Organic and Biological Chemistry

Stereochemistry of Asymmetric Silicon. VII. The Silicon–Nitrogen Bond

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Abstract: Syntheses of four optically active aminosilanes containing the α-naphthylphenylmethylsilyl group, α-NpPhMeSi*, are reported. Relative and absolute configurations have been assigned to these substances and the stereochemistry of their reactions with acidic and basic reagents has been determined. Based on the stereochemical results, mechanism models have been proposed.

Previous papers in this series on the stereochemistry of substitution at asymmetric silicon[2–7] have reported results obtained with optically active compounds containing the α-naphthylphenylmethylsilyl group, α-NpPhMeSi*, designated R_3Si^* below, and having the following leaving groups: alkoxy and siloxy,[3,6] carboxylate and tosylate,[4] halogen (F, Cl, and Br).[2–6] Comparison of results for RPhMeSi*X, in which R = neopentyl, benzhydryl, or ethyl, with those obtained for α-NpPhMeSi*X showed that stereochemical results obtained with the latter system are generally applicable.[7]

In the present paper are reported results obtained with optically active R_3Si^*X compounds in which X is a nitrogen-containing leaving group.[8] Although there is substantial interest in the chemistry of organosilicon amines and their derivatives[9] there also exists a great dearth of information concerning the reaction mechanisms of these compounds. In this circumstance, studies of the dynamic stereochemistry of reactions of Si–N bonds seemed very desirable.

Syntheses and Stereochemical Correlations of Configuration. In pentane solvent, reaction of excess amine with $(+)R_3Si^*Cl$ was used to prepare $(+)$-R_3Si^*NHBu-*i* and $(+)R_3Si^*Pyr$ (Pyr is 1-pyrrolidinyl). Reaction of the latter with $LiAlH_4$ provided the final step in a Walden cycle (eq 1). Since it is known[2] that reaction 1a proceeds with retention, reactions 1b and 1c must include one inversion and one retention. In analogy with the formation and reduction of alkoxysilanes,[2,3]

$$(-)\text{-}R_3Si^*H \xrightarrow[a]{Cl_2} (+)\text{-}R_3Si^*Cl \xrightarrow[b]{C_4H_8NH} (+)\text{-}R_3Si^*Pyr \xrightarrow[c]{LiAlH_4} (+)\text{-}R_3Si^*H \quad (1)$$

the reasonable choice is inversion for 1b and retention for 1c. Also, stereospecific reactions of R_3Si^*Cl in general proceed with inversion of configuration in accord with the SN2–Si stereochemistry rule for good leaving groups.[5] Assignment of an inversion stereochemistry to 1b is also nicely consistent with reaction 2.

(2)

Assignment of an inversion path to reaction 2 is in close analogy to the inversion reactions of R_3Si^*Cl with diverse R′Li reagents[6] and reinforces the above assignment of an inversion stereochemistry to reaction 1b.

The preparation of $R_3Si^*NH_2$ utilized R_3Si^*H as starting material and was carried out with sodium amide in xylene and with lithium amide in the same solvent. The predominant stereochemical course was the same for both reagents, but the yield was much improved in the synthesis with lithium amide *and* ammonia (eq 3).

$$(+)\text{-}R_3Si^*H + NH_3 \xrightarrow[80\text{–}85^\circ]{LiNH_2} (-)\text{-}R_3Si^*NH_2 + H_2 \quad (3)$$

In analogy with the following reaction of potassium hydroxide with R_3Si^*H, which proceeds with retention of configuration,[10] reaction 3 should likewise proceed by a retention stereochemistry.

$$(+)\text{-}R_3Si^*H + KOH(s) \xrightarrow[\sim 100^\circ]{xylene} \xrightarrow{H_2O} (+)\text{-}R_3Si^*OH$$

Also, it has been reported that $(-)$-R_3Si^*Cl reacts with ammonia to give $(+)$-$R_3Si^*NH_2$,[11] an expected result, since ammonolysis of R_3Si^*Cl should proceed with inversion of configuration, and $(-)$-R_3Si^*Cl and $(+)$-R_3Si^*H are known to have the same configuration.[2]

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[1] Department of Chemistry, University of California, Davis, California.

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

[6] L. H. Sommer, W. D. Korte, and P. G. Rodewald, *ibid.*, **89**, 862 (1967).

[7] L. H. Sommer, K. W. Michael, and W. D. Korte, *ibid.*, **89**, 868 (1967).

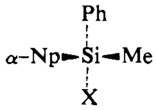
[8] For a preliminary communication, see L. H. Sommer, J. D. Citron, and C. L. Frye, *J. Am. Chem. Soc.*, **86**, 5684 (1964)

[9] For reviews, see C. Eaborn, "Organosilicon Compounds," Butterworth & Co., (Publishers) Ltd., London, 1960, pp 339–343; R. Fessenden and J. S. Fessenden, *Chem. Rev.*, **61**, 361 (1961); U. Wannagat, *Advan. Inorg. Chem. Radiochem.*, **6**, 225 (1964).

[10] L. H. Sommer, C. L. Frye, M. C. Musolf, G. A. Parker, P. G. Rodewald, K. W. Michael, Y. Okaya, and R. Pepinsky, *J. Am. Chem. Soc.*, **83**, 2210 (1961).

[11] K. D. Kaufman, U. Mann, and K. Rühlmann, *Z. Chem.*, **5**, 188 (1965).

Table I. α-NpPhMeSi*X Compounds Having the Configuration



$$\alpha\text{-Np}\blacktriangleright\overset{\text{Ph}}{\underset{\text{X}}{\text{Si}}}\blacktriangleleft\text{Me}$$

Si*X[a]	[α]D, deg (solvent)	Si*X	[α]D, deg (solvent)
(*S*)-(+)-SiPyr	+21.6 (pentane)	(*R*)-(+)-SiH	+34.5 (pentane)
(*S*)-(+)-SiNH-*i*-Bu	+5.1 (pentane)	(*S*)-(+)-SiOCOPh	+17.7 (pentane)
(*S*)-(−)-SiNH$_2$	−4.8 (pentane)	(*S*)-(−)-SiCl	−6.3 (pentane)
(*S*)-(−)-SiNHSi*R$_3$	−8.2 (pentane)	(*S*)-(+)-SiOH	+20.5 (ether)

[a] Names for the above optically active aminosilanes, in the order of listing, are: (*S*)-(+)-α-naphthylphenylmethyl(1-pyrrolidinyl)silane; (*S*)-(+)-N-isobutyl-α-naphthylphenylmethylsilylamine; (*S*)-(−)-α-naphthylphenylmethylsilylamine; (*S*)-(−)-1,3-di-α-naphthyl-1,3-diphenyl-1,3-dimethyldisilazane.

Table II. Hydrolysis of Silylamines with ∼0.25 *M* HCl in Ether Solvent

Eq no.	Reactant	Product	Stereo-specificity[a]	Yield, %
7	(+)-R$_3$Si*Pyr	(−)-R$_3$Si*OH	76%, inversion	100
8	(+)-R$_3$Si*NH-*i*-Bu	(−)-R$_3$Si*OH	95%, inversion	91
9	(+)-R$_3$Si*NH$_2$	(+)-R$_3$Si*OH	96%, inversion	100
	(+)-R$_3$Si*NHSi*R$_3$	No reaction		

[a] A stereospecificity of, say, 90% inversion means that the product was 80% optically pure (20% racemic).

Further evidence for the above assignment of relative configuration for R$_3$Si*NH$_2$ comes from the synthesis of 1,3-di-α-naphthyl-1,3-diphenyl-1,3-dimethyldisilazane, R$_3$Si*NHSi*R$_3$ (eq 4). According to the SN2-Si

$$(+)\text{-R}_3\text{Si*NH}_2 + n\text{-C}_4\text{H}_9\text{Li} \xrightarrow[\text{a}]{} [\text{R}_3\text{Si*NHLi}] \xrightarrow[\text{b}]{(-)\text{-R}_3\text{Si*Cl}} \underset{[\alpha]\text{D} +8.2°}{(+)\text{-R}_3\text{Si*NHSi*R}_3} \quad (4)$$

stereochemistry rule, 4b should proceed with inversion of configuration, and from this it follows that (+)-R$_3$Si*NH$_2$ and (−)-R$_3$Si*Cl are of opposite configuration; if this were not the fact, inactive *meso* product would be formed. Indeed, reaction of the lithio derivative of racemic (±)-R$_3$Si*NH$_2$ with (−)-R$_3$Si*Cl leads to disilazane having optical rotation only one-half of that obtained in reaction 4.

$$(\pm)\text{-R}_3\text{Si*NH}_2 + n\text{-C}_4\text{H}_9\text{Li} \longrightarrow [\text{R}_3\text{Si*NHLi}] \xrightarrow{(-)\text{-R}_3\text{Si*Cl}} meso\text{-R}_3\text{Si*NHSi*R}_3 + \underset{[\alpha]\text{D} +4.1°}{(+)\text{-R}_3\text{Si*NHSi*R}_3} \quad (5)$$

From consideration of reactions 4 and 5, it is clear that the disilazane from 4 and (+)-R$_3$Si*NH$_2$ have the same configuration at all three silicon centers.

The absolute configurations[2] of the aminosilanes plus those of some other compounds which are relevant to subsequent discussion are presented in Table I. These aminosilane configurational assignments receive further support from the similarity of their stereochemistry in reactions described below.

Stereochemistry of the Silicon–Nitrogen Bond. In general, silicon–nitrogen bonds are more reactive than analogous carbon–nitrogen bonds with both acids and bases. However, reactivity of the silicon–nitrogen bond is especially pronounced when the attacking reagent can transform the nitrogen into a better leaving group by preliminary coordination. Thus, acidic reagents react far more rapidly than basic reagents.[9]

In the present work three optically active aminosilanes hydrolyzed rapidly to the corresponding silanols when treated with ∼0.25 *M* hydrochloric acid in ether solvent.

$$\text{R}_3\text{Si*NR}'_2 + \text{H}_2\text{O} \xrightarrow[\text{Et}_2\text{O}]{\text{HCl}} \text{R}_3\text{Si*OH} \quad (6)$$

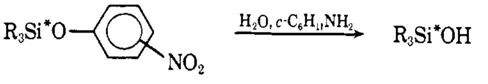
As shown in Table II reaction 6 proceeds with predominant inversion of configuration. Since the reactions in Table II are greatly accelerated by the presence of acid, there can be little doubt that the *actual* leaving group contains protonated nitrogen and that the gross mechanism involves

$$\text{R}_3\text{Si*NR}'_2 \overset{\text{H}^+}{\rightleftharpoons} \text{R}_3\text{Si*}\overset{+}{\text{N}}\text{HR}'_2$$

$$\text{R}_3\text{Si*}\overset{+}{\text{N}}\text{HR}'_2 \xrightarrow{\text{H}_2\text{O}} \text{R}_3\text{Si*OH} + \text{R}'_2\text{NH}$$

Previous work has shown that the basicity of the leaving group, X, is a very important factor in determining the stereochemical course of reaction at asymmetric silicon.[2-7] The pK_a values for the conjugate acids, HX, of the leaving groups involved in reaction 6 are: (CH$_2$)$_4$NH$_2^+$, ∼9.9; *i*-BuNH$_3^+$, 10.43; NH$_4^+$, 9.25.[12] In the same connection, it is interesting to note that previous work has shown that inversion of configuration is the predominant stereochemical course for the following hydrolysis reactions also carried out in ether solvent.[13,14]

$$\text{R}_3\text{Si*SSi*R}_3 \xrightarrow[\text{Et}_2\text{O}]{\text{H}_2\text{O, Et}_2\text{NH}} \text{R}_3\text{Si*OH} + \text{R}_3\text{Si*S}^-\text{Et}_2\text{NH}_2^+ \quad (10)$$



(11)

(*meta* and *para*)

For reaction 10, pK_a for HX is ∼7. For reactions 11: *m*-NO$_2$PhOH has pK_a = 8.35; *p*-NO$_2$PhOH has pK_a = 7.14.[12]

R$_3$Si*OPh, having pK_a of HX equal to 9.95, proved to be quite resistant to hydrolysis under the conditions used in reactions 10 and 11.[14] Since the actual leaving groups in the reactions listed in Table II have pK_a values close to that of phenol, rapid acid-catalyzed hydrolyses of the silylamines may reflect the presence of the positive charge present in the silylamine leaving groups.[15] Table III lists the results obtained from

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(12) For an excellent summary of pK_a values for R$_2$NH$_2^+$, RNH$_3^+$, etc., see H. C. Brown, D. H. McDaniel, and O. Hafliger in "Determination of Organic Structures by Physical Methods," E. A. Braude and F. C. Nachod, Ed., Academic Press Inc., New York, N. Y., 1955, Chapter 14.

(13) L. H. Sommer and J. McLick, *J. Am. Chem. Soc.*, 88, 5359 (1966).

(14) Unpublished work of L. H. Sommer and R. Mason on the stereochemistry of the ≡Si* —OAr bond.

Table III. Reaction of Silylamines with HCl in Pentane

Eq no.	Reactant	Product	Stereo specificity[a]	Yield, %[b]
12	(+)-R_3Si^*Pyr	(−)-R_3Si^*Cl	52%, retention	43
13	(+)-R_3Si^*NH-*i*-Bu	(+)-R_3Si^*Cl	80%, inversion	66
14	(+)-$R_3Si^*NH_2$	(−)-R_3Si^*Cl	91%, inversion	60
15	(+)-$R_3Si^*NHSi^*R_3$	(−)-R_3Si^*Cl	96%, inversion	

[a] The product was shown to be R_3Si^*Cl in each reaction by infrared and was then reduced with lithium aluminum hydride (with inversion of configuration[2]) to give R_3Si^*H. Stereospecificity values are based on the optical purity of the latter. [b] Yields are based on isolated R_3Si^*H.

Table IV. Reaction of Silylamines with Carboxylic Acids

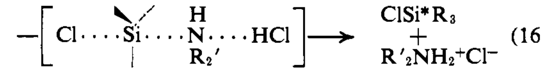
Eq no.	Reactant	Acid	Product	Stereospecificity	Yield, %
18	(+)-$R_3Si^*NH_2$	Benzoic[b]	(−)-R_3Si^*OBz	79%, retention	97
19	(+)-$R_3Si^*NH_2$	Mesitoic[b]	(+)-R_3Si^*OMes	70%, inversion	98
20	(+)-R_3Si^*NH-*i*-Bu	Benzoic[c]	(−)-R_3Si^*OBz[a]	74%, inversion	53

[a] This product was reduced with lithium aluminum hydride to give (by inversion of configuration) a net 53% yield of (+)-R_3Si^*H. [b] Benzene solvent. [c] Pentane solvent.

treatment of the silylamines with hydrogen chloride gas in a pentane solvent.

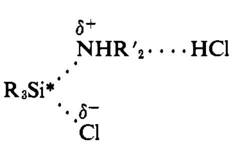
The fact that the reactions listed in Table III proceed as rapidly as hydrogen chloride can be added to the pentane solution of silylamine is, of itself, an interesting mechanistic problem. Protonation of the nitrogen is a reasonable first step, but the displacement of R'_2NH from silicon by Cl^- in a second step clearly would comprise a process in which the leaving group is a stronger base than the entering group by an enormous factor (~15 to 20 pK_a units). In explanation of these facts we wish to advance a mechanistic scheme in which the actual leaving group is partially protonated R'_2NH and the partial formation of $R'_2NH_2^+Cl^-$ in the rate-determining transition state furnishes an additional driving force. For the inversion reactions we propose eq 16.[5] For reaction 12 in Table III, which proceeds

$$R_3Si^*NR'_2 + HCl \xrightleftharpoons{\text{pentane}} \underset{\text{ion pair}}{R_3Si^*\overset{+}{N}HR'_2\ Cl^-} \xrightarrow{HCl}$$



(16)

with slight net retention of configuration, a combination of factors may favor operation of a mechanism for which the rate-determining transition state has the approximate structure



$$R_3Si^* \begin{matrix} \cdot\cdot\overset{\delta+}{N}HR'_2\cdots HCl \\ \cdot\cdot\overset{\delta-}{Cl} \end{matrix} \qquad (17)$$

The slight net retention of configuration in reaction 12 and other considerations prompted an investigation of the reactions of silylamines with carboxylic acids, and Table IV shows the results obtained.

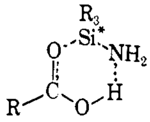
As indicated in Table I, present and previous correlations of configuration assign the same configuration to (+)-R_3Si^*NH-*i*-Bu, (−)-$R_3Si^*NH_2$, and (+)-R_3Si^*OCOPh. In the present work, (−)-R_3Si^*OMes resulted from treatment of (−)-R_3Si^*Cl with cyclohexylammonium mesitoate, and reduction of the mesitoate with lithium aluminum hydride furnished (+)-R_3Si^*H (eq 21 and 22). Based on previous work[2–7]

$$(-)\text{-}R_3Si^*Cl + C_6H_{11}NH_3^+OMes^- \longrightarrow (-)\text{-}R_3Si^*OMes \qquad (21)$$

$$(-)\text{-}R_3Si^*OMes + LiAlH_4 \longrightarrow (+)\text{-}R_3Si^*H \qquad (22)$$

an inversion stereochemistry can be assigned to both 21 and 22 in accord with the SN2–Si stereochemistry rule. This conclusion is also in accord with previous demonstration that (−)-R_3Si^*Cl and (+)-R_3Si^*H have the same configuration, and assigns the same configuration to (+)-R_3Si^*OMes, (+)-R_3Si^*OBz, and (−)-$R_3Si^*NH_2$.

Retention of configuration for $R_3Si^*NH_2$ in reaction 18 compared to inversion of configuration in reactions 9 and 14 may be rationalized in terms of a transition-state structure such as 23 for reaction 18. Relative to



(23)

HCl gas, or H_3O^+ plus H_2O, the benzoic acid reagent provides better opportunity for concerted electrophilic attack on N and nucleophilic attack on Si in a quasi-cyclic transition state such as 23. Thus, an SNi–Si mechanism can lead to retention of configuration.[16]

In reaction 19, use of mesitoic acid, in which the carboxyl group is highly hindered by the *o*-methyl groups, effectively blocks formation of transition state 23,[17] and a mechanism which may utilize one or two molecules of RCOOH per molecule of $R_3Si^*NH_2$ in the transition state results in predominant inversion of configuration. In reaction 20, relative to reaction 18, increased steric requirements in the amino leaving group also lead to a change of mechanism and a change to inversion of configuration.

Based on previous studies of alkoxysilanes, R_3Si^*OR',[3] the present finding of retention of configuration for the reduction of R_3Si^*Pyr with $LiAlH_4$ (reaction 1c) was an expected result. Furthermore, the reaction of powdered KOH with an optically active silylamine has been reported to follow a retention stereo-

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(15) In view of the electronegativity difference between carbon and silicon, and because protonation of the nitrogen should destroy any $d\pi$–$p\pi$ bonding in Si–N, the protonated silylamines should be especially reactive toward nucleophiles as a result of the presence of adjacent positive charges on silicon and nitrogen in $R_3Si^*NHR_2^+$.

(16) For other cases of probable retention of configuration *via* a six-ring transition state in which the entering and leaving groups are both part of the ring, and for general comment on possible duality of stereochemical results in such cases, see ref 3 and 5, and other references cited therein.

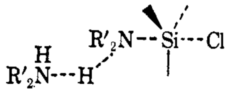
(17) Accurately scaled molecular models clearly show that transition state 23 would be extremely difficult to attain with $R_3Si^*NH_2$ and mesitoic acid, whereas such a transition state should be easily attainable with benzoic acid.

chemistry[11, 18] (eq 24). Reactions analogous to 1c and 24 have been carried out with R_3Si^*OR' and have also

$$(-)\text{-}R_3Si^*NHCH_3 + KOH(s) \longrightarrow$$
$$(+)\text{-}R_3Si^*OK \xrightarrow{H_2O} (-)\text{-}R_3Si^*OH \quad (24)$$

yielded retention stereochemical paths.[3] Reactions 1c and 24 are very slow and probably take place by SNi–Si mechanisms analogous to those already proposed for the corresponding alkoxysilane reactions.[3]

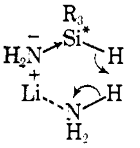
Stereochemistry of Silicon–Nitrogen Bond Formation. Previous studies have demonstrated that diverse types of evidence are in accord with the hypothesis that the most common reaction mechanism for R_3Si^*X in which X is a good leaving group is SN2–Si.[2–7, 19] This generalization coupled with earlier rate studies of the alcoholysis of R_3SiCl compounds[20] and more recent studies which demonstrated general base catalysis for the methanolysis of Ph_3SiOPh in methanol buffers[21] leads to transition-state structure 25 as a reasonable model for aminolysis of R_3Si^*Cl proceeding with inversion of configuration in the present work. Although transition state 25 has precedent and seems quite attractive because both products, $R_3Si^*NR'_2$ and $R'_2NH_2^+Cl^-$, are formed simultaneously, and because partial formation of the amine hydrochloride should assist in breaking the strong Si–Cl bond (formation of $NH_4Cl(s)$ from $NH_3(g)$ and $HCl(g)$ has $\Delta H = -43$ kcal/mole), it is possible that the actual mechanism involves formation of $R_3Si^*NHR'_2{}^+Cl^-$ ion pair as an intermediate. Experiments designed to attempt to distinguish between these mechanistic possibilities are being undertaken.



(25)

Formation of R_3Si^*Pyr from R_3Si^*Cl and PyrLi with inversion of configuration in reaction 2 requires no special comment in view of previous mechanistic discussion of the reactions of R_3Si^*Cl with R'Li[6] which also proceed with inversion of configuration.

In analogy with previously proposed mechanism models for the retention stereochemistry found for reaction of KOH(s) with R_3Si^*H in xylene solvent,[22] mechanism model 26 seems reasonable for the retention stereochemistry found for reaction 3.



$$\longrightarrow R_3Si^*NH_2 + H_2 + LiNH_2 \quad (26)$$

Experimental Section[23]

(+)-N-Isobutyl-α-naphthylphenylmethylsilylamine.[24] (+)-R_3Si^*Cl, $[\alpha]_D$ +6.3°, 3.5 g, was dissolved in 350 ml of pentane, and 4.5 ml of i-$BuNH_2$ was added. A precipitate formed immediately, and after standing 4 hr, the amine hydrochloride was removed by filtration and recovered in 94% yield. Following three washings of the filtrate with 5% K_2CO_3 solution and drying over anhydrous K_2CO_3, the solvent was removed under vacuum, yielding 3.0 g (75%) of a liquid, $[\alpha]_D$ +5.1° (c 3.6, pentane). The infrared spectrum[25] had the following absorption bands characteristic of the isobutylamino moiety: 2.97 (w), 3.42 (s), 6.82 (m), 7.15 (m), and a broadening of the peak at 9.0 μ. Some racemic material was prepared for analysis by molecular distillation, n^{26}_D 1.5970.

Anal. Calcd for $C_{21}H_{25}NSi$: C, 78.94; H, 7.91; N, 4.39; Si, 8.79. Found: C, 78.67; H, 8.07; N, 4.44; Si, 8.84.

(+)-α-Naphthylphenylmethyl(1-pyrrolidinyl)silane. To 5.1 g of (+)-R_3Si^*Cl, $[\alpha]_D$ +6.3°, in 500 ml of pentane was added 6 ml of pyrrolidine. A white precipitate appeared immediately, which was removed by filtration after 10 min. After washing three times with 5% K_2CO_3 solution and drying over anhydrous K_2CO_3, the solvent was removed under vacuum, yielding 5.2 g (90%) of an oil, $[\alpha]_D$ +21.6° (c 1.3, pentane). Infrared absorption bands characteristic of the pyrrolidinyl moiety were at 3.42 (s), 3.58 (m), 7.40 (m), 8.35 (m), 9.27 (s), and 9.90 (s) μ. A sample was prepared for analysis by molecular distillation, n^{24}_D 1.6206.

Anal. Calcd for $C_{21}H_{23}NSi$: C, 79.44; H, 7.30; N, 4.41. Found: C, 78.90; H, 7.72; N, 4.70.

(−)-α-Naphthylphenylmethylsilylamine. Procedure a. To a mixture of 10 g of powdered $NaNH_2$ (Farchan Chemical Co.) and 700 ml of purified xylene at 75–90° in a drybox under helium was added with stirring (magnetic) 10 g of (+)-R_3Si^*H, $[\alpha]_D$ +34.5°. After 5 min gas evolution was visible (H_2?), and this continued for 2 hr. After this period the mixture was allowed to cool and then filtered. Following removal from the drybox, the xylene was taken off under vacuum, and the residual oil was extracted with four 200-ml portions of pentane. The pentane was removed under vacuum, and the residual viscous liquid was transferred to a sublimator containing a wad of glass wool at the bottom. Upon distillation at 50–70° (0.1 mm), the $R_3Si^*NH_2$ crystallized on the sublimator condenser, yield 2.6 g (25%), mp 91.9–94.3° (uncor), $[\alpha]_D$ −4.8° (c 1.2, pentane). An infrared spectrum of the residual viscous oil indicated that it was mainly the disilazane (see below). Absorption bands at 2.95 (m), 3.02 (m), and 6.53 (m) μ were characteristic of the $-NH_2$ moiety.[25, 26]

Anal. Calcd for $C_{17}H_{17}NSi$: C, 77.52; H, 6.51; N, 5.32. Found: C, 77.67, 77.31; H, 6.75, 6.68; N, 5.29.

Procedure b. To a 1 l., three-necked, round-bottomed flask equipped with magnetic stirrer, gas addition tube, addition funnel, and rubber septum was added 450 ml of xylene. Ten grams of (+)-R_3Si^*H, $[\alpha]_D$ +34.7°, in 35 ml of xylene was placed in the addition funnel, and the flask was deaerated with nitrogen. Ten milliliters of ~1.6 M n-BuLi in hexane was added, and then NH_3 was bubbled into the xylene while the solution was stirred, and heated with an oil bath. When the temperature reached 80–85°, the silane solution was added. While ammonia was still bubbling in (~1 bubble/sec), another gas (H_2?) was evolved from the solution for 2 hr. After this time the contents of the flask were cooled and poured into 5% K_2CO_3 solution, with which it was washed three times. After drying over anhydrous K_2CO_3 and filtering, the solvent was stripped.

The resulting oil was diluted with 50 ml of pentane, and a solid formed immediately. After standing in the refrigerator overnight, the solid material (7.8 g) was sublimed at 75° (~0.05–0.03 mm). The yield, 7.1 g, had $[\alpha]_D$ −5.0° (c 1.3, pentane).

The filtrate from the crystallization was freed of solvent, and sublimed in a like manner, yielding an additional 1.4 g of aminosilane. The total yield was 8.5 g, 80%.

(−)-1,3-Di-α-naphthyl-1,3-diphenyl-1,3-dimethyldisilazane. In a three-necked, round-bottomed flask under nitrogen, 10.49 g of (±)-α-naphthylphenylmethylsilylamine was dissolved in 20 ml of ether. n-Butyllithium (2.03 M, 20 ml) in hexane was added with stirring, and after 15 min, a solution of 11.22 g of (+)-R_3Si^*Cl, $[\alpha]_D$ +6.4° (c 1.0, pentane), in 15 ml of ether was added. A white precipitate formed. After 2 hr, the solution was filtered, the solvent stripped, and the residue dissolved in pentane. After filtration, the solvent was again stripped to yield a very viscous clear liquid. A rotation gave $[\alpha]_D$ −4.1° (c 4.4, pentane). The infrared spectrum showed the usual α-NpPhMeSi– system absorptions, plus two strong bands at 8.5 and 10.8 μ characteristic of disilazanes.[25, 26]

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[18] K. Ruhlman, K. D. Kaufmann, and U. Mann, *Z. Chem.*, **5**, 108 (1965).

[19] For a summary of the earlier evidence up to about 1964, see L. H. Sommer, "Stereochemistry, Mechanism and Silicon," McGraw-Hill Book Co., Inc., New York, N. Y., 1965.

[20] A. D. Allen, J. C. Charlton, C. Eaborn, and G. Modena, *J. Chem. Soc.*, 3668 (1957); A. D. Allen and G. Modena, *ibid.*, 3671 (1957).

[21] R. L. Schowen and K. S. Lathan, Jr., *J. Am. Chem. Soc.*, 88, 3795 (1966).

[22] Reference 19, p 105.

[23] Analyses were done by Schwarzkopf Microanalytical Laboratory.

[24] This compound was originally prepared by C. L. Frye.

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A pmr spectrum in CCl_4 showed a multiplet centered at 8.6 ppm (relative to tetramethylsilane) (24 protons), and singlets at 1.8 ppm (one proton) and 0.2 ppm (six protons). Thus the signal at 1.8 ppm is the amino proton.

Part of the product was subject to prolonged vacuum pumping to remove solvent, and an analysis was done on this material.

Anal. Calcd for $C_{34}H_{31}NSi$: C, 80.11; H, 6.13; N, 2.75. Found: C, 80.17; H, 6.24; N, 2.61.

Reduction of (+)-R_3Si^*Pyr with $LiAlH_4$. To 2.54 g of (+)-α-naphthylphenylmethyl(1-pyrrolidinyl)silane, $[\alpha]_D$ +12.8° (*c* 10, pentane), in 25 ml of pentane was added 70 ml of *n*-butyl ether, 45 ml of ethyl ether, and 5 g of $LiAlH_4$. The mixture was refluxed and heated to 75–82° by allowing the lower boiling ethyl ether and pentane to escape. Refluxing was continued for 5 days, at the end of which time the excess hydride was treated with acetone. This reaction was not as vigorous as usual, probably due to the thermal decomposition of the hydride. The mixture was worked up with acid and water and then dried over sodium sulfate. After the solvent was removed, an infrared spectrum indicated that the residue was about 40% silane and 60% disiloxane.

The product was put on a silica gel column and allowed to stand overnight. Elution was accomplished with benzene–pentane (30:70, v/v) to yield 0.98 g (50%) of (+)-R_3Si^*H, $[\alpha]_D$ +9.7° (*c* 3.2, pentane). However, an infrared spectrum showed the presence of minor amounts of other materials, so the silane was rechromatographed in the same manner, yielding 0.41 g of (+)-R_3Si^*H, $[\alpha]_D$ +10.8° (*c* 1.6, pentane), which was shown by infrared spectroscopy to be free of contaminants.

Reaction of (+)-R_3Si^*Cl with Pyrrolidinyllithium. To a 200-ml, round-bottomed flask that had been flushed with nitrogen and equipped with a magnetic stirring bar, condenser, and rubber septum was added successively 30 ml of ether, 0.84 ml (10.0 mmoles) of pyrrolidine, and 5.20 ml (10.5 mmoles) of 2.02 *M* *n*-butyllithium in hexane. A slight cloudiness was perceptible. After stirring for 2 hr, a Michlers ketone test was negative, so 2.85 g (10.1 mmoles) of (+)-R_3Si^*Cl, $[\alpha]_D$ +5.3° (*c* 6.0, pentane), in 15 ml of ether was added. A slight refluxing took place. After 90 min, the solvent was stripped, and 30 ml of pentane was added. Following filtration, the stripping process was repeated twice, finally yielding a clear solution of 2.54 g (82%) of (+)-R_3Si^*Pyr, $[\alpha]_D$ +12.8° (*c* 10, pentane). An infrared spectrum indicated the presence of a small amount of excess aliphatic, possibly R_3Si^*-*n*-Bu.

Reactions of Silylamines with Anhydrous HCl. The reaction of (+)-$R_3Si^*NH_2$ is typical. In a 125-ml filter flask, 0.3 g of (+)-$R_3Si^*NH_2$, $[\alpha]_D$ +4.8° (*c* 1.2, pentane), was dissolved in 50 ml of pentane. The flask was flushed with nitrogen for 2 min, and then HCl (Matheson Co.) was passed through for 30 sec. A precipitate formed immediately, and after this period, nitrogen was again passed through for 2 min. A small sample was removed, and an infrared spectrum showed it to be R_3Si^*Cl (Si–Cl stretch at 19.7 μ). The remainder of the mixture was then reduced with 2 g of $LiAlH_4$ in 100 ml of ether. After 10 min, the $LiAlH_4$ was decomposed with acetone; the solution was treated with dilute aqueous HCl, water, and anhydrous sodium sulfate and the solvent removed on a steam bath. After chromatography over silica gel (see above), pure R_3Si^*H was isolated. Data for this and other reactions are found in Table III.

Acid-Catalyzed Hydrolysis of Silylamines. The reaction of (+)-$R_3Si^*NH_2$ is representative. A solution of 0.2 g of the silylamine ($[\alpha]_D$ +4.8°) in 50 ml of ether was added to 50 ml of ~0.25 *N* HCl solution in a separatory funnel. After shaking 30 sec, the acid was removed; the ethereal solution was washed twice with water and then dried over anhydrous K_2CO_3. The silanol product was usually contaminated with a small amount of disiloxane (estimated to be less than 10% from infrared spectra). Pertinent information about these reactions is given in Table II.

Reactions of $R_3Si^*NH_2$ with Carboxylic Acids. To a solution of 0.501 g of (+)-$R_3Si^*NH_2$, $[\alpha]_D$ +5.0° (*c* 1.2, pentane), in 25 ml of benzene was added a solution of 0.465 g of benzoic acid in 25 ml of benzene. A white solid appeared immediately. After 8 min, the solution seemed to be clearing, so the mixture was filtered and the solvent stripped from the filtrate. A rotation gave $[\alpha]_D$ −11.0° (*c* 3.5, pentane) on 0.68 g of product, a 97% yield. An infrared spectrum showed the product to be α-naphthylphenylmethylbenzoxysilane.[4]

By a similar procedure, (+)-$R_3Si^*NH_2$ reacted with mesitoic acid to give a 98% yield of (+)-α-naphthylphenylmethylmesitoxysilane, $[\alpha]_D$ +3.1° (*c* 3.3, chloroform).

Reaction of (−)-R_3Si^*NHBu with Benzoic Acid. Benzoic acid (0.372 g) was added to a solution of (−)-R_3Si^*NHBu (0.49 g), $[\alpha]_D$ −4.2° (*c* 2.4, pentane), in 20 ml of pentane. A white precipitate appeared immediately. After 2 min, the mixture was poured into a mixture of 2 g of $LiAlH_4$ and 150 ml of ether. The reduced product was worked up in the usual way with acetone, cold dilute acid, water, and sodium sulfate. After chromatography on an 18 × 0.5 in. silica gel column 0.077 g of (−)-R_3Si^*H, $[\alpha]_D$ −7.3° (*c* 0.9, pentane), was obtained. An infrared spectrum indicated that the product was pure.

Preparation of α-Naphthylphenylmethylmesitoxysilane. To a solution of 2.784 g (9.85 mmoles) of (−)-R_3Si^*Cl, $[\alpha]_D$ −5.5° (*c* 1.2, pentane), in 15 ml of chloroform was added a solution of 2.591 g (9.85 mmoles) of cyclohexylammonium mesitoate in 100 ml of chloroform.[4] After 10 min, 650 ml of pentane was added, and a precipitate formed immediately. The mixture was cooled for 30 min in a refrigerator, filtered. washed twice with water, and dried over sodium sulfate. After filtering and stripping the solvent, a rotation gave $[\alpha]_D$ 0.0° (*c* 16, pentane).

However, a rotation in chloroform gave $[\alpha]_D$ −6.9° (*c* 1.7, chloroform). An infrared spectrum was in accord with the structure α-naphthylphenylmethylmesitoxysilane. Assuming 100% inversion for the reaction, and correcting for the optical impurity of the chlorosilane, the mesitoate has $[\alpha]_D$ −7.8° (*c* 1.7, chloroform).

Reduction of (−)-R_3Si^*OMes with $LiAlH_4$. Mesitoxysilane from the preceding experiment ($[\alpha]_D$ −6.9° (*c* 1.7, chloroform)) was dissolved in 20 ml of pentane and added to a mixture of 2.0 g of $LiAlH_4$ in 50 ml of ether. After 45 min, the mixture was worked up in the usual way with acetone, cold dilute hydrochloric acid, water, and sodium sulfate. After filtering and stripping the solvent, the product was placed on an 18 × 0.5 in. silica gel column and eluted with a benzene–pentane (30:70, v/v) mixture. This yielded 0.20 g of (+)-R_3SiH, $[\alpha]_D$ +24.9° (*c* 0.8 pentane). An infrared spectrum confirmed the identity of the product.

Correcting the rotation of the product to optically pure starting material gives $[\alpha]_D$ +28.6°. This is 84% optically pure and corresponds to a stereospecificity of 92% inversion.

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