(10 g, 0.13 mol) in water (3 ml) was mixed with potassium hydroxide (*ca.* 0.5 g) and a catalytic amount of ferric chloride, and air was bubbled through the reaction mixture for 6 hr. Removal of solvent under reduced pressure gave a residue from which the product, bis(2-hydroxyethyl) disulfide, was obtained (*ca.* 4 g) by rapid distillation (kugelrohr) at reduced pressure, bp *ca.* 110° (0.01 mm), mp 22-26° (lit.[56] mp 25-26°).

A sample of (−)-(*R*)-methylphenylpropylphosphine (**14**), which was prepared by the hexachlorodisilane reduction[6] of (+)-(*R*)-methylphenylpropylphosphine oxide (**15**),[57] was reoxidized[6] with hydrogen peroxide to give (−)-(*S*)-**15**, $[\alpha]_D$ −15.0° (methanol), optical purity[58] 75%.

A solution of this same sample of (−)-(*R*)-methylphenylpropylphosphine (50 mg, 0.3 mmol) in benzene (3.3 ml) was added to bis(2-hydroxyethyl) disulfide (46 mg, 0.3 mmol) and the mixture was stirred at *ca.* 50° for 10 hr. Removal of solvent under reduced pressure gave the crude product, which was rapidly distilled (kugelrohr) at reduced pressure, bp *ca.* 110° (0.1 mm). The distillate was chromatographed on silica gel, eluting with ethyl acetate, to give (−)-(*S*)-**15** (39 mg, 71%), $[\alpha]_D$ −14.1° (methanol), optical purity 71%.

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[56] E. J. Gasson, H. McCombie, A. H. Williams, and F. N. Woodward, *J. Chem. Soc.*, 44 (1948).

[57] O. Korpiun, R. A. Lewis, J. Chickos, and K. Mislow, *J. Am. Chem. Soc.*, 90, 4842 (1968).

[58] J. P. Casey, R. A. Lewis, and K. Mislow, *ibid.*, **91**, 2789 (1969).

Stereochemistry of Asymmetric Silicon. XIII. General Demonstration of Stereochemistry Crossover for Reactions Involving Certain Leaving Groups and Alkoxide Reagents[1,2]

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Abstract: Stereochemistry crossover from retention to inversion of configuration (or *vice versa*) in individual reaction series involving alkoxide reagents is reported for the leaving groups OPh, SMe, and F. The reactant is R_3Si^*X (R_3Si^* is α-naphthylphenylmethylsilyl). Mechanistic implications of this work are discussed and further support for the SNi–Si and SN2–Si mechanisms is adduced.

Two previous publications have reported that (a) stereochemistry crossover from *inversion* to *retention* of configuration (or *vice versa*) in coupling reactions is a sensitive function of the nature of the organometallic reagent (RLi or RMgX) and the basicity of the leaving group (X = Cl, F, OMe, or H);[3] (b) stereochemical variation (per cent *retention vs.* per cent *inversion*) and stereochemistry crossover in alkoxide–alkoxide exchange reactions are a sensitive function of the alcoholic content of the solvent and the nature of the cation;[4] (c) the relationships that were revealed in both studies are consistent with earlier conclusions that *inversion* reactions of R_3Si^*X with strong nucleophiles proceed by mechanism SN2–Si and that *retention* reactions follow a quasicyclic SNi–Si mechanism.[3-5]

For SNi–Si, which operates with leaving groups that are usually highly basic and are classed as "poor,"[5] the only previous extensive and systematic study of solvent and reagent effects on the operation or nonoperation of this mechanism has involved alkoxide leaving groups in alkoxide–alkoxide exchange reactions. We now report additional extensive studies which encompass a variety of leaving groups (X = OPh, F, or SCH_3) with alkoxide reagents, for the purpose of extending our detailed knowledge concerning the factors which are critical for operation of the SNi–Si mechanism.

Stereochemical Studies of the Phenoxide Leaving Group. The phenoxide group in $(+)R_3Si^*OPh$ (R_3Si^* is α-naphthylphenylmethylsilyl) gives replacement with predominant retention of configuration yielding (+)-R_3Si^*H when treated with lithium aluminum hydride. Relative configurations for the products of reduction and alkoxide replacement of phenoxide were assigned on the basis of the SN2–Si stereochemistry rule with particular reference to the inversion path always followed by reactions of R_3Si^*Cl with strong nucleophiles.[4-6]

The phenoxide group can be classed as a borderline leaving group (poor leaving groups have pK_a of HX larger than *ca.* 10 and PhOH has $pK_a \sim 10$) and it is, of course, far less basic than an alkoxide group (MeOH has $pK_a \sim 16$). Thus, a comparison of OMe and OPh as leaving groups with alkoxide reagents is of considerable interest. (It may be noted that alkoxide groups are also reduced with lithium aluminum hydride with predominant retention of configuration.)

The first studies concern reaction of R_3Si^*OPh with *n*-butoxide in mixed benzene–butanol solvent and results are presented in Table I. In detail, the reactions studied are

$$R_3Si^*OPh + n\text{-BuOM} \xrightarrow[\text{benzene}]{n\text{-BuOH}} R_3Si^*O\text{-}n\text{-Bu} \qquad \text{(I)}$$

where M = Li, Na.

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[1] For the preceding paper in this series, see L. H. Sommer, J. D. Citron, and G. A. Parker, *J. Am. Chem. Soc.*, **91**, 4729 (1969).

[2] We are grateful for vital support of this work by National Science Foundation.

[3] L. H. Sommer and W. D. Korte, *J. Am. Chem. Soc.*, **89**, 5802 (1967).

[4] L. H. Sommer and H. Fujimoto, *ibid.*, 90, 982 (1968).

[5] L. H. Sommer, "Stereochemistry, Mechanism, and Silicon," McGraw-Hill Book Co., Inc., New York, N. Y., 1965; see Chapter 11 for a summary.

[6] L. H. Sommer, G. A. Parker, N. C. Lloyd, C. L. Frye, and K. W. Michael, *J. Am. Chem. Soc.*, **89**, 857 (1967).

Table I. Stereochemical Studies of Reactions I

Run[a]	Reaction[b] time, hr	Metal alkoxide[c] (mol × 10^3)	n-BuOM (mol)/ R_3SiOPh (mol)	n-BuOH (mol)/ n-BuOM (mol)	n-BuOH, vol % in solvent	Predominant stereochemistry, %[d]
I-1	3.5	n-BuOLi (2.1)	1.25	1.6	2.2	Ret, 94
I-2	2.5	n-BuOLi (2.2)	1.32	6.3	8.7	Ret, 75
I-3	2.0	n-BuOLi (2.1)	1.24	39.6	50	Inv, 84
I-4	1.5	n-BuONa (2.2)	1.30	2.4	3.2	Inv, 62
I-5	4.0	n-BuONa (2.4)	1.40	6.3	8.7	Inv, 84

[a] The specific rotation of optically pure R_3Si^*OPh was taken to be an experimental maximum value of 9.75° obtained by the authors. [b] Runs I-1, -2, and -4 were carried out at reflux temperature. The rest were run at room temperature. The times listed were actual reaction times, but do not comprise *minimal* times required for complete reaction. [c] Excess alkoxide over phenoxysilane was used because phenoxide stays in solution and takes up cations due to the acidity of phenol. [d] For the explicit definition of, and reasons for, the use of the term "predominant stereochemistry," see ref 1. For example, ret, 94% means that configuration was retained 94% and inverted 6%, giving an optical purity of the product of 88%.

Table II. Stereochemical Studies of Reactions II

Run[a]	Reaction time, hr	Metal alkoxide (mol × 10^4)	n-BuOH (mol)/n-BuOM (mol)	n-BuOH (mol)/R_3Si^*-OMe (mol)	n-BuOH, vol %, in solvent	Predominant stereochemistry, %[b,c]
II-1	12	n-BuOLi (3.8)	10	2.6	2.3	Ret, 100
II-2	3.8	n-BuOLi (22)	10	15	16.7	Ret, 89
II-3	3.5	n-BuOLi (9.5)	72	47	51.2	Inv, 65
II-4	0.14	n-BuOLi (5.5)	210	79	100	Inv, >81[d]
II-5	6.5	n-BuONa (2.6)	15	2.6	2.3	Ret, 95
II-6	1.0	n-BuONa (7.8)	28	15	16.7	Inv, 76
II-7	2.5	n-BuONa (3.9)	180	49	52.0	Inv, 82
II-8	0.25	n-BuONa (2.7)	450	83	100	Inv, >77[d]

[a] Runs II-1, II-5 were at refluxing temperature; others were at room temperature. [b] See Table I, footnote *d*. [c] Predominant stereochemistry is based on optically pure (+)R_3Si^*OMe, $[\alpha]_D$ +17.2°, and (+)R_3Si^*O-n-Bu, $[\alpha]_D$ +9.0° in pentane. [d] n-Butoxysilane was partially racemized during the reaction and the exact stereospecificity could not be estimated.

Table III. Stereochemical Studies of Reactions III

Run	Reaction[a] time, hr	Metal alkoxide (mol × 10^3)	i-PrOM (mol)/ R_3Si^*OPh (mol)	i-PrOH (mol)/ i-PrOM (mol)	i-PrOH, vol % in solvent	Predominant stereochemistry, %[b]
III-1	4.0	i-PrOLi (2.2)	1.31	4.9	5.6	Ret, 88
III-2	2.5	i-PrOLi (2.2)	1.28	17	19	Ret, 84
III-3	2.0	i-PrOLi (2.1)	1.20	70	96	Inv, 77
III-4	3.0	i-PrONa (2.2)	1.30	4.9	5.6	Ret, 53
III-5	2.0	i-PrONa (2.2)	1.32	17	19	Inv, 83
III-6	1.5	i-PrONa (2.2)	1.33	70	96	Inv, 75

[a] Runs III-1, -2, -4, and -5 were carried out at refluxing temperature; the rest were at room temperature. [b] See footnote *d* in Table I.

The reactions in Table I could not be carried out under conditions completely parallel to those used in alkoxide–alkoxide exchanges. For the latter, a catalytic amount of $ROM(ROM/R_3Si^*OR' \cong 0.2)$ sufficed, whereas the greater acidity of phenol relative to n-BuOH made necessary the use of excess ROM ($ROM/R_3Si^*OPh \cong 2$). However, outside the limits imposed by this situation, very similar conditions were used, and the reactions in mixed benzene–1-butanol solvent of R_3Si^*OMe with n-BuOM (M = Li, Na) can be compared with the reactions in Table I. For convenient discussion, some of the data previously reported for reactions II are given in Table II. The solvent is mixed benzene–1-butanol.

$$R_3Si^*OMe + n\text{-BuOM} \xrightarrow[\text{benzene}]{n\text{-BuOH}} R_3Si^*O\text{-}n\text{-Bu} \qquad \text{(II)}$$

Comparing Tables I and II it is exceedingly interesting to note that (a) stereochemistry crossover from retention to inversion occurs in I-3 and II-3, and both of these have ~50 vol % butanol in the solvent; (b) a striking difference is found for the two series when comparing reactions I-4 (62% inversion) for n-BuONa, with II-5 (95% retention) for n-BuONa, thus indicating that with the sodium alkoxide OPh has a greater preference for inversion than OMe; (c) the last point receives some additional support from comparison of I-5 with II-6, noting here, as before,[4] that increased alcoholic content of the solvent favors inversion. In both Table I and Table II, the change from ROLi to the more ionic RONa favors inversion. Both the solvent and cation effects are extremely interesting from a mechanistic standpoint (see below).

Our next series of studies concerned change of the alkoxide reagent to isopropoxide. Again, the comparison of R_3Si^*OPh with R_3Si^*OMe is quite instructive. For the former, in reactions III (M = Li, Na), the solvent was isopropyl alcohol–benzene (Table III). For R_3Si^*OMe, refluxing isopropyl alcohol–toluene was used in order to obtain practical rates in reactions IV.

$$R_3Si^*OPh + i\text{-PrOM} \xrightarrow[\text{benzene}]{i\text{-PrOH}} R_3Si^*O\text{-}i\text{-Pr} \qquad \text{(III)}$$

For convenience in discussion, some of the data previously reported for reactions IV[4] (M = Li, Na) are given in Table IV. The solvent is mixed toluene–isopropyl alcohol.

Table IV. Stereochemical Studies of Reactions IV

Run	Reaction time, hr	Metal alkoxide (mol × 10^4)	*i*-PrOH (mol)/ *i*-PrOM (mol)	*i*-PrOH (mol)/ R_3Si^*OMe	*i*-PrOH, vol % in solvent	Predominant stereochemistry, %[a]
IV-1	2.5	*i*-PrOLi (15)	13	9.2	9.1	Ret, 100
IV-2	2.5	*i*-PrOLi (12)	55	31	31.2	Ret, 89
IV-3	1.3	*i*-PrOLi (11)	120	61	100	Ret, 77
IV-4	2.5	*i*-PrONa (4.4)	18	3.7	3.8	Ret, 89
IV-5	2.5	*i*-PrONa (7.0)	28	9.2	9.1	Ret, 73

[a] See Table I, footnote *d*.

Table V. Stereochemical Studies of Reactions V

Run	Reaction time, hr	Metal alkoxide (mol × 10^3)	*n*-BuOM/(mol)/ $R_3Si^*SCH_3$ (mol)	*n*-BuOH (mol)/ *n*-BuOM (mol)	*n*-BuOH, vol % in solvent	Predominant stereochemistry, %[a]
V-1[b]	22.0	*n*-BuOLi (2.0)	1.15	0.7	0.8	Ret, 70
V-2[b]	2.0	*n*-BuOLi (1.9)	1.13	3.0	3.4	Inv, 61
V-3	1.2	*n*-BuOLi (2.1)	1.22	39	50	Inv, 85
V-4	2.0	*n*-BuONa (2.2)	1.30	2.4	3.2	Inv, 58
V-5	1.2	*n*-BuONa (2.2)	1.32	36	50	Inv, 72

[a] Based on the specific rotation of optically pure $R_3Si^*SCH_3$, 12.3°. [b] Runs V-1 and -2 were carried out at reflux temperature; the rest were run at room temperature.

Table VI. Stereochemical Studies of Reactions VI

Run	Reaction[a] time, hr	Metal alkoxide (mol × 10^3)	*n*-PrOM (mol)/ $R_3Si^*SCH_3$ (mol)	*n*-PrOH (mol)/ *n*-PrOM (mol)	*n*-PrOH, vol % in solvent	Predominant stereochemistry, %
VI-1	5.5	*n*-PrOLi (2.2)	1.31	4.9	5.2	Ret, 71
VI-2	2.5	*n*-PrOLi (2.2)	1.31	44	50	Inv, 68
VI-3	0.5	*n*-PrOLi (2.2)	1.32	64	92	Inv, 64
VI-4	2.0	*n*-PrONa (2.2)	1.30	5.0	5.2	Ret, 64
VI-5	2.5	*n*-PrONa (2.4)	1.38	42	50	Inv, 53

[a] Runs VI-1 and -4 were carried out at reflux temperature; the rest were run at room temperature.

$$R_3Si^*OMe + i\text{-PrOM} \xrightarrow[\text{toluene}]{i\text{-PrOH}} R_3Si^*O\text{-}i\text{-Pr} \qquad \text{(IV)}$$

Concerning the relative stereochemistries of R_3Si^*-OPh and R_3Si^*OMe with isopropoxide, it is interesting to compare Tables III and IV and note that (a) stereochemistry crossover from retention to inversion occurs with the phenoxysilane but *not* with the methoxysilane; (b) in runs made under conditions which are comparable, III-3 (77% inversion) with IV-3 (77% retention), III-4 and III-5 (53% retention and 83% inversion, respectively) with IV-5 (73% retention), III-1 and III-2 (88% retention and 84% retention, respectively) with IV-1 (100% retention), that the phenoxysilane relative to the methoxysilane shows a substantially greater preference for the inversion path.

While detailed discussion of the mechanistic implications of the phenoxysilane work are deferred to a later section of this paper, it seems appropriate to note here that a difference of 6 log units in the pK_a values for OPh and OMe has given rise to significant stereochemical effects.

Stereochemical Studies of the Methylmercaptide Leaving Group. The pK_a of CH_3SH[7] is close to that of phenol, being 10.3. Thus, it was of interest to see what effects the presence of sulfur would have on the stereochemical path taken by R_3Si^*SMe[8] with alkoxide reagents. Table V gives results of studies concerning reactions V (M = Li, Na).

$$R_3Si^*SMe + n\text{-BuOM} \xrightarrow[\text{benzene}]{n\text{-BuOH}} R_3Si^*O\text{-}n\text{-Bu} \qquad \text{(V)}$$

Table VI gives results of studies concerning reactions VI (M = Li, Na).

$$R_3Si^*SMe + i\text{-PrOM} \xrightarrow[\text{benzene}]{i\text{-PrOH}} R_3Si^*O\text{-}i\text{-Pr} \qquad \text{(VI)}$$

For data concerning the change from S to O as the leaving atom in the leaving group, Table V should be compared with I, and also Table VI with IV. Comparison of Tables V and I clearly shows the greater preference for an inversion path of R_3Si^*SMe compared to R_3Si^*OPh with butoxide and butanol–benzene solvent. For example, compare V-1 and V-2 (70% retention and 61% inversion, respectively) with I-1 (94% retention).

Although Table VI nearly conforms internally to the general patterns of stereochemical variation and stereochemical crossover for other reactions, the use of *i*-PrOM and *i*-PrOH in the solvent seems to have decreased the difference between the stereochemical behavior of R_3Si^*OPh and R_3Si^*SMe. Although a difference certainly exists it is not nearly so striking as the butoxide studies indicated. Difference in the hydrogen-bonding capacities of 1-butanol and 2-propanol may be responsible. The latter is not as effective in favoring the change to inversion.[4]

Stereochemical Studies of the Fluoride Leaving Group. Despite the fact that the pK_a of HF, ~3.5, places F in the category of good leaving groups (which generally have pK_a of HX less than *ca.* 6), the high bond energy of Si–F (~140 kcal/mol), the small size of F, and the capacity of F for coordination with the electrophilic

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(7) M. M. Kreevoy, B. E. Eichinger, F. F. Stary, E. A. Katz, and J. H. Sellstedt, *J. Org. Chem.*, 29, 1641 (1964).

(8) L. H. Sommer and J. McLick, *J. Am. Chem. Soc.*, 89, 5806 (1967).

Table VII. Stereochemical Studies of Reactions VII

Run	Reaction[a] time, hr	Metal alkoxide (mol × 10^3)	n-BuOM (mol)/ R_3Si^*F (mol)	n-BuOH (mol)/ n-BuOM (mol)	n-BuOH, vol % in solvent	Predominant stereochemistry, %[b]
VII-1	3.3	n-BuOLi (2.5)	1.31	2.0	3.0	Ret, 92
VII-2	3.0	n-BuOLi (2.1)	1.11	14.8	15.8	Ret, 62
VII-3	2.5	n-BuOLi (2.6)	1.37	32	50.0	Inv, 88
VII-4	2.5	n-BuONa (2.2)	1.16	1.5	2.0	Ret, 94
VII-5	2.0	n-BuONa (2.3)	1.23	13.7	15.8	Ret, 56
VII-6	1.3	n-BuONa (2.2)	1.19	38	46.8	Inv, 80

[a] The runs VII-1 and -4 were carried out at reflux temperature. The rest were at room temperature. [b] Based on a specific rotation of optically pure R_3Si^*F of 47.0° (in Et_2O).

Table VIII. Stereochemical Studies of Reactions VIII

Run	Reaction[a] time, hr	Metal alkoxide (mol × 10^3)	i-PrOM (mol)/ R_3Si^*F (mol)	i-PrOH (mol)/ i-PrOM (mol)	i-PrOH, vol % in solvent	Predominant stereochemistry, %
VIII-1	2.0	i-PrOLi (2.3)	1.22	4.7	5.6	Ret, 96
VIII-2	2.5	i-PrOLi (2.3)	1.23	34	37.5	Ret, 77
VIII-3	1.0	i-PrOLi (2.5)	1.34	60	95.9	Inv, 77
VIII-4	2.0	i-PrONa (2.5)	1.30	4.3	5.6	Ret, 100
VIII-5	2.5	i-PrONa (2.3)	1.18	35	37.5	Ret, 73
VIII-6	1.0	i-PrONa (2.3)	1.22	66	95.9	Inv, 57[b]

[a] Runs VIII-1 and -4 were carried out at reflux temperature. The rest were carried out at room temperature. [b] Decreased per cent inversion probably was due to greater incursion of racemization relative to run VIII-3.

center of an attacking reagent frequently cause R_3Si^*F to react with retention of configuration by an SNi–Si mechanism.[6,9] The latter is true for example in the reactions of simple alkyl- or aryllithium reagents[9] and also, of particular interest for the present work, for the reaction of R_3Si^*OK with R_3Si^*F in xylene solvent,[9] as formulated in the reaction

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

However, lithium aluminum hydride reduction of R_3Si^*F proceeds with predominant inversion of configuration,[10] as do its reactions with "charge-delocalized" organometallic reagents.[3] Thus, despite the pK_a of HF, the F leaving group has behaved stereochemically as though it were a poor leaving group, because of the nature of F and the nature of the SNi–Si mechanism. Thus, it was of considerable interest to note whether *for the first time*, stereochemistry crossover could be effected with R_3Si^*F by varying the nature of the medium as well as the reagent in alkoxide reactions.

Table VII gives results of studies relating to reactions VII (M = Li, Na).

$$R_3Si^*F + n\text{-BuOM} \xrightarrow[\text{benzene}]{n\text{-BuOH}} R_3Si^*O\text{-}n\text{-Bu} \qquad \text{(VII)}$$

Table VIII gives results of studies concerning reactions VIII (M = Li, Na).

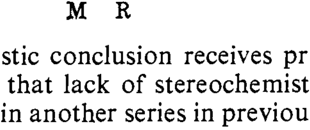
$$R_3Si^*F + i\text{-PrOM} \xrightarrow[\text{benzene}]{i\text{-PrOH}} R_3Si^*O\text{-}i\text{-Pr} \qquad \text{(VIII)}$$

Thus, from Tables VII and VIII it is clear that increasing the alcoholic content of the medium gives rise to stereochemistry crossover for both ROLi and RONa in both tables. This is in line with the other alkoxide series reported above. However, a very interesting aspect of the F leaving group work is the absence of effects engendered by changing from ROLi to RONa (which usually shifts stereochemistry toward more inversion). Perhaps the hydrogen bonding of F to ROH in both cases is such a dominant factor in determining per cent inversion *via* SN2–Si that cation effects on SNi–Si, which must be considerable, are overbalanced by the hydrogen-bonding effect which determines the per cent inversion and hence (by difference) the per cent retention by SNi–Si. Perhaps these considerations apply also to a dominant hydrogen bonding of SMe to ROH which results in no significant cation effects for the reactions reported in Tables V and VI.

Some General Mechanism Considerations. With the exception of Table IV, stereochemistry crossover occurs in all the other tabulated reaction series, and even in Table IV stereochemical variation follows the expected pattern. The solvent effect of increased inversion with increased alcoholic content is generally dramatic and true, except for some minor exceptions which may be due to racemization.

The general pattern of the results reported herein for alkoxide reactions at asymmetric silicon centers leaves little doubt that the actual leaving group in the inversion path reactions of R_3Si^*X is X---H–OR, in which hydrogen bonding converts the normally poor leaving group into a group sufficiently activated to leave *via* the type of SN2–Si mechanism shown below (Scheme I) which has been proposed before for the alkoxide–alkoxide exchanges[4] (X is the leaving atom in OPh, SMe, F).

Scheme I. General SN2–Si *Inversion* Transition State for Alkoxide Reactions



This mechanistic conclusion receives probable support from the fact that lack of stereochemistry crossover in Table IV and in another series in previous work[4] is associated with the changes from 1-butanol to cyclohexanol

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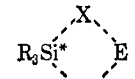
(9) L. H. Sommer, W. D. Korte, and P. G. Rodewald, *J. Am. Chem. Soc.*, **89**, 862 (1967).

(10) L. H. Sommer, C. L. Frye, G. A. Parker, and K. W. Michael, *ibid.*, **86**, 3271 (1964).

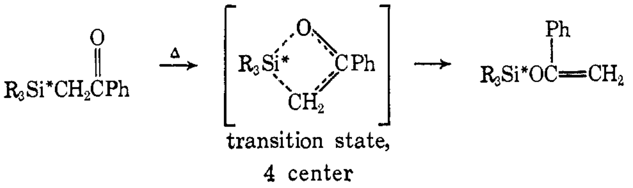
and to 2-propanol. The latter two alcohols may have decreased hydrogen-bonding capacity resulting from steric and/or electronic factors. It is extremely interesting and probably of substantial significance that this lack of stereochemistry crossover with the branched alcohols is noted only with the poorer, less reactive leaving groups, such as the alkoxysilanes,[4] R_3Si^*OR'. In the present work (Tables I, III, V–VII) stereochemistry crossover was noted for all three leaving groups with both *n*-butyl alcohol and isopropyl alcohol.

For the alkoxide–alkoxide exchanges proceeding along the retention path we earlier proposed simply an SNi-Si mechanism model and we wish now to extend that model to the present retention reactions. In the approximate formulation given in Scheme II, E is the electrophilic part of an attacking reagent EY in a four-center, polar mechanism for R_3Si^*X. For the reactions reported herein E is Li or Na and Y is OR′.

Scheme II. SNi-Si *Retention* Transition State for Alkoxide Reactions



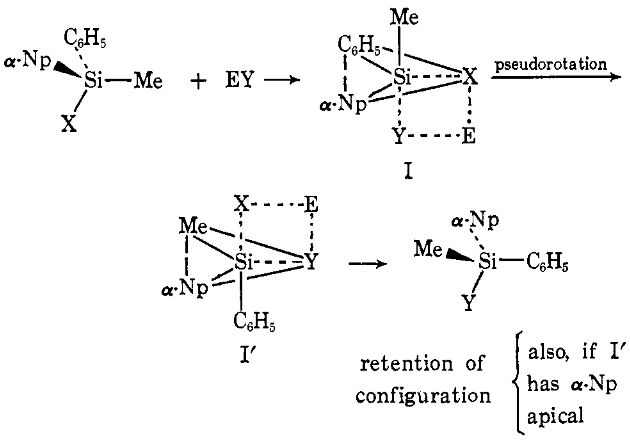
A very probable four-center mechanism has been proposed by Brook to explain the interesting rearrangement given below which proceeds with retention of configuration.[11]



Previously,[4] for the alkoxide–alkoxide exchanges, we proposed, in accord with even earlier proposals,[5,12] that SNi-Si transition states can have over-all tetragonal-pyramid or trigonal-bipyramid geometries with both formulations having a near pyramidal arrangement of R groups and Si.

At the moment we consider the following mechanism unlikely, but it must be noted here that SNi-Si could *conceivably* involve intermediates having *part bonds* to X and Y which are trigonal-bipyramids and undergo *pseudorotation* to permit *apical exit* of X, as in Scheme III.[13,14]

Scheme III. SNi-Si Involving Pseudorotation and Apical Entry of Y and Apical Exit of X



Experimental Section

Preparations of (−)R_3Si^*F and (−)$R_3Si^*SCH_3$. These syntheses were described previously.[8,10]

Preparation of (+)α-Naphthylphenylmethylphenoxysilane. Phenoxysilane has been characterized,[15] but a modified method was used herein to prepare it and is described. A solution of 11.4 mmol of phenol (1.07 g) in 3 ml of ethyl ether was diluted with 80 ml of pentane in a 300-ml erlenmeyer flask. To the solution was added 11.4 mmol of cyclohexylamine (1.30 ml). Into the magnetically stirred solution, 10.4 mmol of (+)R_3Si^*Cl (2.96 g), [α]D +6.4° (*c* 1.74, pentane), was added dissolved in 50 ml of pentane. Immediately, a white precipitate appeared, and the solution was stirred for 0.5 hr. The reaction mixture was washed with water and dried over sodium sulfate. After taking off the solvent, the crude product was chromatographed on a 8 × 1.9 cm silica gel column with elution by 200 ml of 80% pentane–20% benzene solvent. Evaporation of the solvent left the liquid product, 2.52 g (72% yield), which had [α]D +9.75° (*c* 2.29, cyclohexane) and an infrared spectrum identical with that of the authentic phenoxysilane.[15]

***n*-Butoxide–Phenoxysilane Exchange Reactions.** Lithium or sodium *n*-butoxide was prepared by heating *n*-butyl alcohol in benzene with lithium or sodium metal, except for run I-1. *n*-Butyllithium in hexane (1.60 *M*) was used for run I-1. As a typical example, a procedure for I-2 is described. A 50-ml three-necked flask equipped with a condenser, a thermometer, and an addition funnel was used. The small magnetic bar was used for stirring. The whole system was contained in a system protected from air and moisture. Benzene (11 ml) was deaerated with nitrogen and 1.5 ml of *n*-butyl alcohol was added, then the whole system was flushed with nitrogen. This standard procedure was used in all of the following experiments. Lithium *n*-butoxide was prepared by dissolving 15.6 mg of lithium wire (2.25 mmol) in the solution at elevated temperature. After cooling the solution to room temperature, 1.70 mmol of phenoxysilane (0.58 g), [α]D +9.02° (*c* 3.14, cyclohexane), was added in 2.5 ml of benzene. Nothing visible happened and the solution was heated to reflux. After 5 min at reflux temperature the precipitate (PhOLi?) rapidly started to come out and the solution was refluxed for 2.5 hr. The whole solution was then taken up in 60 ml of pentane, washed with water, and dried over sodium sulfate. An infrared spectrum of the crude product showed it to be completely free from phenoxysilane and the presence of a very small amount of silanol. It was chromatographed on a 5 × 1.3 cm silica gel column with elution by 20 ml of 75% pentane–25% benzene. Evaporation of the solvent left 0.36 g of (+)R_3Si^*O-*n*-Bu, [α]D +4.09° (*c* 3.09, pentane), identified by an infrared spectrum.

Isopropoxide–Phenoxysilane Exchange Reactions. Lithium and sodium isopropoxides were prepared by heating isopropyl alcohol with lithium or sodium metal. As a typical example, a procedure for III-5 is described. Sodium isopropoxide was prepared by heating 3 ml of isopropyl alcohol and 51.7 mg of sodium (2.24 mmol) in 10 ml of benzene at 60° for 1 hr. At 30°, 1.70 mmol of (+)R_3Si^*OPh (0.58 g), [α]D +9.02° (*c* 3.14, cyclohexane), was added dissolved in 2 ml of benzene. No apparent change was observed and the reaction mixture was refluxed for 2 hr at72–73°. After cooling the solution to room temperature, the reaction mixture was washed with water and dried over sodium sulfate. The crude product had a considerable amount of silanol and was chromatographed on a 17 × 1.3 cm silica gel column using 100 ml of 50% pentane–50% benzene. The recovered material (0.28 g) identified as isopropoxysilane by an infrared spectrum had [α]D +3.67° (*c* 2.62, pentane).

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(11) A. G. Brook, D. M. MacRae, and W. W. Limburg, *J. Am. Chem. Soc.*, 89, 5493 (1967).

(12) Reference 5, pp 56–66.

(13) For an excellent general reference to pseudorotation in the hydrolysis of phosphate esters, see F. H. Westheimer, *Accounts Chem. Res.*, 1, 70 (1968).

(14) For nmr evidence that pseudorotation occurs in SiF_5^- and $RSiF_4^-$, but not in $Ph_2SiF_3^-$ due to incursion of rapid intermolecular F–F exchange, and for evidence that $R_3SiF_2^-$ cannot be made and is too unstable to exist under the conditions used to prepare the former species, see F. Klanberg and E. Y. Muetterties, *Inorg. Chem.*, 7, 155 (1968).

(15) Unpublished studies of L. H. Sommer and R. Mason: see R. Mason, Ph.D. Thesis, The Pennsylvania State University, 1966.

***n*-Butoxide–Methylmercaptide Exchange Reactions.** Lithium and sodium *n*-butoxides were prepared by heating lithium or sodium metal and *n*-butyl alcohol in benzene except for V-1. As an example, a procedure for V-1 is described. Lithium *n*-butoxide was prepared from 1.95 mmol of *n*-butyllithium (1.60 *M* in hexane) and 0.30 ml of *n*-butyl alcohol in 12 ml of benzene. The solution was stirred for 1 hr at room temperature. Into the solution, which remained clear, 1.70 mmol of (−)$R_3Si^*SCH_3$ (0.50 g), [α]D −10.0° (*c* 2.44, pentane), was added in 3 ml of benzene. No apparent change was observed and it was refluxed for 22 hr, during which time a suspension (CH_3SLi?) appeared. The reaction mixture was worked up in the usual manner. An infrared spectrum of the crude product (0.51 g) showed that the reaction was complete. It was chromatographed in the manner mentioned before. The recovered (+)-R_3Si^*O-*n*-Bu (0.41 g) had [α]D +2.95° (*c* 4.59, pentane).

Isopropoxide–Methylmercaptide Exchange Reactions. As a typical example, a procedure for VI-2 is described. Lithium isopropoxide was prepared by heating 15.4 mg of lithium (2.22 mmol) and 7.5 ml of isopropyl alcohol in 5 ml of benzene for 0.5 hr. At room temperature, 1.70 mmol of (−)$R_3Si^*SCH_3$ (0.50 g), [α]D −9.6° (*c* 0.91, pentane), was added dissolved in benzene. There was a small amount of solid suspended (*i*-PrOLi?). This suspension soon disappeared and the solution became clear. The solution was stirred for 2.5 hr. An infrared spectrum of the crude product showed that the reaction was complete and the products were chromatographed in the manner mentioned before. The recovered (+)R_3Si^*O-*i*-Pr (0.31 g) had [α]D +2.18° (*c* 2.89, pentane).

***n*-Butoxide–Fluoride Exchange Reactions.** As a typical example, a procedure for VII-3 is described. Lithium *n*-butoxide was prepared by heating 18 mg of lithium metal and 7.5 ml of *n*-butyl alcohol in 5 ml of benzene. When the solution was cooled to room temperature, the solution became opaque because of a suspension, presumably lithium *n*-butoxide. Into the solution, 1.9 mmol of (+)R_3SiF (0.51 g), [α]D +38.9° (*c* 1.20, pentane), was added in 2.5 ml of benzene. The solution immediately cleared and started to become cloudy again. Presumably, lithium *n*-butoxide dissolved in the initial stage and lithium fluoride started to appear. Although the reaction seemed fast, it was magnetically stirred for 2.5 hr at room temperature. The reaction mixture was worked up in the usual manner. The crude product was chromatographed in the manner mentioned before. The recovered (−)R_3Si^*O-*n*-Bu (0.39 g) identified by an infrared spectrum had [α]D −6.47° (*c* 4.06, pentane).

Isopropoxide–Fluoride Exchange Reactions. As a typical example, a procedure for VIII-5 is described. Sodium isopropoxide was prepared by heating 51.9 mg of sodium (2.26 mmol) and 7.5 ml of isopropyl alcohol in 10 ml of benzene. In 2 hr, sodium was dissolved and the solution was cooled to room temperature. The solution remained clear. A solution of 0.51 g of (+)R_3Si^*F (1.9 mmol), [α]D +38.9° (*c* 1.20, pentane), in 2.5 ml of benzene was added into the solution. The solution immediately became cloudy and was magnetically stirred for 2.5 hr. The reaction mixture was worked up in the usual manner. An infrared spectrum of the crude product showed it to be exclusively isopropoxysilane except for some silanol. It was chromatographed in the manner mentioned before and the recovered (−)R_3Si^*O-*i*-Pr had [α]D −2.61° (*c* 3.44, pentane).

Stereochemistry of Asymmetric Silicon. XIV. The SN2*–Si Mechanism and Racemization of an Optically Active Fluorosilane without Displacement of Fluoride Ion[1,2]

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Abstract: A kinetic study of the alcohol-induced racemization of optically active α-naphthylphenylmethylfluorosilane, R_3Si^*F, has been carried out. The data have been rationalized in terms of mechanism SN2*–Si which involves the equilibrium formation of an expanded-octet addition complex between the reagent and the fluorosilane.

As proposed in previous publications, mechanism SN2–Si commonly operates for stereospecific *inversion* reactions of optically active R_3Si^*X, and mechanism SNi–Si is usual for *retention* of configuration at an asymmetric silicon center in triorgano monofunctional silanes. Furthermore, neither of these mechanisms involve formation of a full-fledged *Si-5* intermediate having *five full bonds to central silicon.*[3–6]

The extensive evidence for operation of mechanisms SN2–Si and SNi–Si in a very large number (∼100) of stereospecific reactions of α-NpPhMeSi*X and PhMeRSi*X (R = neopentyl, benzhydryl, or ethyl) stands in interesting contrast to the elegant studies by Frye which have resulted in isolation of special structures containing pentacoordinate silicon.[7] These substances comprise nitrilotriethoxysilanes, Z-$Si(OCH_2CH_2)_3N$, and related pentacoordinate silicon derivatives of 2,2′,2′′-nitrilophenol, (o-$HOC_6H_4)_3N$, in which the silicon is part of *neutral* triptych structures having transannular dative bonding between nitrogen and silicon, and pentacoordinate silicon derivatives of catechol in which the silicon is part of the *anionic* component of salts. However, these structures, which are formally analogous to expanded-octet intermediates derived from addition of an

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[1] For the preceding paper in this series see L. H. Sommer and H. Fujimoto, *J. Am. Chem. Soc.*, **91**, 7040 (1969).

[2] For a report of preliminary results obtained at the Pennsylvania State University, see L. H. Sommer and P. G. Rodewald, *ibid.*, **85**, 3898 (1963).

[3] For a recent detailed treatment of mechanism SN2–Si, see L. H. Sommer, G. A. Parker, N. C. Lloyd, C. L. Frye, and K. W. Michael, *ibid.*, **89**, 857 (1967).

[4] For a recent paper on mechanism SNi–Si, see L. H. Sommer and H. Fujimoto, *ibid.*, **90**, 982 (1968).

[5] For general treatments of mechanisms SN2-Si and SNi–Si, see L. H. Sommer, "Stereochemistry, Mechanism, and Silicon," McGraw-Hill Book Co., Inc., New York, N. Y., 1965.

[6] It should be noted that, as defined in ref 5, mechanisms SN2–Si and SNi–Si may or may not involve formation of an unstable intermediate whose structure and free energy closely approximate the structures and free energies of the transition state maxima which precede and follow it along the reaction coordinate. In short, for SN2–Si or SNi–Si an unstable intermediate is a shallow minimum having long and weak bonds between Si and the entering and leaving groups.

[7] C. L. Frye, G. E. Vogel, and J. A. Hall, *J. Am. Chem. Soc.*, **83**, 996 (1961); C. L. Frye, *ibid.*, **86**, 3170 (1964); C. L. Frye, G. A. Vincent, and G. L. Hanschildt, *ibid.*, **88**, 2727 (1966).