68.6; H, 9.05; F, 9.05. Found: C, 68.6; H, 9.28; F, 9.03.

Treatment of (+)-benzhydrylphenylmethylchlorosilane (1.65 g), $[\alpha]_D$ +10.9° (*c* 9.0 in pentane), with cyclohexylammonium fluoride (0.70 g) in chloroform solvent gave (−)-benzhydrylphenylmethylfluorosilane (1.46 g) in 84% yield. Several recrystallizations from pentane gave 0.37 g of material with mp 80–81°, and $[\alpha]_D$ −11.6° (*c* 1.8 in pentane). The infrared spectrum showed all of the bands characteristic of the benzhydrylphenylmethylsilyl group.

Anal. Calcd for $C_{20}H_{19}FSi$: C, 78.4; H, 6.25. Found: C, 78.4; H, 6.65.

Treatment of (+)-phenylneopentylmethylbromosilane (1.49 g), $[\alpha]_D$ +8.4° (*c* 14.9 in CCl_4), with cyclohexylammonium fluoride (0.65 g) in chloroform solvent gave (−)-phenylneopentylmethylfluorosilane (0.97 g) in 85% yield with $[\alpha]_D$ −1.8° (*c* 8.9 in pentane) and having the expected infrared spectrum.

Treatment of (−)-benzhydrylphenylmethylbromosilane (1.54 g), $[\alpha]_D$ −11.7° (*c* 31.4 in pentane), with cyclohexylammonium fluoride (0.50 g) in chloroform solvent gave (+)-benzhydrylphenylmethylfluorosilane (1.16 g) in 90% yield with $[\alpha]_D$ +6.6° (*c* 8.6 in pentane).

Preparation of PhMeRSi*OMe. Reaction of (+)-phenylneopentylmethylchlorosilane (2.35 g), $[\alpha]_D$ +4.7° (*c* 12.5 in CCl_4), with sodium tetramethoxyborane (2.0 g) in 25 ml of dry ether gave (−)-phenylneopentylmethoxysilane, $[\alpha]_D$ −8.6° (*c* 9.4 in pentane), in 72% yield (1.66 g) after 3 hr at room temperature. The infrared spectrum was consistent with the assigned structure and had bands at 3.60 and 9.15 μ characteristic of the $SiOCH_3$ moiety.

Anal. Calcd for $C_{13}H_{22}OSi$: C, 70.3; H, 9.91; Si, 12.6. Found: C, 70.1; H, 9.99; Si, 12.6.

Reaction of (+)-benzhydrylphenylmethylchlorosilane (4.25 g), $[\alpha]_D$ +13.1° (*c* 12.1 in pentane), with sodium tetramethoxyborane (6.0 g) in 30 ml of dry ether gave (−)-benzhydrylphenylmethylmethoxysilane, $[\alpha]_D$ −24.5° (*c* 12.8 in pentane), in 84% yield (3.54 g) after 7 hr at room temperature. The infrared spectrum of this material gave clear confirmation of the expected product.

Anal. Calcd for $C_{21}H_{22}OSi$: C, 79.2; H, 6.96; Si, 8.82. Found: C, 78.9; H, 6.85; Si, 8.69.

Preparation of PhMeRSi*OOCCH$_3$. 1. Reactions with Mercuric Acetate. Reaction of (+)-phenylneopentylmethylchlorosilane (2.35 g), $[\alpha]_D$ +4.7° (*c* 12.5 in CCl_4), with mercuric acetate (3.06 g) in benzene (25 ml) gave (−)-phenylneopentylmethylacetoxysilane (1.93 g) in 74% yield after 1 hr at reflux temperature. The acetoxysilane had $[\alpha]_D$ −0.94° (*c* 1.0 in pentane) and the infrared spectrum was consistent with the assigned structure and had the following bands characteristic of the $SiOOCCH_3$ moiety: 5.8, 8.0, and 9.8 μ.

Anal. Calcd for $C_{14}H_{22}O_2Si$: C, 76.2; H, 8.80; Si, 11.2. Found: C, 76.1; H, 8.81; Si, 11.4.

Reaction of (−)-benzhydrylphenylmethylchlorosilane (5.65 g), $[\alpha]_D$ −11.3° (*c* 31.4 in pentane), with mercuric acetate (5.65 g) in benzene (25 ml) gave (−)-benzhydrylphenylmethylacetoxysilane (5.55 g) in 91% yield after 1.5 hr at the reflux temperature. The acetoxysilane had $[\alpha]_D$ −6.5° (*c* 25.6 in pentane) and the infrared spectrum was consistent with the assigned structure.

Anal. Calcd for $C_{22}H_{22}O_2Si$: C, 76.3; H, 6.40; Si, 8.11. Found: C, 76.1; H, 6.35; Si, 8.23.

2. Reaction with Potassium Acetate. Reaction of (−)-benzhydrylphenylmethylchlorosilane (4.92 g), $[\alpha]_D$ −13.8° (*c* 10.5 in pentane), with potassium acetate (8.90 g) in 35 ml of benzene gave (−)-benzhydrylphenylmethylacetoxysilane (4.28 g) in 81% yield after 66 hr at room temperature. The product had $[\alpha]_D$ −4.9° (*c* 25.6 in pentane) and had the expected infrared spectrum.

Preparation of (+)Ph$_2$CHPhMeSi*O-cyclo-C$_6$H$_{11}$. Treatment of (−)-benzhydrylphenylmethylchlorosilane (6.48 g), $[\alpha]_D$ −14.1° (*c* 10.6 in pentane), with cyclohexanol (8.2 g) and cyclohexylamine (8.2 g) in pentane for 2 hr gave, after washing with water, drying over potassium carbonate, and fractional distillation, (+)-benzhydrylphenylmethylcyclohexoxysilane (2.77 g) in 30% yield with $[\alpha]_D$ +25.6° (*c* 9.7 in pentane) and bp 160–165° (0.7 mm). The infrared spectrum showed the bands characteristic of the benzhydrylphenylmethylsilyl group and also bands at 3.45, 7.30, 9.30, 11.52, and 12.05 μ attributed to the SiO-cyclo-C_6H_{11} group.

Anal. Calcd for $C_{26}H_{30}OSi$: C, 80.8; H, 7.82; Si, 7.27. Found: C, 80.6; H, 8.12; Si, 7.16.

Preparation of (−)Ph$_2$CHPhMeSi*OOCC$_6$H$_5$. Reaction of (−)-benzhydrylphenylmethylchlorosilane (5.14 g), $[\alpha]_D$ −13.7° (*c* 28 in ether), with cyclohexylammonium benzoate (3.52 g) in chloroform solvent gave (−)-benzhydrylphenylmethylbenzoxysilane (5.46 g) in 84% yield with $[\alpha]_D$ −16.4° (*c* 22.4 in pentane). The infrared spectrum showed the bands characteristic of the benzhydrylphenylmethylsilyl group and also bands at 5.90, 7.62, 7.78, and 8.55 μ attributed to the $SiOOCC_6H_5$ group.

Anal. Calcd for $C_{27}H_{24}O_2Si$: C, 79.4; H, 5.92; Si, 6.88. Found: C, 78.9; H, 6.11; Si, 6.82.

Methanolysis Reactions. The procedure used for the following methanolysis reactions has been described in detail for the methanolysis of α-naphthylphenylmethylbenzoxysilane.[4c] Treatment of (+)-phenylneopentylmethylchlorosilane (1.42 g), $[\alpha]_D$ +4.7° (*c* 12.5 in CCl_4), with methanol (5.0 g) and cyclohexylamine (10.0 g) in pentane gave (−)-phenylneopentylmethylmethoxysilane (1.0 g) in 72% yield with $[\alpha]_D$ −6.5° (*c* 10.0 in pentane). The infrared spectrum of this methoxysilane was identical with that of the authentic phenylneopentylmethylmethoxysilane.

Methanolysis of (+)-benzhydrylphenylmethylchlorosilane (2.42 g), $[\alpha]_D$ +13.4° (*c* 12.4 in pentane), gave (+)-benzhydrylphenylmethylmethoxysilane (1.86 g) in 77% yield with $[\alpha]_D$ −26.4° (*c* 10.2 in pentane).

Methanolysis of (+)-phenylneopentylmethylbromosilane (3.06 g), $[\alpha]_D$ +8.4° (*c* 14.9 in CCl_4), gave (−)-phenylneopentylmethylmethoxysilane (2.03 g) in 81% yield with $[\alpha]_D$ −8.1° (*c* 13.5 in pentane).

Methanolysis of (−)-benzhydrylphenylmethylbromosilane (1.54 g), $[\alpha]_D$ −11.7° (*c* 31.4 in pentane), gave (+)-benzhydrylphenylmethylmethoxysilane (1.27 g) in 95% yield with $[\alpha]_D$ + 19.1° (*c* 5.1 in pentane).

Methanolysis of (−)-phenylneopentylmethylacetoxysilane (0.33 g), $[\alpha]_D$ −0.94° (*c* 11.0 in pentane), gave a 96% yield (0.28 g) of

(+)-phenylneopentylmethylmethoxysilane, $[\alpha]_D$ +4.8° (*c* 2.6 in pentane).

Methanolysis of (+)-benzhydrylphenylmethylacetoxysilane (0.59 g), $[\alpha]_D$ +4.9° (*c* 3.3 in pentane), gave a 92% yield (0.50 g) of (+)-benzhydrylphenylmethylmethoxysilane, $[\alpha]_D$ +9.4° (*c* 3.2 in pentane).

Methanolysis of (−)-benzhydrylphenylmethylbenzoxysilane (1.82 g), $[\alpha]_D$ −16.0° (*c* 22.4 in pentane), was carried out in the usual way except that the product was chromatographed over silica gel. After chromatography, there was obtained a 25% yield (0.36 g) of (−)-benzhydrylphenylmethylmethoxysilane, $[\alpha]_D$ −18.4° (*c* 1.1 in pentane).

Lithium Aluminum Hydride Reductions. 1. PhMeRSi*Cl. The procedure used was similar to that previously reported for the reduction of α-naphthylphenylmethylchlorosilane with lithium aluminum hydride.[4g] Reduction of (+)-phenylneopentylmethylchlorosilane (1.18 g), $[\alpha]_D$ −7.5° (*c* 18.3 in CCl_4), with lithium aluminum hydride in ether solvent gave (+)-phenylneopentylmethylsilane (1.80 g) in 100% yield with $[\alpha]_D$ +2.5° (*c* 12.5 in CCl_4), and having the expected infrared spectrum.

Reduction of (+)-benzhydrylphenylmethylchlorosilane (2.18 g), $[\alpha]_D$ +14.1° (*c* 10.5 in pentane), gave (−)-benzhydrylphenylmethylsilane (1.77 g) in 91% yield with $[\alpha]_D$ −7.1° (*c* 12.8 in CCl_4).

Reduction of (+)-phenylethylmethylchlorosilane (1.70 g), $[\alpha]_D$ +3.0° (*c* 13.0 in CCl_4), gave (−)-phenylethylmethylsilane (1.36 g) in 98% yield with $[\alpha]_D$ −2.5° (*c* 11.0 in CCl_4).

2. PhMeRSi*Br. By a procedure similar to that used for the reduction of the chlorosilane, (+)-phenylneopentylmethylbromosilane (1.79 g), $[\alpha]_D$ +10.1° (*c* 11.9 in CCl_4), was reduced with lithium aluminum hydride and gave (−)-phenylneopentylmethylsilane (1.23 g) in 97% yield with $[\alpha]_D$ −2.5° (*c* 7.2 in CCl_4).

Reduction of (+)-benzhydrylphenylmethylbromosilane (1.41 g), $[\alpha]_D$ +16.2° (*c* 12.8 in pentane), gave (−)-benzhydrylphenylmethylsilane (0.64 g) in 58% yield with $[\alpha]_D$ −7.0° (*c* 4.3 in CCl_4).

3. PhMeRSi*F. By a procedure similar to that used for the reduction of the chlorosilane except that the reaction time was extended to 1 hr (−)-phenylneopentylmethylfluorosilane (0.97 g), $[\alpha]_D$ −1.8° (*c* 8.8 in pentane), was reduced with lithium aluminum hydride and gave (+)-phenylneopentylmethylsilane (0.83 g) in 91% yield with $[\alpha]_D$ +0.94° (*c* 12.0 in CCl_4).

Treatment of (+)-benzhydrylphenylmethylfluorosilane (1.96 g), $[\alpha]_D$ +8.4° (*c* 12.8 in pentane), with lithium aluminum hydride for 3 hr gave (−)-benzhydrylphenylmethylsilane (1.10 g) in 59% yield with $[\alpha]_D$ −2.1° (*c* 7.1 in pentane).

4. PhMeRSi*OMe. By a procedure similar to that used for the reduction of the chlorosilane except that the reaction time was extended to 20 hr, (−)-phenylneopentylmethylmethoxysilane (0.65 g), $[\alpha]_D$ −13.7° (*c* 10.0 in pentane), was reduced with lithium aluminum hydride and gave (−)-phenylneopentylmethylsilane (0.57 g) in 100% yield, with $[\alpha]_D$ −2.5° (*c* 7.2 in CCl_4).

Reaction of (+)-benzhydrylphenylmethylmethoxysilane (0.98 g), $[\alpha]_D$ +19.1° (*c* 5.1 in pentane), with lithium aluminum hydride for 1 hr gave (+)-benzhydrylphenylmethylsilane contaminated with unreacted methoxysilane. After chromatography over silica gel with 40% benzene–pentane, (+)-benzhydrylphenylmethylsilane (0.56 g) was obtained in 63% yield with $[\alpha]_D$ +2.5° (*c* 3.3 in pentane).

5. PhMeRSi*OH. To a solution of lithium aluminum hydride (1.50 g) in 15 ml of dry ether was added a solution of (−)-phenylneopentylmethylsilanol (2.49 g), $[\alpha]_D$ −4.6° (*c* 6.2 in ether), in 25 ml of di-*n*-butyl ether. The flask contents were then heated and the solvent distilled until a temperature of 138° was reached. After 3 hr at this elevated temperature, the reaction mixture was hydrolyzed with dilute HCl, dried over potassium carbonate, and chromatographed over silica gel. Removal of the solvent left (−)-phenylneopentylmethylsilane (1.05 g) in 46% yield with $[\alpha]_D$ −0.90° (*c* 4.6 in pentane).

By a procedure similar to that above except that the temperature was maintained at 130° for 1 hr, (−)-benzhydrylphenylmethylsilanol (2.71 g), $[\alpha]_D$ +17.9° (*c* 5.1 in pentane), gave (−)-benzhydrylphenylmethylsilane, $[\alpha]_D$ −3.3° (*c* 9.1 in pentane), in an 87% yield (2.16 g).

6. Reduction of PhMeRSi*OOCCH$_3$. The procedure used was similar to that previously reported for the reduction of α-naphthylphenylmethylacetoxysilane with lithium aluminum hydride.[4e] Reduction of (−)-phenylneopentylmethylacetoxysilane (0.87 g), $[\alpha]_D$ −0.94° (*c* 11.0 in pentane), with lithium aluminum hydride at −78° in ether gave (+)-phenylneopentylmethylsilane (0.32 g) in 48% yield with $[\alpha]_D$ +0.63° (*c* 6.4 in pentane).

Reduction of (+)-benzhydrylphenylmethylacetoxysilane (3.12 g), $[\alpha]_D$ +16.3° (*c* 14.0 in ether), with lithium aluminum hydride at −78° gave (+)-benzhydrylphenylmethylsilane (0.26 g) in 10% yield with $[\alpha]_D$ +3.1° (*c* 1.8 in pentane).

Reduction of (+)Ph$_2$CHPhMeSi*O-cyclo-C$_6$H$_{11}$. By a procedure similar to that described above for the reduction of benzhydrylphenylmethylsilanol, except that the reaction time at 130° was 3 hr, (+)-benzhydrylphenylmethylcyclohexoxysilane (1.69 g), $[\alpha]_D$ +19.1° (*c* 9.7 in pentane), was reduced with lithium aluminum hydride and gave (+)-benzhydrylphenylmethylsilane (0.46 g) in 36% yield with $[\alpha]_D$ +2.6° (*c* 3.8 in pentane).

Reduction of (+)Ph$_2$CHPhMeSi*OOCC$_6$H$_5$. The procedure is similar to that described above for the reduction of the acetoxysilane. Reduction of (+)-benzhydrylphenylmethylbenzoxysilane (1.19 g), $[\alpha]_D$ +12.7° (*c* 6.0 in pentane), with lithium aluminum hydride at −60° gave (+)-benzhydrylphenylmethylsilane (0.40 g) in 48% yield with $[\alpha]_D$ +1.9° (*c* 2.1 in pentane).

Reactions with KOH(s). 1. (+)-Phenylneopentylmethylsilanol. By the procedure used for the preparation of α-NpPhMeSi*OK,[4g] (+)-phenylneopentylmethylsilanol, $[\alpha]_D$ +4.6° (*c* 10.2 in pentane), was treated with powdered potassium hydroxide and gave a 99% yield of a 0.604 *N* solution of the potassium silanolate in xylene. The (−)-potassium silanolate had $[\alpha]_D$ −2.3° (*c* 15.1 in xylene) and was not isolated.

2. (−)-Phenylneopentylmethylmethoxysilane. Treatment of a xylene solution of (−)-phenylneopentylmethylmethoxysilane (0.42 g), $[\alpha]_D$ −8.6° (*c* 10.0 in pentane), with potassium hydroxide (4.0 g) for 1 hr on the steam bath gave a cloudy solution from which the optical activity could not be determined. The xylene solution was therefore hydrolyzed by adding it to a 250-ml separatory funnel containing ether (100 ml) and water (100 ml), shaking vigorously for a few seconds, washing with water, and drying over potassium carbonate. Removal of the solvent gave (−)-phenylneopentylmethylsilanol (0.35 g) in 90% yield with $[\alpha]_D$ −4.7° (*c* 3.5 in pentane) and having an infrared spectrum identical with that of the authentic silanol.

3. (−)-Phenylneopentylmethylacetoxysilane. Treatment of (−)-phenylneopentylmethylacetoxysilane (0.47 g), $[\alpha]_D$ −0.94° (*c* 11 in pentane), with potassium hydroxide, as described above for the methoxysilane, gave a 92% yield (0.35 g) of (+)-phenylneopentylmethylsilanol, $[\alpha]_D$ +3.1° (*c* 2.4 in pentane).

Reactions of Potassium Phenylneopentylmethylsilanolate. 1. Hydrolysis. A xylene solution (5.0 ml) of (−)-potassium phenylneopentylmethylsilanolate (0.604 *N*, 3.02 mmoles), $[\alpha]_D$ −2.34° (*c* 15.1 in xylene), was diluted with dry ether (20 ml) and poured into a 250-ml separatory funnel containing cold water (100 ml). After shaking vigorously, washing with water, and drying over potassium carbonate, the solvent was removed leaving (+)-phenylneopentylmethylsilanol (0.59 g) in 94% yield with $[\alpha]_D$ +4.6° (*c* 2.7 in pentane).

2. With Dimethyl Sulfate. To 4.0 ml of a xylene solution of (−)-potassium phenylneopentylmethylsilanolate (0.604 *N*, 2.42 mmoles), $[\alpha]_D$ −2.3° (*c* 15.1 in xylene), was added purified dimethyl sulfate (2.00 g) resulting in immediate formation of a precipitate. The material was shaken for a few seconds, then diluted with pentane (100 ml) and washed with sodium bicarbonate solution and four times with water before drying over potassium carbonate. Removal of the volatiles under vacuum gave (+)-phenylneopentylmethylmethoxysilane (0.33 g) in 62% yield with $[\alpha]_D$ +8.1° (*c* 3.3 in pentane) and having the expected infrared spectrum.

3. With Acetyl Chloride. To a xylene solution (7.0 ml) of (−)-potassium phenylneopentylmethylsilanolate (0.604 *N*, 4.2 mmoles, $[\alpha]_D$ −2.3° [*c* 15.1 in xylene]) was added acetyl chloride (4.0 g) resulting in an immediate formation of a precipitate. Removal of xylene and excess acetyl chloride under vacuum left a residue which was diluted with pentane. Filtration and removal of the pentane gave (+)-phenylneopentylmethylacetoxysilane (0.83 g) in 78% yield with $[\alpha]_D$ +1.4° (*c* 11.0 in pentane).

Reactions with Ethyllithium. Details of the procedure used have been reported for the coupling of ethyllithium with α-naphthylphenylmethylchlorosilane.[1] Addition of (−)-benzhydrylphenylmethylchlorosilane (6.60 g), $[\alpha]_D$ −13.9° (*c* 32.4 in ether), to ethyllithium gave an 89% yield (5.72 g) of (+)-benzhydrylphenylethylmethylsilane, $[\alpha]_D$ +11.0° (*c* 27.0 in pentane), bp 190–192° (2.5 mm), after fractional distillation.

Anal. Calcd for $C_{22}H_{24}Si$: C, 83.5; H, 7.64; Si, 8.88. Found: C, 83.2; H, 8.08; Si, 8.65.

Reaction of ethylllithium with (−)-benzhydrylphenylmethylfluorosilane (3.5 g), $[\alpha]_D$ −11.6° (*c* 12.2 in pentane), gave an 88% yield (3.24 g) of (−)-benzhydrylphenylethylmethysilane with $[\alpha]_D$ −10.2° (*c* 18.6 in pentane).

Reaction of Cycyohexylammonium Chloride with (+)-Phenylneopentylmethylbromosilane. Treatment of (+)-phenylneopentylmethylbromosilane (1.71 g), $[\alpha]_D$ +3.8° (c 11.4 in CCl_4), with cyclohexylammonium chloride (0.85 g) in chloroform (60 ml) gave (−)-phenylneopentylmethylchlorosilane (1.17 g) in 82% yield with $[\alpha]_D$ −1.6° (c 5.9 in CCl_4) and having the expected infrared spectrum.

Reaction of Lithium Dimethoxyaluminum Hydride with (+)-Phenylneopentylmethylchlorosilane. Reaction of (+)-phenylneopentylmethylchlorosilane (1.18 g), $[\alpha]_D$ +7.5° (c 11.8 in CCl_4), with excess lithium dimethoxyaluminum hydride (prepared from the hydride and methanol)[4g] for 2 hr gave 1.07 g of product shown to be ~55% methoxysilane and 45% silane by an infrared spectrum. The rotation of the mixture was $[\alpha]_D$ −4.9° (c in 10.7 in pentane). The mixture was placed on a column of silica gel and allowed to stand for 12 hr. Elution with pentane–benzene (50%) gave (−)-phenylneopentylmethylsilane (0.49 g) in 49% yield with $[\alpha]_D$ −2.3° (c 4.9 in CCl_4). Therefore, by difference, the (−)-methoxysilane (0.58 g) had $[\alpha]_D$ −8.2° (c 5.8 in pentane).

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Stereochemistry of Electrophilic Substitutions on 2-Norbornyllithium

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Abstract: It has been demonstrated that brominolysis of *exo-* and *endo-*2-norbornyllithium occurs with predominant inversion of configuration, while carboalkoxylation (with chloroformate esters) occurs with preferred (but not complete) retention. It is concluded that concerted aliphatic electrophilic substitutions, in contrast with nucleophilic substitutions, have both inversion and retention pathways available, and the pathway chosen depends upon subtle factors not yet elucidated.

The stereochemistry of concerted electrophilic aliphatic substitutions has been studied by a number of workers in the past two decades, and the result has been a considerable body of data to indicate that such substitutions prefer retention of configuration. Examples are the carbonations of secondary alkyllithiums,[1,2] alkenyllithiums,[2,3] and cyclopropyllithiums;[4,5] the halogen–metal interchanges in the same systems;[1,3–5] metal–metal exchanges of saturated[2,6,7] and olefinic[2] organomercurials; and brominolysis of cyclohexylmercuric bromides[8] and cyclopropyllithiums.[4] In the last-named case, Applequist and Peterson found that *cis-* and *trans-*2-methylcyclopropyllithium reacted with bromine with preferential but incomplete retention of configuration. The experiments herein described were conceived to explore the reason for this incomplete retention.

Absence of stereospecificity in a substitution reaction first suggests an intermediate carbanion, radical, or cation. Arguments against the carbanion had been raised[4] in the cyclopropyl case, where the lithium reagents show no tendency to epimerize at the lithiated carbon, so the most probable possibilities seemed to be the free radical, which had already been found[8] in organomercurial brominolyses under certain conditions, and the carbonium ion, which might react under some conditions with a nucleophile before it can open to the allylic cation. The radical and cation possibilities, it was thought, could be differentiated in the 2-norbornyl case, which should give considerable *endo*-norbornyl bromide in any reaction of norbornyl radical with bromine,[9] but exclusively *exo* product from the norbornyl cation with bromide.[10] Furthermore, from an optically active norbornyllithium, only the cation mechanism should lead to racemized product.[10–12] Because of the unexpected results obtained in this work with the racemic norbornyllithiums, it proved unnecessary to examine the optically active forms.

Results and Discussion

2-Norbornyllithium was prepared from *exo*-2-norbornyl chloride and lithium metal in refluxing pentane in yields as high as 33%, but averaging about 10%. *endo*-2-Norbornyl chloride also gave yields of about 10%. The same *exo*/*endo* mixture of lithium reagents was formed in either case, as shown by the near identities of the product ratios from reactions with various electrophiles at −70° (Table I). Also to be noted in Table I (footnotes) is that several efforts to change the composition of the cold epimeric lithium reagent mixture by selective destruction of the more reactive epimer failed to change the final product mixtures significantly. Finally, and most importantly, the data show that the different reagents give very different product mixtures, which means that at least some of the reactions do not proceed with simple retention of configuration.

Suitable controls, described in the Experimental Section, were done to establish the stabilities of all

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