Organic and Biological Chemistry

Stereochemistry of Asymmetric Silicon. IV. The SN2–Si Stereochemistry Rule for Good Leaving Groups

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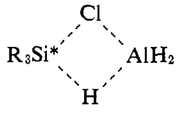
Abstract: The stereochemistry of 14 reactions of optically active α-naphthylphenylmethylhalosilanes, R_3Si^*Cl and R_3Si^*Br, has been studied and all were found to proceed with predominant *inversion* of configuration. On the basis of these and previous studies the SN2–Si stereochemistry rule of inversion of configuration for displacement of good leaving groups from silicon is proposed for acyclic R_3SiX compounds.

Previous papers in this series on the stereochemistry of substitution at asymmetric silicon[2-4] have reported that: (a) 11 reactions of optically active α-naphthylphenylmethylchlorosilane, α-NpPhMeSi*Cl, designated R_3Si^*Cl below, proceed with predominant *inversion* of configuration;[2,3] (b) acyloxysilanes, R_3Si^*OCOR, likewise react with predominant *inversion* of configuration[4] (in contrast to R_3Si^*OR);[3] (c) the tosylate group in R_3Si^*OTs is displaced by R_3Si^*OK with *inversion* of configuration.[4]

The present paper reports further studies of the stereochemistry of displacement of Cl from asymmetric silicon and some parallel studies of the Br leaving group. These new data plus earlier reports on the Cl, OCOR, and OTs leaving groups are sufficiently diversified (with respect to solvent, nature of the nucleophile, etc.) to permit formulation of a general stereochemistry rule.

Table I summarizes the results of treatment of $(-)R_3Si^*Cl$ with seven new reagents and also includes the 11 reactions reported in previous papers. All 18 reactions are presented in Table I for convenient reference in discussion.

Reaction 17 in Table I proceeds with high stereospecificity,[2] and it was of interest to determine whether a change in reagent from lithium aluminum hydride to aluminum hydride (prepared from 1:3 $AlCl_3$–$LiAlH_4$)[5] would engender a change from inversion to retention of configuration. In fact, reaction 1 takes place with 92% inversion of configuration,[6] despite the possibility of operation of mechanism SNi–Si in the nonpolar medium[2]



Thus, the above quasi-cyclic transition state is not valid for reaction 1. Even in polymeric form, $(AlH_3)_x$, aluminum hydride would be expected to be more electrophilic and less nucleophilic, as a reagent, than is lithium aluminum hydride. Nevertheless, reaction 1 proceeds with predominant *inversion* of configuration.

Reaction 2 in Table I comprises halide–halide exchange at an asymmetric silicon atom for the case of an entering group that is more basic than the leaving group.

Reactions 3, 4, and 5 in Table I show that an acyloxy entering group, like the more basic alkoxy, hydroxy, and silanolate groups, also displaces Cl from R_3Si^*Cl with *inversion* of configuration.

It is very interesting to note that mercuric acetate, containing the highly electrophilic mercuric ion, also gives the acyloxysilane with 76% *inversion* of configuration. Thus, using a benzene solvent and mercuric acetate, it is clear that nucleophilic displacement of Cl by acetate with *inversion* of configuration proceeds at a faster rate than ionization of Si–Cl by mercuric ion and consequent racemization.

Assignment of inversion of configuration to reactions 1–7 is based on previously reported correlations of configuration by a variety of methods.[2-4]

It will be evident from examination of Table I that predominant inversion of configuration obtains for replacement of Cl in R_3Si^*Cl with: (a) groups of widely varying basicity, H > OH, OR, OSi*R > F, OCOR; (b) groups of widely varying steric requirements, *i.e.*, O-t-C_4H_9 and H; (c) groups which form bonds to silicon in which dπ–pπ dative bonding is probably significant,[7] *e.g.*, $\equiv\text{Si}-\underset{..}{\ddot{\text{O}}}\text{R}$, $\equiv\text{Si}-\underset{..}{\ddot{\text{F}}}$, etc.; (d) a group which forms bonds to silicon in which dπ–pπ bonding is not possible, *e. g.*, H.

These relationships, plus the widely varied nature of the reagents and solvents in Table I, offer convincing evidence for *the importance of inversion of configuration as a common stereochemical path for reactions of* R_3Si^*Cl.

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

[3] L. H. Sommer, C. L. Frye, and G. A. Parker, *ibid.*, **86**, 3276 (1964).

[4] L. H. Sommer, G. A. Parker, and C. L. Frye, *ibid.*, **86**, 3280 (1964).

[5] A. E. Finholt, A. C. Bond, and H. I. Schlesinger, *ibid.*, **69**, 1199 (1947).

[6] Optical purity of the product was 84%.

[7] *Cf.*, C. Eaborn, "Organosilicon Compounds," Butterworth and Co., London, 1960.

Table I. Inversion Reactions of (−)-α-Naphthylphenylmethylchlorosilane, (−)R_3Si^*Cl[a]

Reaction no.	Reagent	Solvent	Product
1	$AlCl_3$–$LiAlH_4$	Ether	(−)R_3Si^*H
2	Cyclo-$C_6H_{11}NH_3F$	Chloroform	(−)R_3Si^*F
3	Cyclo-$C_6H_{11}NH_3OCOCH_3$	Chloroform	(−)$R_3Si^*OCOCH_3$
4	Cyclo-$C_6H_{11}NH_3OCOC_6H_5$	Chloroform	(−)$R_3Si^*OCOC_6H_5$
5	Cyclo-$C_6H_{11}NH_3OCOC_6H_4$-*p*-NO_2	Chloroform	(−)$R_3Si^*OCOC_6H_4$-*p*-NO_2
6	$Hg(OCOCH_3)_2$	Benzene	(−)$R_3Si^*OCOCH_3$
7	KOH(s)	Xylene	(+)R_3Si^*OK
8[c]	H_2O	Ether	(−)R_3Si^*OH
9	CH_3OH	Pentane[b]	(−)$R_3Si^*OCH_3$
10	$NaB(OCH_3)_3H$	Diglyme	(−)$R_3Si^*OCH_3$
11	$NaB(OCH_3)_4$	Ether	(−)$R_3Si^*OCH_3$
12	Cyclo-$C_6H_{11}OH$	Pentane[b]	(+)R_3Si^*O-cyclo-C_6H_{11}
13	*t*-C_4H_9OK	*t*-Butyl alcohol	(+)R_3Si^*O-*t*-C_4H_9
14	(−)-Menthol	Pentane[b]	(+)R_3Si^*O-(−)-Men
15	$LiAl(OCH_3)_2H_2$	Ether	(−)R_3Si^*H, (−)$R_3Si^*OCH_3$
16	(+)R_3Si^*OK	Xylene	(−)$R_3Si^*OSi^*R_3$
17	$LiAlH_4$	Ether	(−)R_3Si^*H
18	$NaBH_4$	Diglyme	(−)R_3Si^*H

[a] In some cases the (+)R_3Si^*Cl enantiomer was used and gave the enantiomer of the product listed. [b] An amine was used as an acceptor for formed HCl. [c] Reactions 8–18 have been reported previously.[2,3]

In Table II are summarized the results of investigation of seven reactions of optically active α-naphthylphenylmethylbromosilane, R_3Si^*Br. In all seven cases, paralleling the corresponding reactions of R_3Si^*Cl, *inversion* of configuration was the predominant stereochemical path.

Table II. Inversion Reactions of (−)-α-Naphthylphenylmethylbromosilane, (−)R_3Si^*Br[a]

Reaction no.	Reagent	Solvent	Product
1	$LiAlH_4$	Ether	(−)R_3Si^*H
2	H_2O	Ether	(−)R_3Si^*OH
3	$NaB(OCH_3)_3H$	Ether	(−)$R_3Si^*OCH_3$
4	*t*-C_4H_9OK	*t*-C_4H_9OH	(+)R_3Si^*O-*t*-C_4H_9
5	(+)R_3Si^*OK	Xylene	(−)$R_3Si^*OSi^*R_3$
6	Cyclo-$C_6H_{11}NH_3Cl$	Chloroform	(+)R_3Si^*Cl
7	Cyclo-$C_6H_{11}NH_3F$	Chloroform	(−)R_3Si^*F

[a] In some cases the (+)R_3Si^*Br enantiomer was used and gave the enantiomer of the product listed. Reaction 1 has been reported.[2]

Assignment of an *inversion* stereochemistry to the reactions in Table II is based on correlations of configuration reported in previous papers.[2–4]

The 25 reactions of R_3Si^*Cl and R_3Si^*Br listed in Tables I and II all comprise replacement of good leaving groups by entering groups which are more basic than the leaving groups.[8] In combination with the previously reported *inversion* reactions for R_3Si^*Cl, R_3Si^*OCOR, and R_3Si^*OTs with diverse reagents in a variety of solvents, the present results for Cl and Br lead to the following general stereochemistry rule:

Good leaving groups X, whose conjugate acids have pK_a less than ∼6, 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.[9]

For *acyclic systems*, this rule has been designated "the SN2–Si stereochemistry rule" in previous discussion.[10] It states a striking general aspect of organosilicon stereochemistry and deserves amplified discussion here, especially in view of recent developments concerning: accurate determination of the structures of PF_5, CH_3PF_4, and $(CH_3)_2PF_3$ by the electron diffraction method;[11] strong evidence concerning the structure of $(CH_3)_3PF_2$ from F^{19} nmr spectra;[12] and recent discussions[13,14] of bonding theories for phosphorus(V) compounds based on the structures of $(CH_3)_nPF_{5-n}$ and related compounds such as SF_4 and ClF_3.

In beginning the discussion of the SN2–Si stereochemistry rule and its mechanistic implications it is important to note that *the rule emphasizes basicity rather than electronegativity of X*. This implies that the capacity of X to stabilize a negative charge (the stability of X^-) is critical for the stereochemistry of R_3Si^*X. Table III summarizes the stereochemical trends which have been found experimentally and compares them with orders of electronegativity and basicity. The last column lists references in which the designated trends have been found.

The general stereochemical trends summarized in Table III represent experimental findings in something more than 200 reactions of R_3Si^*X, including those containing *neo*-$C_5H_{11}PhMeSi^*$–, $Ph_2CHPhMeSi^*$–, and $PhEtMeSi^*$ -systems.[15] They clearly indicate the parallelism between decreased basicity of X^- and increased stereochemical preference for reaction with inversion of configuration. No such correlation is found for electronegativity of X.

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[8] Cases in which R_3Si^*Cl and R_3Si^*Br are treated with salts whose anions are not more basic than Cl or Br are discussed in a later paper; for a preliminary communication on this subject, see: L. H. Sommer, F. O. Stark, and K. W. Michael, *J. Am. Chem. Soc.*, **86**, 5683 (1964).

[9] Despite the fact that the pK_a of HF places F in the category of good leaving groups, the high bond energy of Si–F (∼150 kcal/mole), the small size of 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. The above rule is for acyclic R_3SiX.

[10] L. H. Sommer, "Stereochemistry, Mechanism and Silicon," McGraw-Hill Book Co., Inc., New York, N. Y., 1965, pp 184–186.

[11] L. S. Bartell and K. W. Hansen, *Inorg. Chem.*, **4**, 1775 (1965).

[12] E. L. Muetterties, W. Mahler, and R. Schmutzler, *ibid.*, **2**, 613 (1963).

[13] R. J. Gillespie, *ibid.*, **5**, 1634 (1966).

[14] L. S. Bartell, *ibid.*, **5**, 1635 (1966).

[15] L. H. Sommer, K. W. Michael, and W. D. Korte, *J. Am. Chem. Soc.*, **89**, 868 (1967).

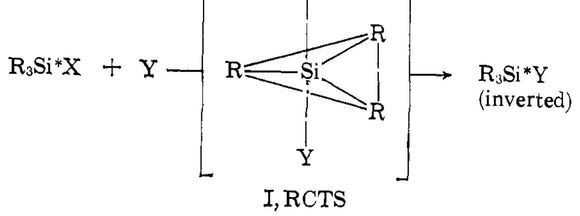
Table III. Stereochemistry of R_3Si^*X and Basicity and Electronegativity of X

Entry no.	Basicity order for X^-	Stereochemical preference of X for inversion	Electronegativity of X	Ref
1	$Br < Cl \ll F$	$Br, Cl \gg F$	$F \gg Cl > Br$	*a*
2	$RS \ll RO$	$RS \gg RO$	$RO > RS$	*b*
3	$RCO_2 \ll RO$	$RCO_2 \gg RO$	$RCO_2 \cong RO$	4
4	$ArO < RO$	$ArO > RO$	$ArO \cong RO$	*c*
5	$RO \ll H$	$RO \gg H$	$RO > H$	*d*
6	$Ph_2CH < PhCH_2$	$Ph_2CH > PhCH_2$	$Ph_2CH \cong PhCH_2$	*d*

[a] L. H. Sommer, W. D. Korte, and P. G. Rodewald, *J. Am. Chem. Soc.*, **89**, 862 (1967). [b] L. H. Sommer and J. McLick, *ibid.*, **88**, 5359 (1966). [c] Unpublished results of L. H. Sommer and R. Mason: R. Mason, Ph.D. Thesis, The Pennsylvania State University, 1966. [d] Unpublished studies of L. H. Sommer and W. D. Korte: W. D. Korte, Ph.D. Thesis, University of California, Davis, 1966.

Critical dependence of stereochemistry on basicity of X^-, rather than on electronegativity of X, must mean that considerable ionic stretching has taken place in the transition state placing substantial negative charge on X. A review of many reaction series involving structure and reactivity relationships of R_3SiX leads to the same mechanistic conclusion concerning the majority of reactions of R_3SiX with strong nucleophiles.[16] Thus, reaction rates as well as reaction stereochemistry correlate well with bascity of X^-; increased capacity of X to bear a negative charge leads to increased reaction rates with strong nucleophiles. Trends such as these have previously led to the conclusion that the SN2–Si inversion mechanism is the most common mechanism for polar reactions of R_3SiX and that, for an entering group Y, a reasonable model for an SN2-Si mechanism is one whose rate-controlling transition state: (a) has an over-all trigonal bipyramidal geometry with X and Y occupying apical positions; (b) has "bonds" to X and Y that are longer and weaker than those between silicon and the nonreacting organic (R) groups; (c) may or may not precede or follow an unstable intermediate whose structure and free energy are very similar to those of the rate-controlling transition state.[17]

Equation 1 below expresses characteristics a and b of mechanism SN2–Si. Sequences 2 and 3 express alternates c (RCTS = rate-controlling transition state, INT = unstable intermediate).



(1)

I, RCTS

$$R_3Si^*X + Y \longrightarrow [\text{I, RCTS} \longrightarrow \text{II, INT}] \longrightarrow R_3Si^*Y \text{ (inverted)} \qquad (2)$$

$$R_3Si^*X + Y \longrightarrow [\text{II, INT} \longrightarrow \text{I, RCTS}] \longrightarrow R_3Si^*Y \text{ (inverted)} \qquad (3)$$

In sequences 2 and 3 the free energy of activation for transformation of I to II, or the reverse, is very small, and II is only a small dip (minimum) in the usual plot of reaction coordinate *vs.* free energy. Relative to 2 and 3, mechanisms involving *Si-5 intermediates having five full bonds to silicon* and having significant deviation from the concerted (direct) displacement in 1 have been formulated as SN2*-Si and SN2**-Si.[18]

Returning to the recent developments mentioned above concerning the structures of $(CH_3)_nPF_{5-n}$ compounds, the significant facts for purposes of the present discussion are: (1) The molecules are either trigonal bipyramids or somewhat distorted trigonal bipyramids. (2) Methyl groups occupy equatorial positions. (3) Apical bonds are longer than the corresponding equatorial bonds. (4) All the bond lengths increase, and the difference in bond length, $[r(\text{P–F})_{\text{ap}} - r(\text{P–F})_{\text{eq}}]$, increases as the number of methyl groups increases. Relationships 3 and 4 are not quantitatively known for $(CH_3)_3PF_2$, but F^{19} nmr and infrared spectra indicate that they are qualitatively correct and that this substance has longer apical P–F bonds than CH_3PF_4 and $(CH_3)_2PF_3$.[12]

Clearly, relationships 1–4 for the $(CH_3)_nP_{5-n}$ structures are in general harmony with postulated structure I for SN2–Si transition states. In its general aspects structure I also resembles the widely accepted structure for SN2 transition states for carbon centers.

That the similarity of structure I extends not only to SN2 transition states for carbon but also to stable pentacoordinate organic compounds of phosphorus provides additional support for previous conclusions concerning I.[17]

Gillespie's valence-shell, electron-pair repulsion (VSEPR) theory simply and directly predicts the above features, 1–4, of the $(CH_3)_nPF_{5-n}$ structures.[13] One of the important rules of the VSEPR theory for predicting molecular shapes is that for trigonal bipyramidal geometry the apical electron pairs are not equivalent to the equatorial electron pairs. Apical electron pairs have three nearest neighbor pairs at 90° and equatorial pairs have only two such 90° neighboring pairs. Thus, according to VSEPR, at equilibrium the apical pairs are displaced to a greater distance from the nucleus than equatorial pairs. For equivalent ligands, then, apical bonds are longer than equatorial bonds.[19] It is possible that this VSEPR rule has important stereochemical implications for all trigonal bipyramidal transition states. Extension of VSEPR theory to such transition states predicts that: *in the absence of other important factors,*[20] *the long bonds to X and Y tend to be apical bonds.* The latter situation obviously leads to inversion of configuration.

Bonding in SN2-Si transition-state structure I may be formulated in different ways. It has previously[17] been approximated by the "idealized" structures III and IV. In III, X and Y use appropriate filled orbitals for overlap with two hybrid $3p_z3d_z{}^2$ orbitals to form two covalent bonds between X, Si, and Y.[21] For the

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(16) Reference 10, Chapter 8.

(17) Reference 10, Chapter 11.

(18) For general discussion of SN2*-Si and SN2**-Si see ref 10, Chapter 11; for evidence against *common* operation of these mechanisms, see footnote *a*, Table III.

(19) For general reviews of VSEPR theory, see: R. J. Gillespie and R. S. Nyholm, *Quart. Rev.* (London), **11**, 339 (1957); R. J. Gillespie, *J. Chem. Educ.*, **40**, 295 (1963).

(20) In the case of silicon centers such factors lead to quasi-cyclic transition states which give retention of configuration by mechanism SNi-Si.

(21) The combinations of wave functions which give the two $3p_z3d_z{}^2$

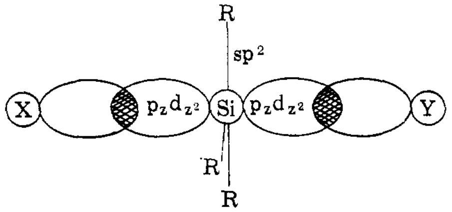
nontransitional elements, it seems likely that pd hybrid orbitals are capable of forming only very weak covalent bonds, and this would accord with III as one alternative for the bonding in I. In III, the R groups use sp^3 hybrid orbitals for overlap with 3s3p^2 hybrid orbitals of the central silicon atom. This is a valence-bond description of I.

Structure IV is a pictorial representation of the combination of a 3p$_z$ orbital of the silicon with an orbital of both the entering and leaving groups. From application of the usual LCAO approximation three molecular orbitals will be formed, and if p$_z$ orbitals of X and Y are involved, MO formation may be pictured as involving the processes[22]

$$\psi_{\mathrm{B}} = \frac{1}{2}[\psi_{\mathrm{p}_z}(\mathrm{X}) - \psi_{\mathrm{p}_z}(\mathrm{Y}) + \sqrt{2}\psi_{\mathrm{p}_z}(\mathrm{Si})]$$

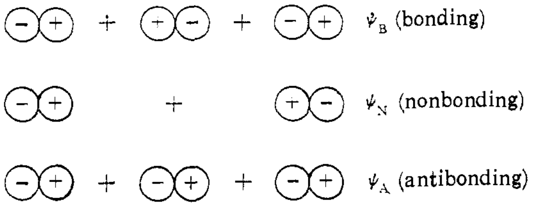
$$\psi_{\mathrm{N}} = \frac{1}{\sqrt{2}}[\psi_{\mathrm{p}_z}(\mathrm{X}) + \psi_{\mathrm{p}_z}(\mathrm{Y})]$$

$$\psi_{\mathrm{A}} = \frac{1}{2}[\psi_{\mathrm{p}_z}(\mathrm{X}) - \psi_{\mathrm{p}_z}(\mathrm{Y}) - \sqrt{2}\psi_{\mathrm{p}_z}(\mathrm{Si})]$$

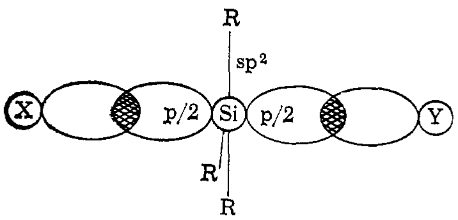


III

covalent-bond representation of S$_N$2–Si transition state involving two hybrid 3p$_z$3d$_{z^2}$ orbitals of Si



For structure IV, the bonding three-center MO, ψ_{B}, contains only two electrons and this would result in bonds between X, Si, and Y which would be longer than simple localized electron pair bonds, since in ψ_{B} there is only one bonding pair for two bonds. In ψ_{N} the two other electrons are associated with X and Y only. Thus transition-state model IV is a second alternative that seems to have the essential features of transition state structure I.



IV

three-center, four-electron MO representation of an S$_N$2–Si transition state; no d orbital participation; two electrons in ψ_{N}

The present work provides no basis for choosing between III and IV and it is possible that the amount of d-orbital participation varies from reaction to reaction and may possibly be zero in many cases. Indeed, Bartell[11,14] prefers a bonding formulation for (CH$_3$)$_n$PF$_{5-n}$, originally proposed by Rundle, which neglects d orbitals altogether and pictures bonds to the apical ligands as involving mainly p orbitals (with perhaps some s orbital contribution) in three-center four-electron bonds having the four electrons contained in ψ_{B} and ψ_{N} as described above.

In the above discussion, bonding proposals for stable, isolable organo-substituted phosphorus(V) fluorides have been applied to S$_N$2–Si transition states. Because of the difference in nuclear charge of phosphorus and silicon centers, III and IV may represent transition states (or unstable intermediates) for many silicon species, whereas corresponding phosphorus species are stable molecules. In the latter connection, it should be noted that elegant studies by Frye[23] and by West[24] have provided evidence for pentacoordinate silicon in isolable special structures containing one and three organic groups, respectively. The latter[24] is a cation containing silicon bonded to three phenyl groups and two nitrogens.

It seems appropriate to conclude this discussion by predicting that common operation of the S$_N$2 reaction mechanism for carbon centers and of the S$_N$2–Si mechanism for silicon centers will be found to extend to many other atomic centers, and that the direct displacement mechanism (essentially concerted bond making and bond breaking) proceeding with Walden inversion will prove to be of substantial importance for many elements.

Experimental Section

Reactions of (−)-α-Naphthylphenylmethylchlorosilane. Reduction with Aluminum Hydride. Aluminum hydride was prepared by reaction of 0.90 g (6.7 mmoles) of anhydrous aluminum chloride with 0.73 g (19 mmoles) of lithium aluminum hydride in 40 ml of dry ether. The reactants were stirred for 6 hr to ensure complete reaction. To the reducing mixture, with aluminum hydride as the active species, 0.80 g (2.8 mmoles) of (−)-chlorosilane, $[\alpha]_{\mathrm{D}}$ −6.1°, dissolved in 20 ml of dry ether, was added. After standing at room temperature for 2.5 hr, the reaction mixture was hydrolyzed, extracted with pentane, and then dried. Isolation gave 0.69 g (99% yield) of (−)-α-naphthylphenylmethylsilane, $[\alpha]_{\mathrm{D}}$ −29° (*c* 4.3 in pentane). The product was identified by its infrared spectrum which was identical with that of an authentic sample[2] and had the strong Si–H maximum at 4.7 μ. The product was formed with 92% net inversion of configuration.

Conversion to Fluorosilane. To a solution of the (−)-chlorosilane (0.370 g, 1.31 mmoles), $[\alpha]_{\mathrm{D}}$ −5.7° (*c* 3.70 in pentane), in

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hybrid orbitals are

$$\psi_{\mathrm{p}_z\mathrm{d}_{z^2}} = \frac{1}{\sqrt{2}}(\psi_{\mathrm{d}_{z^2}} + \psi_{\mathrm{p}_z})$$

$$\psi'_{\mathrm{p}_z\mathrm{d}_{z^2}} = \frac{1}{\sqrt{2}}(\psi_{\mathrm{d}_{z^2}} - \psi_{\mathrm{p}_z})$$

$\psi_{\mathrm{p}_z\mathrm{d}_{z^2}}$ will resemble an sp hybrid in shape (to a first approximation) and will project strongly in the $-z$ direction and $\psi'_{\mathrm{p}_z\mathrm{d}_{z^2}}$ will have the same shape and will project strongly in the $+z$ direction. Overlap of these hybrid orbitals with, say, p$_z$ orbitals of X and Y is, of course, perfectly sound on symmetry grounds.

(22) The pictorial representation and conventions follow those of Rundle for three-center, four-electron bonds using p orbitals: R. E. Rundle, *J. Am. Chem. Soc.*, **85**, 112 (1963). The three molecular orbitals are obtained by taking the following sums and differences, that is, linear combinations of the atomic orbitals.

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

(24) J. Y. Corey and R. West, *ibid.*, **85**, 4043 (1963).

purified chloroform was added cyclohexylammonium fluoride (0.156 g, 1.31 mmoles) with stirring. During a 10-min period the fluoride salt had dissolved with reaction, and the solution was added to 150 ml of pentane at −78°. The chloride salt was removed by filtration, and removal of solvents under vacuum afforded (−)-α-naphthylphenylmethylfluorosilane (89% yield) having $[\alpha]_D$ −32.7° (*c* 12.9 in pentane) with 90% net inversion of configuration. The fluorosilane had an infrared spectrum identical with that of an authentic sample.[2]

Conversion to Acyloxysilanes with Cyclohexylamine Salts. To a 2.5-dm polarimeter tube were added 0.40 g (1.4 mmoles) of (−)-chlorosilane, $[\alpha]_D$ −5.4° (*c* 2.4 in pentane), and 10 ml of dry chloroform. The resulting solution had α_{obsd} −0.53°. Then 0.25 g (1.6 mmoles) of cyclohexylammonium acetate was added to the polarimeter tube. It was necessary to shake the reaction mixture for about 4 min in order to dissolve the salt. When the solution became clear, it had α_{obsd} −3.60°. The rotation decreased to −3.50° over a 10-min period (owing to slow racemization). Then the chloroform solution was poured into a 250-ml suction flask containing 75 ml of pentane. The salts precipitated immediately and were filtered. The filtrate was then washed twice with cold water and dried over anhydrous sodium sulfate. Solvent removal afforded 0.37 g (86% yield) of (−)-α-naphthylphenylmethylacetoxysilane, $[\alpha]_D$ −13° (*c* 2.1 in pentane). The acetoxysilane was formed with 91% net inversion of configuration. It was characterized by comparison of its infrared spectrum with that of an authentic sample.[4]

By a procedure similar to the above, (−)-chlorosilane was converted to (−)-α-naphthylphenylmethylbenzoxysilane in 77% yield with 100% net inversion of configuration. The product had an infrared spectrum identical with that of an authentic sample.[4]

By a procedure similar to the above, (−)-chlorosilane was converted to (−)-α-naphthylphenylmethyl-*p*-nitrobenzoxysilane. When pentane was added to the reaction mixture as soon as the cyclohexylammonium *p*-nitrobenzoate had dissolved, the product isolated was formed with 73% net inversion of configuration. However, this low stereospecificity reflects racemization of the product during the 5 min required for the reagent to dissolve. In a similar experiment, the reaction mixture was allowed to stand for several minutes after the reagent had dissolved; the isolated product then had an optical purity of only 20%. This indicates that the product is racemized readily under the reaction conditions. The (−)-α-naphthylphenylmethyl-*p*-nitrobenzoxysilane was characterized by comparison of its infrared spectrum with that of an authentic sample.[4]

Reaction with Mercuric Acetate. Heating (80°) of a mixture of 0.50 g (1.8 mmoles) of (−)-chlorosilane, $[\alpha]_D$ −6.1° (*c* 4.0 in pentane), 10 ml of benzene, and 0.56 g (1.8 mmoles) of mercuric acetate was continued for 3.5 hr until most of the mercuric acetate had reacted. Isolation gave a 92% yield of (−)-acetoxysilane, $[\alpha]_D$ −9.1° (*c* 3.2 in pentane). The infrared spectrum was identical with that of a sample of authentic acetoxysilane.[4] The (−)-actoxysilane was formed with 76% net inversion of configuration.

Reaction with Powdered Potassium Hydroxide, KOH(s). To 4 g (70 mmoles) of powdered potassium hydroxide (containing about 12% water) and 18 ml of dry xylene was added 1.4 g (5.0 mmoles) of (−)-α-naphthylphenylmethylchlorosilane, $[\alpha]_D$ −6.0° (*c* 5.0 in pentane). The reactants were vigorously shaken in a stoppered, 50-ml flask, and the chlorosilane appeared to react as rapidly as it dissolved, producing a sharp temperature increase. The formed silanolate was not isolated. Upon hydrolysis, 1.2 g of (−)-α-naphthylphenylmethylsilanol was isolated, $[\alpha]_D$ −16° (*c* 1.2 in ether). The product was characterized by its infrared spectrum[2] and was formed with 92% net inversion of configuration.

Reactions of (−)-α-Naphthylphenylmethylbromosilane. Hydrolysis. A solution of 1.00 g of (+)-α-naphthylphenylmethylsilane, R_3Si^*H, $[\alpha]_D$ +32° (*c* 3.4 in pentane), in 30 ml of purified carbon tetrachloride was cooled in an ice bath and then carefully treated with a solution of bromine in carbon tetrachloride under a stream of dry nitrogen until a faint permanent bromine color was obtained. Carbon tetrachloride and hydrogen bromide were then removed from the reaction flask under vacuum until the volume of the solution was reduced to 12.0 ml. The resulting (−)-bromosilane solution had a rotation of α_{obsd} −7.04°, $[\alpha]_D$ −25.6°. This (−)-bromosilane solution was diluted with 30 ml of anhydrous pentane and injected rapidly, with a glass syringe, into a solution of 10 ml of 30% aqueous ammonium hydroxide in 500 ml of cold water, contained in a 1-l. separatory funnel. The funnel was immediately stoppered and vigorously shaken for 1 min. The organic layer was separated, diluted with an additional 30 ml of pentane, and washed once with 100 ml of cold water. After drying with anhydrous potassium carbonate and filtering, the solvent was removed by evaporation under reduced pressure. There was obtained a 67% yield of (−)-α-naphthylphenylmethylsilanol, $[\alpha]_D$ −19.9° (*c* 4.5 in benzene), 72% optically pure, with 86% net inversion of configuration. The product had an infrared spectrum identical with that of authentic silanol,[2] and optically pure silanol has $[\alpha]_D$ 27.6° in benzene.[2]

Reaction with Sodium Trimethoxyborohydride. A solution of (−)-bromosilane in carbon tetrachloride was prepared from 1 g of (+)-silane and had $[\alpha]_D$ −25.1°. The bromosilane solution was diluted with 30 ml of anhydrous ether and 1.0 g of powdered sodium trimethoxyborohydride was added directly to the flask and stirred into suspension. The reaction was allowed to proceed for 15 min at room temperature. The solution was then filtered, diluted with 50 ml of pentane, and washed with dilute hydrochloric acid for approximately 30 sec in a separatory funnel. Isolation gave a 71% yield of (−)-methoxysilane, $[\alpha]_D$ −16.1° (*c* 2.3 in pentane), 97% optically pure, with 98% net inversion of configuration. The product had an infrared spectrum identical with that of authentic methoxysilane.[2] Optically pure methoxysilane has $[\alpha]_D$ 16.5° in pentane.

Reaction with Potassium *t*-Butoxide. A solution of (−)-bromosilane in carbon tetrachloride was prepared from 1 g of (+)-silane as described above and had $[\alpha]_D$ −22.3°. To this was added 10 ml of a solution prepared from 0.5 g of potassium and 10 ml of anhydrous *t*-butyl alcohol, and also 10 ml of xylene plus 10 ml of hexane. The reaction mixture became opaque almost immediately. The reaction mixture was refluxed gently for 1 min (80°), cooled, diluted with 50 ml of pentane, and then washed five times with cold water. Isolation gave a 50% yield of (+)-α-naphthylphenylmethyl-*t*-butoxysilane, $[\alpha]_D$ +14.4° (*c* 2.6 in pentane), 52% optically pure, with 76% net inversion of configuration. (The bromosilane is exceedingly sensitive toward racemization with a variety of reagents.) The product was characterized by comparison of its infrared spectrum with that of an authentic sample.[3]

Reaction with (+)-Potassium α-Naphthylphenylmethylsilanolate. Reaction of xylene solution of (+)-silanolate[3] (5 mmoles) with (−)-bromosilane prepared from 1 g (5 mmoles) of (+)-silane, as described above, was allowed to proceed for 5 min at room temperature. The reaction mixture was then diluted with pentane, washed with water, dried, and filtered. After removal of solvents there was obtained a 77% yield of optically active 1,3-di-α-naphthyl-1,3-diphenyl-1,3-dimethyldisiloxane having $[\alpha]_D$ −8.8° (*c* 7.6 in pentane), 89% optically pure, whose infrared spectrum was identical with that of an authentic sample of the disiloxane.[3] The product was formed with 94% net inversion of configuration.

Reaction with Cyclohexylammonium Chloride. A solution of (−)-α-naphthylphenylmethylbromosilane (1.31 g, 4.02 mmoles), $[\alpha]_D$ −22°, in 46 ml of purified chloroform was treated with cyclohexylammonium chloride (0.543 g, 4.02 mmoles). After 30 min the reaction was quenched in pentane (200 ml) at −78°. Isolation gave a 94% yield of (+)-α-naphthylphenylmethylchlorosilane, $[\alpha]_D$ +3.3°, 54% optically pure, which was identified by comparison of its infrared spectrum, 2–25 μ, with that of authentic chlorosilane.[2] The infrared spectrum showed *no* bromosilane. Reaction proceeded with 77% net inversion of configuration.

Reaction with Cyclohexylammonium Fluoride. A solution of (−)-α-naphthylphenylmethylbromosilane (0.327 g, 1.00 mmole), $[\alpha]_D$ −22.1° (*c* 2.7 in pentane), in 11.5 ml of purified chloroform was treated with cyclohexylammonium fluoride (0.119 g, 1.00 mmole). After stirring for a few seconds the (initially insoluble) amine salt dissolved with reaction, and the solution was quenched with pentane (200 ml) at −78°. Isolation afforded a 96.2% yield of pure fluorosilane having $[\alpha]_D$ −37.5°, 92% optically pure, with 96% net inversion of configuration. The infrared spectrum of the product was identical with that of authentic fluorosilane.[2]

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