Stereochemistry of Asymmetric Silicon. V. Coupling Reactions with Organometallic Reagents and Displacements of Chloride and Fluoride Leaving Groups[1]

L. H. Sommer,[2] W. D. Korte, and P. G. Rodewald

Contribution from the Departments of Chemistry, The Pennsylvania State University, University Park, Pennsylvania, and the University of California, Davis, California.
Received October 6, 1966

Abstract: The stereochemistry of displacement of chloride and fluoride leaving groups from asymmetric silicon in optically active compounds containing the α-naphthylphenylmethylsilyl group, α-NpPhMeSi*-, has been studied for reactions which comprise coupling with organometallic reagents. *Inversion* of configuration was found to be the predominant stereochemical path for R_3Si^*Cl with all the R′Li compounds studied. In contrast, R_3Si^*F gives predominant *retention* of configuration in its reactions with simple alkyllithium reagents. However, with reagents like allyllithium, benzyllithium, α-methylbenzyllithium, benzhydryllithium, and 9-fluorenyllithium, R_3Si^*F gives *inversion* of configuration. Ethylmagnesium bromide couples with $R_3Si^*OCH_3$ with *retention* of configuration, and benzylmagnesium chloride gives *inversion* of configuration with R_3Si^*Cl and R_3Si^*F. *The general significance of these results for organosilicon mechanisms is examined.* An SN2-Si mechanism for the *inversion* reactions, and a quasi-cyclic SNi-Si mechanism for the *retention* reactions, seem most reasonable.

One of the most useful methods for formation of carbon-silicon bonds is the coupling reaction of organometallic reagents with silicon-halogen compounds.[3] In this paper are reported the first stereochemical data which relate to the mechanisms of these interesting reactions and which also serve to demonstrate *retention* of configuration as an important stereochemical path for displacement of fluoride from asymmetric silicon in optically active α-naphthylphenylmethylfluorosilane, designated R_3Si^*F below.[4]

Reaction of R_3Si^*OMe with ethylmagnesium bromide in ether is slow at room temperature. Removal of most of the ether and heating at 90° for several hours gave[4]

$$(+)R_3Si^*OMe + EtMgBr \longrightarrow (+)R_3Si^*Et \qquad (1)$$

Reaction of the methoxysilane with ethyllithium in ether took the same stereochemical course.

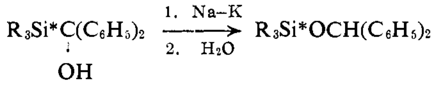
$$(+)R_3Si^*OMe + EtLi \longrightarrow (+)R_3Si^*Et \qquad (2)$$

Reaction of R_3Si^*Cl with ethyllithium proceeds rapidly at room temperature and gave the following result.

$$(-)R_3Si^*Cl + EtLi \xrightarrow{\text{ether}} (-)R_3Si^*Et \qquad (3)$$

On the basis of assignment of the same configuration to $(+)R_3Si^*OMe$ and $(-)R_3Si^*Cl$,[5] reactions 1 and 2 pursue stereochemical paths opposite to that of reaction 3. The previous findings of retention of configuration for the lithium aluminum hydride reduction of R_3Si^*OMe to R_3Si^*H and for the Grignard reduction of R_3Si^*OMe to R_3Si^*H by *t*-butylmagnesium chloride[5b] suggest *retention* of configuration for reactions 1 and 2. The general stereochemical rule—arrived at on the basis of many reactions of R_3Si^*Cl with diverse nucleophiles—of inversion of configuration for reactions of R_3Si^*Cl with bases stronger than chloride[1] suggests inversion of configuration for reaction 3. Two elegant studies by Brook and co-workers reinforce this conclusion.[6,7]

The reasonable assignment of a retention stereochemistry to the following rearrangement



$$R_3Si^*\underset{\displaystyle OH}{C}(C_6H_5)_2 \xrightarrow[\text{2. } H_2O]{\text{1. Na–K}} R_3Si^*OCH(C_6H_5)_2$$

plus assignment of a retention stereochemistry to lithium aluminum hydride reduction of the rearrangement product to R_3Si^*H, in analogy to earlier known examples of retention for reduction of R_3Si^*OR,[5b] led to assignment of an inversion stereochemistry for the coupling reaction of benzhydryllithium with R_3Si^*Cl.[6]

$$(+)R_3Si^*Cl + (C_6H_5)_2CHLi \xrightarrow{\text{ether}} (-)R_3Si^*CH(C_6H_5)_2 \qquad (4)$$

On the basis of similar evidence, an inversion stereochemistry has been assigned to the coupling reaction of R_3Si^*Cl with benzylsodium.[7]

$$(-)R_3Si^*Cl + PhCH_2Na \xrightarrow[\text{toluene}]{\text{ether}} (-)R_3Si^*CH_2C_6H_5 \qquad (5)$$

On balance, the evidence for inversion of configuration as the stereochemical path for coupling reactions of R_3Si^*Cl with R′Li is quite convincing and is in accord with the general stereochemical rule of *inversion* of configuration in many displacement reactions of R_3Si^*Cl.

Although the lithium aluminum hydride reduction of R_3Si^*F to R_3Si^*H proceeds with *inversion* of configuration,[5a] it was found in the present work that reaction

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[1] For the preceding paper in this series, see: L. H. Sommer, G. A. Parker, N. C. Lloyd, C. L. Frye, and K. W. Michael, *J. Am. Chem. Soc.*, **89**, 857 (1967).

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

[3] *Cf.* C. Eaborn, "Organosilicon Compounds," Butterworths and Co. London, 1960, Chapter 2.

[4] For a preliminary report on a few of the reactions reported herein, see: L. H. Sommer, P. G. Rodewald, and G. A. Parker, *Tetrahedron Letters*, 18, 821 (1962).

[5] (a) L. H. Sommer, C. L. Frye, G. A. Parker, and K. W. Michael, *J. Am. Chem. Soc.*, **86**, 3271 (1964); (b) L. H. Sommer, C. L. Frye, and G. A. Parker, *ibid.*, **86**, 3276 (1964).

[6] A. G. Brook and C. M. Warner, *Tetrahedron Letters*, **18**, 815 (1962).

[7] A. G. Brook and W. W. Limburg, *J. Am. Chem. Soc.*, **85**, 832 (1963).

Table I. Stereochemistry of Coupling Reactions of α-NpPhMeSi*X, R_3Si*X, with Organolithium Reagents

No.	R_3Si*X reactant	Reagent[a]	Product	$[\alpha]$D, deg[b]	Stereo-chemistry, %[c,d]
1	(+)SiCl	EtLi	(+)SiEt	+6.1	100 inv
2	(−)SiF	EtLi	(−)SiEt	−1.2	60 ret
3	(+)SiCl	*n*-PrLi	(+)Si-*n*-Pr	+1.5	94 inv
4	(−)SiF	*n*-PrLi	(−)Si-*n*-Pr	−1.7	100 ret
5	(+)SiCl	*n*-BuLi	(−)Si-*n*-Bu	−0.6	59 inv
6	(−)SiF	*n*-BuLi	(+)Si-*n*-Bu	+3.2	100 ret
7	(+)SiCl[e]	*i*-PrLi	(+)Si-*i*-Pr	+2.2	67 inv
8	(−)SiF[e]	*i*-PrLi	(−)Si-*i*-Pr	−6.4	100 ret
9	(+)SiCl	*i*-BuLi	(−)Si-*i*-Bu	−6.4	100 inv
10	(−)SiF	*i*-BuLi	(+)Si-*i*-Bu	+5.9	96 ret
11	(+)SiCl	*neo*-C_5H_{11}Li	(−)Si-*neo*-C_5H_{11}	−23.1	100 inv
12	(−)SiF	*neo*-C_5H_{11}Li	(+)Si-*neo*-C_5H_{11}	+19.0	91 ret
13	(+)SiCl	Ph_2CHLi	(−)Si-$CHPh_2$	−16.6[f]	97 inv[g]
14	(−)SiF	Ph_2CHLi	(−)Si-$CHPh_2$	−16.8[f]	97 inv[g]
15	(+)SiCl	$PhCH_2Li$	(+)Si-CH_2Ph	+6.9	100 inv
16	(−)SiF	$PhCH_2Li$	(+)Si-CH_2Ph	+4.9	85 inv
17	(+)SiCl	$Ph(CH_3)CHLi$	(+)Si-$CH(CH_3)Ph$	+36.2	100 inv
18	(−)SiF	$Ph(CH_3)CHLi$	(+)Si-$CH(CH_3)Ph$	+8.3	61 inv
19	(+)SiCl	(*p*-$CH_3OC_6H_4$)CH_2Li	(−)Si-CH_2($C_6H_4OCH_3$-*p*)	−14.1	100 inv
20	(−)SiF	(*p*-$CH_3OC_6H_4$)CH_2Li	(−)Si-CH_2($C_6H_4OCH_3$-*p*)	−14.0	100 inv
21	(+)SiCl	$CH_2{=}CHCH_2Li$	(+)Si-$CH_2CH{=}CH_2$	+12.8	100 inv
22	(−)SiF	$CH_2{=}CHCH_2Li$	(+)Si-$CH_2CH{=}CH_2$	+5.5	71 inv
23	(+)SiCl	9-Fluorenyllithium[h]	(+)Si-9-fluorenyl	+6.4	65 inv
24	(−)SiF	9-Fluorenyllithium[h]	(+)Si-9-fluorenyl	+21.5	100 inv

[a] Reactions were run in dry ethyl ether unless otherwise noted. [b] Rotations were taken on pentane solutions unless otherwise noted. For consistency of presentation, data are given for (+)R_3Si*Cl and (−)R_3Si*F, although sometimes their enantiomers were used. [c] A stereospecificity of, say, 90% means that the product was 80% optically pure (20% racemic), if an optically pure reactant was used. [d] In the case of the benzhydryl and benzyl derivatives, the products could be crystallized up to optical purity, thus indicating high stereospecificity for these reactions. In other cases, the product of highest rotation from reaction with a given R′Li compound was assumed to be optically pure. [e] Reactions run in a pentane solvent. [f] Chloroform solvent. [g] Based on optically pure (+)R_3Si*$CHPh_2$, $[\alpha]$D +17.9°. [h] Reactions run in pentane–benzene solvent.

of the fluorosilane with R_3Si*OK in xylene proceeds with *retention* of configuration.

$$(+)R_3Si^*F + (-)R_3Si^*OK \xrightarrow{\text{xylene}} (+)R_3Si^*OSi^*R_3 \qquad (6)$$

Retention in reaction 6 follows from previous assignment of the same configuration to the reactants and product.[5b] Reaction 6, proceeding with *retention* of configuration, is in striking contrast to the *inversion* stereochemistry which obtains for the reaction of R_3Si*Cl with R_3Si*OK under the same conditions.[5b]

In view of the change in stereochemistry of reaction with R_3Si*OK engendered by the change from a chloride to a fluoride leaving group, it was of interest to compare R_3Si*Cl and R_3Si*F in their reactions with R′Li compounds.

Table I gives the results of comparison of R_3Si*Cl and R_3Si*F in their reactions with a wide variety of organolithium reagents. Most of these reagents were used in ether solvent, but *i*-PrLi was used in pentane and 9-fluorenyllithium in pentane–benzene solvent.

In reactions 1–12 which involved simple alkyllithium reagents the stereochemistry for R_3Si*F was opposite to that found for R_3Si*Cl. The same configuration obtains for (+)R_3Si*Cl and (−)R_3Si*F.[5a] For these reactions, the assignment of an inversion stereochemistry for R_3Si*Cl is based on evidence summarized above. *Thus, the reactions of R_3Si*F with six simple alkyllithium reagents pursue a predominant retention stereochemistry.*

In reactions 13–24 which involved allyllithium and benzyl-type lithium reagents the predominant stereochemistry of reaction for R_3Si*Cl is inversion of configuration. However, *the stereochemistry of reaction for R_3Si*F is changed to inversion of configuration.*

In addition to the above reactions reported in Table I, the coupling reactions of α-naphthyllithium with Ph_2CHPhMeSi*Cl and the corresponding fluoride were studied. Based on previous assignments of relative configuration, reaction of the chlorosilane proceeded with predominant inversion of configuration.[8] Stereospecificity is 70% inversion.

$$(-)Ph_2CHPhMeSi^*Cl + \alpha\text{-NpLi} \xrightarrow{\text{ether}} (+)Ph_2CHPhMeSi^*\text{-}\alpha\text{-Np} \qquad (7)$$

Based on wide-ranging parallelism between the stereochemistry of the α-NpPhMeSi*- and Ph_2CHPhMeSi*- systems, multidirectional evidence exists[9] for assignment of the same configuration to (−)Ph_2CHPhMeSi*Cl and (−)Ph_2CHPhMeSi*F.

$$(-)Ph_2CHPhMeSi^*F + \alpha\text{-NpLi} \xrightarrow{\text{ether}} (-)Ph_2CHPhMeSi^*\text{-}\alpha\text{-Np} \qquad (8)$$

Thus, reaction 8 in contrast to 7 proceeds with retention of configuration. Stereospecificity for (7) is 70% net inversion of configuration. Reaction 8 proceeds with 99% net retention of configuration. Optically pure benzhydrylphenylmethyl-α-naphthylsilane[6] has $[\alpha]$D 17.9°, and the assigned stereochemistry values are based on that figure. The product from (7) had $[\alpha]$D +7.0°, and that from 8 had $[\alpha]$D −17.4°.

It is probable that deviation from 100% inversion of configuration for the reactions of R_3Si*Cl in Table I and for reaction 7 is not due to simultaneous opera-

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(8) L. H. Sommer, K. W. Michael, and W. D. Korte, *J. Am. Chem. Soc.*, **85**, 3712 (1963).

(9) From data in ref 8 and unpublished work of L. H. Sommer, K. W. Michael, and W. D. Korte.

tion of a slower retention mechanism. We believe that such deviation usually results from racemization of R_3Si^*Cl prior to coupling in most cases. This is almost certainly the situation for reactions 7 and 23 in Table I which take place relatively slowly.

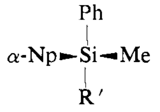
Reactions of benzylmagnesium chloride in ether solvent with R_3Si^*Cl and R_3Si^*F (R_3Si^* is a α-Np-PhMeSi*) were found to be quite stereospecific.

$$(+)R_3Si^*Cl + C_6H_5CH_2MgCl \xrightarrow{Et_2O} (+)R_3Si^*CH_2C_6H_5 \quad (9)$$

$$(-)R_3Si^*F + C_6H_5CH_2MgCl \xrightarrow{Et_2O} (+)R_3Si^*CH_2C_6H_5 \quad (10)$$

Stereochemistry for these reactions was 93 and 94% inversion for (9) and (10), respectively. In (9), conditions were about 20 hr at ambient temperature. Reaction 10 was carried out by heating at reflux temperature for 14 hr.

It is interesting to tabulate in Table II the R_3Si^*R' compounds which are assigned the same configuration as $(+)R_3Si^*H$, on the basis of the stereochemistry assignments in Table I plus the earlier demonstration that $(+)R_3Si^*H$, $(-)R_3Si^*Cl$, and $(+)R_3Si^*F$ have the same configuration.[5] The R_3Si^*R' compounds in Table II which have the same configuration as $(+)R_3Si^*H$ also have the *absolute configuration*



$$\alpha\text{-Np}-\underset{\text{R}'}{\overset{\text{Ph}}{\text{Si}}}-\text{Me}$$

Table II. R_3Si^*R' Enantiomers Having the $(+)R_3Si^*H$ Configuration

α-NpPh-MeSi*–R′ R′	[α]D, deg[a]	α-NpPh-MeSi*–R′ R′	[α]D, deg[a]
H	+34	9-Fluorenyl[b]	+22
Et	+6	$(C_6H_5)_2CH$[c]	−17
n-Pr	+2	$(C_6H_5)CH_2$	−7
n-Bu	−3	$(C_6H_5)(CH_3)CH$	+36
i-Pr	+6	$CH_2{=}CHCH_2$	+12
i-Bu	−6	*p*-$CH_3OC_6H_4CH_2$	−14
neo-C_5H_{11}	−23		

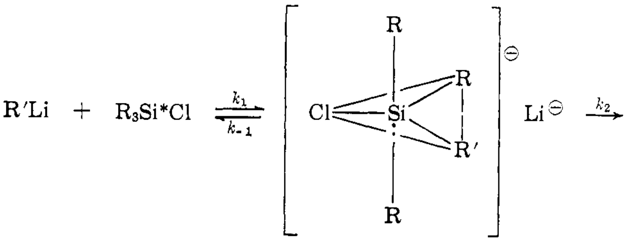
[a] Pentane solvent except as noted. [b] Ether solvent. [c] Chloroform solvent.

The importance of conformation as well as polarizability of groups in determining sign of rotation of R_3Si^*R' is evident from examination of Table II.

General Mechanism Considerations. In this section, it is proposed to examine the general mechanistic significance of the above studies for organosilicon chemistry. Possible mechanism models are discussed in the next section.

Against the background of earlier studies which revealed inversion of configuration to be the common stereochemical path for reactions of R_3Si^*Cl with diverse nucleophiles,[1] the finding of an inversion stereochemistry for the reactions of R_3Si^*Cl with R′Li would appear to be unexceptional. However, the fact that, regardless of the detailed mechanism, the entering group in these reactions is formally R'^- leads to some important mechanistic conclusions.

Excellent yields and high stereospecificity are characteristic of the reactions of α-NpPhMeSi*Cl with R′Li, and these findings serve to dispose of possible operation of an SN2*-Si mechanism for which $k_{-1} \gg k_2$ would obtain in the formulation[10]



I

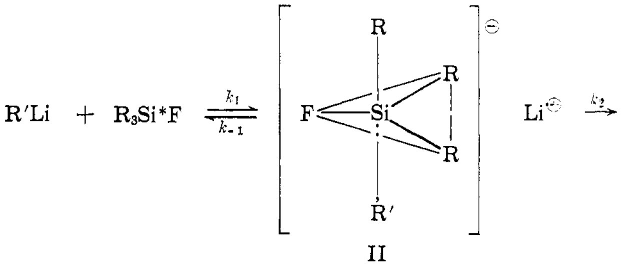
R_3Si^*R' (inverted) + LiCl

In the intermediate I, the entering group R′ and one of the nonreacting organic groups occupy equivalent equatorial positions in a trigonal bipyramid and are bonded to silicon by equally full bonds. According to the previous definition of an SN2*-Si mechanism,[10] intermediate I is a full-fledged pentacovalent silicon species containing *five full bonds to silicon*. For convenience, *such an intermediate is designated Si-5* in subsequent discussion. For mechanism SN2*-Si, formation of Si-5 is rapid and breakup to products is slower than return to starting reactants.

For the particular geometry of Si-5 shown in I, which involves "equatorial entry" of the entering group R′, it seems entirely unreasonable to expect that Si-5 could return many times to R′Li and R_3Si^*Cl without accompanying extensive exchange of organic groups and formation of optically inactive mixed products.

Structure I for Si-5, both entering and leaving groups equatorial, is one possible geometry which would lead to inversion of configuration if the over-all geometry about the silicon center is trigonal bipyramidal.[11] The other disposition of entering and leaving groups for an inversion stereochemistry would be for R′ and Cl to occupy both apical positions. For this geometry, the argument can still be made that an SN2*-Si mechanism could give exchange of organic groups by a retention stereochemistry—apical R′ exchanging with equatorial R—but this argument is weakened by the implied assumption of nearly equal rates of expulsion of apical and equatorial organic groups.

A very convincing case can be made *against* Si-5 in an SN2*-Si mechanism for the *retention* reactions of R_3Si^*F and R′Li. For "apical entry" of R′Li in a reaction giving *retention* of configuration, the formulation would be



II

R_3Si^*R' (retained config) + LiF

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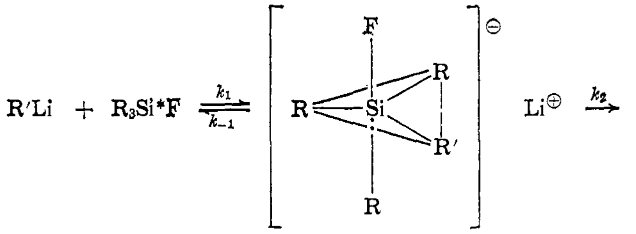
(10) For previous discussion of mechanism SN2*-Si, see: L. H. Sommer, "Stereochemistry, Mechanism and Silicon," McGraw-Hill Book Co., Inc., New York, N. Y., 1965.

(11) This has been pointed out for phosphorus centers by P. C. Haake and F. H. Westheimer, *J. Am. Chem. Soc.*, **83**, 1102 (1961), and for silicon, independently, by C. Eaborn, *J. Organometal. Chem.* (Amsterdam), **1**, 37 (1963), and by L. H. Sommer, ref 10, pp 183–184.

As before, for SN2*–Si $k_{-1} \gg k_2$, and for II as for I, optically inactive mixed products should result from exchange of R′ and R. *This is not observed.* For "equatorial entry" of R′Li in a reaction giving *retention* of configuration with R_3Si^*F, the formulation would be



III

R_3Si^*R' (retained config) + LiF

For III, extensive exchange of equatorial R′ with equatorial R in an SN2*–Si mechanism should result in optically inactive mixed products.

Thus, the retention reactions of R_3Si^*F with R′Li are shown not to involve an SN2*–Si mechanism, despite the fact that on any grounds this would be the class of reactions of R′Li most expected to involve formation of Si-5. From this, and the above considerations of the inversion reactions of R_3Si^*Cl with R′Li, it seems unlikely that mechanism SN2*–Si obtains for any of the coupling reactions being reported.

Operation of an SN2**–Si mechanism,[12] for which formation of Si-5 is slow (k_1) and rate controlling and $k_2 \gg k_{-1}$, is also highly improbable for the reactions of R_3Si^*X with R′Li. Previous work has shown that the ability of a leaving group to stabilize a negative charge is a critical factor in determining the reaction stereochemistry of R_3Si^*X.[1] For mechanism SN2**–Si there is no significant breaking of Si–X in the rate-controlling step.[12]

In the present work, the dramatic change from a retention stereochemistry for R_3Si^*F with alkyllithium or aryllithium reagents, to an inversion stereochemistry when allyllithium and benzyl-type organolithiums are used, is exceedingly difficult to rationalize in terms of mechanism SN2**–Si which would simply involve rate-controlling addition of R'^- to the silicon center without significant stretching of the Si–F bond.

Bond-energy considerations (see below) also argue strongly against operation of SN2**–Si in the coupling reactions.

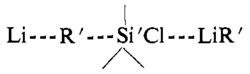
It is proposed that the inversion reactions reported in this paper for R_3Si^*X and R′Li proceed by an SN2–Si mechanism. It should be emphasized that such a mechanism may or may not involve an unstable intermediate. However, if such an intermediate is involved, its structure is very different from that of Si-5. Instead of five full bonds to silicon, the "bonds" to the entering and leaving groups, Y and X, are long and weak relative to those between silicon and the nonreacting groups. Also, an unstable intermediate in a reaction proceeding by an SN2–Si mechanism has a structure and free energy very similar to those of the rate-controlling transition state. For SN2–Si, an over-all trigonal bipyramidal geometry with X and Y occupying apical positions seems most probable.[13]

It is proposed that the retention reactions reported in this paper for R_3Si^*X and R′Li proceed by an SNi–Si mechanism.[14] Like SN2–Si, such a mechanism may or may not involve an unstable intermediate which has long and weak "bonds" to the entering and leaving groups. Over-all geometry for SNi–Si may be a tetragonal pyramid or a trigonal bipyramid. In the former geometry both X and Y are basal. In the latter, one is apical and the other is equatorial. Mechanism SNi–Si involves quasi-cyclic, rate-controlling transition states which are usually four center.

Mechanism Models. Any discussion of coupling reactions of R_3Si^*Cl or R_3Si^*F with organometallic reagents must take into consideration the fact that replacements of Cl or F on silicon by R′ are, of themselves, quite endothermic. From studies of the bond dissociation energies of $(CH_3)_3Si–Y$ by electron impact, where Y is CH_3, CH_3CH_2, $(CH_3)_2CH$, $(CH_3)_3C$, Cl, and F, it was found that D(Si–Cl) exceeds D(Si–C) by about 40 kcal/mole, and that D(Si–F) is greater than D(Si–C) by about 100 kcal/mole.[15] Although the latter value may be too high, Cottrell's values[16] and Margrave's value for D(Si–F)[17] still lead to a value of about 70 kcal/mole higher bond energy for Si–F than for Si–C. In these circumstances it is reasonable to conclude that (1) the rate-controlling transition states for the coupling reactions must involve considerable stretching of the high-energy Si–Cl and Si–F bonds, and (2) that stretching of these bonds must be accompanied by a concerted formation of LiCl and LiF whose high heats of formation ($\Delta H_f°$), −97 and −145 kcal/mole, respectively, are certainly needed to offset the high energy cost of replacing Cl and F on silicon by R′. It is clear that these considerations make it necessary to include substantial electrophilic attack on the Si–X bond in any reasonable transition-state structures for these reactions.

Since detailed elucidation of the structures and reaction mechanisms of organolithium compounds is in an early and active stage of development,[18] only relatively simple and nondetailed mechanism models can be proposed in the present paper. These will be limited to suggestions of approximate transition-state structures for the inversion and retention reactions reported above. In the structures given below, it must be emphasized that *the R′Li units may or may not be components of larger (R′Li)$_n$ aggregates. Also, donor solvent molecules are not shown.*

Within the limits just prescribed, structure IV constitutes a reasonable model for the inversion reactions of R_3Si^*Cl with simple alkyl- and aryllithium reagents.



$$\mathrm{Li{-}{-}{-}R'{-}{-}{-}\overset{|}{\underset{\wedge}{Si}}{'}Cl{-}{-}{-}LiR'}$$

IV, R′ = alkyl or aryl

Structure IV is very similar to the transition state proposed by Eastham and co-workers[19] for the coupling

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[12] For previous discussion of mechanism SN2**–Si, see ref 10.

[13] For previous detailed discussion of mechanism SN2–Si see ref 1 and 10.

[14] For previous detailed discussion of mechanism SNi–Si see ref 5b and 10.

[15] G. G. Hess, F. W. Lampe, and L. H. Sommer, *J. Am. Chem. Soc.*, 87, 5327 (1965).

[16] T. Cottrell, "The Strength of Chemical Bonds," 2nd ed, Butterworth and Co., London, 1958, pp 270–280.

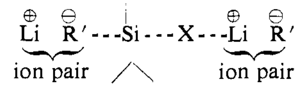
[17] T. C. Ehlert and J. L. Margrave, *J. Chem. Phys.*, **41**, 1066 (1964).

[18] For a recent review, see: T. L. Brown, *Advan. Organometal. Chem.*, 3, 365 (1965).

[19] J. F. Eastham and G. W. Gibson, *J. Am. Chem. Soc.*, **85**, 2171 (1963).

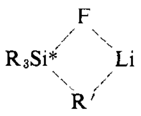
reaction of *n*-butyllithium with 1-bromooctane in hexane–ether solvents. Rate studies and evidence in accord with a solvated dimer, $Et_2O(\cdot BuLi)_2$, are consistent with their conclusion.[19]

A substantial increase in the ionic character of the carbon–lithium bond would be expected for the benzyl-type R'Li compounds because of delocalization of negative charge, and various recent studies confirm this expectation.[20] For such reagents, structure V (X = Cl) seems reasonable for *inversion* with R_3Si^*Cl in ether solvent.



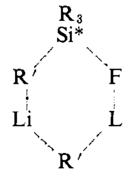
V, R' = benzyl-type group

For the *inversion* reactions of R_3Si^*F with charge-delocalized R'Li reagents, structure V (X = F), because of high ionic character of the carbon–lithium bond and delocalization of negative charge, can provide sufficient electrophilic assistance (by formation of LiF) to overcome the high bond energy of Si–F. However, sufficient electrophilic assistance cannot be supplied by simple alkyl- or aryllithium reagents using structure IV. Instead, an SNi-Si mechanism is proposed, in which breaking of Si–F and breaking of Li–C are mutually helpful in promoting formation of Si–C and LiF. The simplest version of such a mechanism would involve transition-state structure VI which may have over-all trigonal bipyramid or tetragonal pyramid geometry about the silicon center.[5b]



VI, R' = alkyl or aryl

However, the real reasons for a retention stereochemistry in the reactions of R_3Si^*F with alkyl- or aryllithium reagents may not be as simple as the one just advanced, and may lead to preferred formation of a quasi-six-ring transition state which has over-all tetragonal pyramid geometry about the silicon center and would give retention of configuration. Grignard reduction of R_3Si^*OR' to R_3Si^*H by *t*-butylmagnesium chloride proceeds with retention of configuration in an assigned SNi-Si mechanism which involves a quasi-six-ring analogous to VII.[5b]



VII, R' = alkyl or aryl

Several papers have emphasized *inversion* of configuration for ~120° displacement of the leaving group by the entering group, both groups equatorial in an over-all trigonal bipyramid geometry.[11,21] However, it is also true that *retention* of configuration would result from the same disposition of entering and leaving groups (~120°), if the over-all geometry involves a pyramidal arrangement of the nonreacting groups about the reaction center.[22]

Experimental Section

Reactions with Ethyllithium. To a solution of 2.0 g of (+)-α-naphthylphenylmethylchlorosilane, $[\alpha]_D$ +6.1° (*c* 10.1 in pentane),[5a] in 10 ml of anhydrous ether was added 1.42 g of ethyllithium in 50 ml of ether. Reaction was rapid and exothermic. After standing overnight at ambient temperature the product was isolated by the following procedure. The contents of the reaction flask were poured into a 1-l. separatory funnel containing 200 ml of pentane. After addition of ice, the mixture was extracted with cold, dilute hydrochloric acid. The organic layer was repeatedly extracted with water until the water extracts were no longer acidic. The combined aqueous layers were neutralized and extracted three times with 50-ml quantities of pentane. The organic layers were then combined, dried over anhydrous potassium carbonate, and then filtered. Removal of solvent under vacuum gave 1.87 g (96% yield) of (+)-α-naphthylphenylethylmethylsilane as an oil having $[\alpha]_D$ +6.1° (*c* 8.8 in pentane). The infrared spectrum (neat) of this material showed the absorption bands characteristic of the α-naphthylphenylmethylsilyl system[5a] and new maxima at 3.51, 6.90, 9.98, 10.07, and 15.0 μ attributed to the ethyl group on silicon. In a larger preparation which gave 25 g of the same product, the α-naphthylphenylethylmethylsilane was distilled and had bp 195–197° at 3.8 mm and n^{25}_D 1.6183.

Anal. Calcd for $C_{19}H_{20}Si$: C, 82.7; H, 7.24; Si, 10.2. Found: C, 82.8; H, 7.48; Si, 10.1.

In the above reactions and in all subsequent reactions of R'Li, where R' is alkyl, described below, the organolithium reagent was allowed to stand in a dry nitrogen atmosphere for some hours in order to allow insoluble salts to settle out and was then transferred to a separatory funnel using dry nitrogen. The organolithium reagent was usually added very rapidly to the halosilane solution in the reaction flask.

The product from the reaction of the (+)-chlorosilane with ethyllithium in pentane for 16 hr at 38° had an infrared spectrum which showed the presence of a small amount of silicon hydride, R_3Si^*H, resulting from reduction of the silicon halide by the organolithium reagent. (Infrared showed no Si–H in the starting halosilane.) The Si–H impurity was removed by the following procedure. The product was treated with dry chlorine in carbon tetrachloride solvent until the appearance of a yellow-green color indicated that Si–H had been converted to Si–Cl. After hydrolysis, chromatography over silica gel separated the desired product from R_3SiOH. There was obtained 1.59 g (81% yield) of product having $[\alpha]_D$ +4.8° (*c* 11.0 in pentane) which had an infrared spectrum identical with that of authentic α-naphthylphenylethylmethylsilane.

By the above procedures and reaction for 13 hr at 38°, (−)-α-naphthylphenylmethylfluorosilane, $[\alpha]_D$ −46.0° (*c* 3.6 in ethyl ether),[5a] gave a 95% yield of (−)-α-naphthylphenylethylmethylsilane having $[\alpha]_D$ −3.2° (*c* 7.5 in pentane) whose infrared spectrum was identical with that of the authentic substance.

Addition of (+)-α-naphthylphenylmethylmethoxysilane (1.95 g), $[\alpha]_D$ +16.5° (*c* 2.8 in pentane),[5a] to ethyllithium in ether solvent gave after work-up, as described above, and elution chromatography through a 30 × 1 in. column of silica gel with a 50% benzene–pentane solvent blend the (+)-ethylsilane in 79% yield (1.55 g) with $[\alpha]_D$ +2.9° (*c* 7.5 in pentane). The infrared spectrum of the material was identical with that of the authentic ethylsilane.

Reactions with *n*-Propyllithium. By the procedures described above the reaction of the (+)-chlorosilane with *n*-propyllithium in ether solvent gave a 94% yield of (+)-α-naphthylphenyl-*n*-propylmethylsilane, $[\alpha]_D$ +1.5° (*c* 8.4 in pentane), as an oil whose infrared spectrum had the bands characteristic of the α-naphthylphenylmethylsilyl group and also had bands at 3.43, 3.53, 6.90, 7.12, and 9.42 μ; no silanol, siloxane, or silicon hydride bands were present. From the (−)-fluorosilane in ether solvent, the product had $[\alpha]_D$ −1.7° (*c* 5.7 in pentane) and was obtained in 92% yield.

Anal. Calcd for $C_{20}H_{22}Si$: Si, 9.66. Found: Si, 9.63.

Reactions with *n*-Butyllithium. By the procedures described above the reaction of the (+)-chlorosilane with *n*-butyllithium in ether solvent gave a 95% yield of (−)-α-naphthylphenyl-*n*-butylmethylsilane, $[\alpha]_D$ −0.58° (*c* 9.7 in pentane), as an oil whose infrared

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(20) *Cf.* V. R. Sandel and H. H. Freedman, *J. Am. Chem. Soc.*, **85**, 2328 (1963); R. Waack and M. A. Doran, *ibid.*, **85**, 1651 (1963), and subsequent papers by Waack and co-workers.

(21) J. Day and D. J. Cram, *ibid.*, **87**, 4398 (1965); R. L. Schowen and K. S. Latham, Jr., *ibid.*, **88**, 3795 (1966).

(22) For retention reactions proceeding by mechanism SNi-Si, the advantages of a pyramidal arrangement of nonreacting groups are discussed in ref 10, pp 61–64.

spectrum had the bands characteristic of the α-naphthylphenylmethylsilyl system and also had bands at 3.42, 3.45, 3.53, 6.89, 9.30, and 11.50 μ. From the (−)-fluorosilane in ether solvent, the product had $[\alpha]_D$ +3.2° (*c* 10.5 in pentane) and was obtained in 99% yield.

Anal. Calcd for $C_{21}H_{24}Si$: Si, 9.23. Found: Si, 9.16.

Reactions with Isobutyllithium. By the procedures described above the reaction of the (+)-chlorosilane with isobutyllithium in ether solvent gave an 89% yield of (−)-α-naphthylphenylisobutylmethylsilane, $[\alpha]_D$ −6.4° (*c* 2.1 in pentane), as an oil whose infrared spectrum had the bands characteristic of the α-naphthylphenylmethylsilyl group and also had bands at 3.42, 3.53, 6.88, 7.27 (weak), 7.36 (weak), 9.20, and 9.66 μ. From the (−)-fluorosilane in ether solvent, the product had $[\alpha]_D$ +5.9° (*c* 2.50 in pentane) and was obtained in 94% yield.

Anal. Calcd for $C_{21}H_{24}Si$: Si, 9.23. Found: Si, 9.29.

Reactions with Neopentyllithium. By the procedures described above the reaction of the (+)-chlorosilane with neopentyllithium in ether solvent gave a 97% yield of (−)-α-naphthylphenylneopentylmethylsilane, $[\alpha]_D$ −23.2° (*c* 4.5 in pentane), as an oil whose infrared spectrum had the bands characteristic of the α-naphthylphenylmethylsilyl group and also had bands at 3.43, 3.50, 3.53, 6.85, 7.37, and 8.12 μ attributed to the neopentyl group on silicon. In a large run which gave 30.73 g of product, the product was distilled and had bp 188–190° at 1.8 mm, $n^{27.5}D$ 1.5993. From the (−)-fluorosilane in ether solvent, the product had $[\alpha]_D$ +19.0° (*c* 3.2 in pentane).

Anal. Calcd for $C_{22}H_{26}Si$: C, 83.0; H, 8.18; Si, 8.85. Found: C, 83.2; H, 8.02; Si, 8.80.

Reactions with Isopropyllithium in Pentane. By the procedures described above the reaction of (+)-chlorosilane with isopropyllithium in pentane gave an 84% yield of (+)-α-naphthylphenylisopropylmethylsilane, $[\alpha]_D$ +2.2° (*c* 4.16 in pentane), as an oil whose infrared spectrum had the bands characteristic of the α-naphthylphenylmethylsilyl group and also had the following bands attributed to the isopropyl group on silicon: 3.43, 3.51, 6.83, and 10.02 μ. From the (−)-fluorosilane in pentane solvent, the product was obtained in 87% yield and had $[\alpha]_D$ −6.4° (*c* 8.56 in pentane).

Anal. Calcd for $C_{20}H_{22}Si$: Si, 9.66. Found: Si, 9.71.

Reaction with 9-Fluorenyllithium. The lithium reagent was prepared by treatment of fluorene with *n*-butyllithium in a solvent containing equal volumes of pentane and benzene. Addition of the (+)-chlorosilane was followed by heating at 49° for 17 hr. In addition to the usual work-up, the product was obtained as an orange-red, glassy substance whose infrared spectrum had the bands characteristic of the α-naphthylphenylmethylsilyl group and also had bands at 3.32, 6.82, and 6.94 μ attributed to the presence of the 9-fluorenyl group. The product had $[\alpha]_D$ +6.4° (*c* 1.4 in ether). From the (−)-fluorosilane, by a similar procedure, the product obtained had $[\alpha]_D$ +21.5° (*c* 2.9 in ether).

Anal. Calcd for $C_{30}H_{24}Si$: Si, 6.82. Found: Si, 6.78.

Reaction of (+)-α-Naphthylphenylmethylmethoxysilane with Ethylmagnesium Bromide.[23] Addition of the (+)-methoxysilane to excess ethylmagnesium bromide in ether solvent was followed by removal of as much ether as possible by heating on the steam bath and "baking" the reactants at steam-bath temperature overnight. After hydrolysis and isolation there was obtained an 89% yield of (+)-α-naphthylphenylethylmethylsilane, $[\alpha]_D$ +4.1° (*c* 12 in pentane), havng an infrared spectrum identical with that of the authentic substance.

Reaction of (+)R_3Si^*F with (−)R_3Si^*OK.[24] By the procedure already reported[5b] for reaction of R_3Si^*Cl with R_3Si^*OK, treatment of the (+)-fluorosilane with (−)R_3Si^*OK gave (+)-1,3-di-α-naphthyl-1,3-diphenyl-1,3-dimethyldisiloxane, mp 86–88°, $[\alpha]_D$ +8.1° (*c* 2.2 in pentane), whose infrared spectrum was identical with that of authentic disiloxane.

Reactions with Benzhydryllithium. The procedure of Brook and Warner[6] when applied to the (−)-chlorosilane (46.5 g) gave (+)-α-naphthylphenylbenzhydrylmethylsilane, $[\alpha]_D$ +16.6° (*c* 6.1 in $CHCl_3$), in 96% yield (65.0 g) after fractional distillation, bp 200–210° (1.0 mm). A portion recrystallized from heptane had mp 123–124° and $[\alpha]_D$ +17.7° (*c* 12.1 in $CHCl_3$) (lit.[6] mp 123–125°, $[\alpha]_D$ +17.89°). Addition of the (−)-fluorosilane to benzhydryllithium in ether solvent gave a product having an infrared spectrum identical with that of the authentic substance and $[\alpha]_D$ −16.8° (*c* 15.1 in $CHCl_3$).

Reactions with Benzyllithium. The lithium reagent was prepared by dropwise addition of benzyl ether (13.3 g) to a rapidly stirred mixture of ethyl ether (250 ml) and lithium wire (5 g) cut into 0.125-in. lengths.[25] The straw-colored mixture was stirred for 2 hr, after which a straw-colored material settled, leaving a bright red solution of benzyllithium which was removed from the solid and the unreacted lithium by means of nitrogen pressure. One hour after the addition of the (−)-chlorosilane (3.68 g), the reaction mixture was worked up in the same manner as described above. After elution chromatography through a 30 × 1 in. column of silica gel with 300 ml of a 50% benzene–pentane solvent blend and subsequent removal of solvent, the viscous oil was fractionally distilled. (−)-α-Naphthylphenylbenzylmethylsilane was obtained in 82% yield (3.62 g) with $[\alpha]_D$ −5.3° (*c* 3.4 in cyclohexane), $[\alpha]_D$ +6.9° (*c* 2.8 in pentane), and bp 190–195° (10 mm) (lit.[7] $[\alpha]_D$ −6.68° [*c* 6.0 in cyclohexane], mp 69–70°). Reaction of the (+)-fluorosilane (3.33 g) with benzyllithium gave, after fractional distillation, a 62% yield (2.62 g) of the benzylsilane having the expected infrared spectrum and with $[\alpha]_D$ −4.5° (*c* 9.5 in cyclohexane).

Anal. Calcd for $C_{24}H_{22}Si$: Si, 8.30. Found: Si, 8.37.

Reactions with Benzylmagnesium Chloride. Benzylmagnesium chloride was prepared by slowly adding a solution of benzyl chloride in anhydrous ethyl ether (50 ml) to magnesium turnings (5 g) in ethyl ether (50 ml) with a trace of iodine present. To the dark green Grignard reagent, a solution of the (−)-chlorosilane (3.09 g) in ethyl ether (50 ml) was added. After 24 hr at ambient temperature, the reaction mixture was worked up using the procedure described above. Elution chromatography through a 26 × 0.5 in. column of silcia gel with a 50% benzene–pentane solvent blend and subsequent distillation using a micro column gave (+)-α-naphthylphenylbenzylmethylsilane in a 55% yield (2.12 g) and with $[\alpha]_D$ +5.90 (*c* 8.8 in pentane) and $[\alpha]_D$ −5.8° (*c* 8.6 in cyclohexane). The infrared spectrum was identical with that of the benzylsilane prepared from reaction with the lithium reagent. Reaction of the (−)-fluorosilane (4.20 g) with benzylmagnesium chloride for 14 hr at 35° gave the benzylsilane (3.74 g) with $[\alpha]_D$ −6.0° (*c* 3.0 in pentane), $[\alpha]_D$ +6.6° (*c* 4.7 in cyclohexane), and mp 66–68° (uncorrected). Recrystallization from pentane gave the benzylsilane with $[\alpha]_D$ −6.4° (*c* 4.3 in pentane), $[\alpha]_D$ +6.9° (*c* 4.5 in cyclohexane), and mp 68–70°.

Reactions with α-Methylbenzyllithium. The lithium reagent was prepared by adding bis-α-methylbenzyl ether (6.3 g) to lithium wire (4 g) and ethyl ether (250 ml) and then stirring rapidly while heating the mixture to reflux for 8 hr.[25] After allowing the mixture to stand for 30 min, the bright red lithium reagent was removed from a brown solid and the unreacted lithium by means of nitrogen pressure. Addition of (+)-chlorosilane (2.31 g) to the reagent gave, after work-up and elution chromatography, as described earlier for the benzylsilane, (+)-α-naphthylphenyl-(α-methylbenzyl)methylsilane (2.42 g) as a viscous gum in 84% yield and with $[\alpha]_D$ +36.2° (*c* 11.5 in pentane). The infrared spectrum had the bands characteristic of the α-naphthylphenylmethylsilyl group and also had bands at 3.45, 6.90, 8.60, 7.88, and 10.0 μ attributed to the presence of the α-methylbenzyl group on silicon. From the (+)-fluorosilane (2.41 g) the α-methylbenzylsilane was obtained in 95% yield (3.03 g) with $[\alpha]_D$ −8.30° (*c* 10.7 in pentane) and having the expected infrared spectrum.

Anal. Calcd for $C_{25}H_{24}Si$: C, 85.2; H, 6.86; Si, 7.97. Found: C, 85.5; H, 6.89; Si, 7.98.

Reactions of *p*-Methoxybenzyllithium. *p*-Methoxybenzyllithium was prepared by heating and rapidly stirring for 4 hr a mixture of di-*p*-anisyl ether (7.1 g), dry ethyl ether (300 ml), and lithium metal wire (5.0 g), cut into small pieces. The red-orange lithium reagent was separated from the excess lithium metal by means of nitrogen pressure. A solution of (−)-α-naphthylphenylmethylchlorosilane (1.59 g) in ethyl ether (50 ml) was added to the reagent. After 10 min, the reaction was worked up using the procedure described above. The crude product was chromatographed through a 24 × 0.5 in. column of silca gel with benzene (300 ml). Removal of the solvent under vacuum left (+)-α-naphthylphenyl(*p*-methoxybenzyl)methylsilane (0.25 g) with $[\alpha]_D$ +12.3° (*c* 0.9 in pentane). The infrared spectrum showed bands characteristic of the α-naphthylphenylmethylsilyl group and also strong bands at 3.40, 3.55, 6.20, 6.80, 7.67, 8.45, and 9.58 μ attributed to the *p*-methoxybenzyl group on silicon.

Reaction of the (−)-fluorosilane (0.91 g) with *p*-methoxybenzyllithium gave the (−)-*p*-methoxybenzylsilane (0.22 g) with $[\alpha]_D$

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[23] This experiment was performed by G. A. Parker.

[24] This experiment was performed by C. L. Frye.

[25] H. Gilman and H. A. McNinch, *J. Org. Chem.*, **26**, 3723 (1961).

−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]

L. H. Sommer,[3] K. W. Michael, and W. D. Korte

Contribution from the Department of Chemistry, The Pennsylvania State University, University Park, Pennsylvania. *Received October 6, 1966*

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]