Using cyclo-$C_6H_{11}NH_3Cl^{36}$ in chloroform solvent it was found that for

$$R_3Si^*Cl + cyclo\text{-}C_6H_{11}NH_3Cl^{36} \rightleftharpoons$$
$$R_3Si^*Cl^{36} + cyclo\text{-}C_6H_{11}NH_3Cl$$
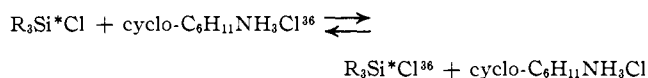
the rate of racemization and the rate of chloride–radio-chloride exchange are the same within experimental error. Polarimetric and exchange rate data were obtained on the same reaction mixture and the agreement in duplicate runs was good. For run 1 $k(rac.)/k(ex.) = 1.1 \pm 0.1$. For run 2, $k(rac.)/k(ex.) = 1.0 \pm 0.1$. Our rationale of these results involves formation of a siliconium ion pair which undergoes *fast* retention, and inversion exchanges whose rates exceed return to reactants with inversion of configuration. In this mechanism, formation of the siliconium ion pair is rate controlling and the exchanges, which proceed rapidly, take place equally fast by retention or inversion reactions of the siliconium ion pairs.

It appears that in chloroform solvent cyclohexylammonium chloride, bromide, and iodide promote ionization of silicon–chlorine bonds (to ion pairs) at a rate which can become competitive with displacement by an S_N2-Si mechanism[3] when the anionic part of the salt is not more basic than –Cl. It has been shown that added salts can have a very large rate-enhancing effect on carbonium ion formation in nonpolar media and that the rate enhancement produced by salts is frequently approximately first order in added salt.[4] It appears that the dramatic effects of salts on the rates of carbonium ion pair formation in nonpolar media are paralleled by their effects on siliconium ion pair formation from R_3Si^*Cl. The latter is optically stable indefinitely in chloroform solvent in the absence of added salts.

It should not be assumed that chloride–radiochloride exchange at asymmetric silicon will, in all circumstances, give a ratio of one for $k(rac.)/k(ex.)$. The situation is probably much more complex than that. In polar solvents of higher ion-solvating power, which would promote a concentration of free chloride ion much larger than is present in chloroform and thereby give faster rates by an S_N2-Si mechanism, the classical S_N2 pattern might be observed,[5] *i.e.*, $k(rac.)/k(ex.) = 2.0$. Indeed, it seems probable that an S_N2-Si mechanism and perhaps also an ionization (S_N1-Si) mechanism were operative in some chloride–chloride exchange studies reported for Ph_3SiCl and Et_4NCl^{36} in dioxane–nitromethane solvents.[6]

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

(3) L. H. Sommer, G. A. Parker, and C. L. Frye, *J. Am. Chem. Soc.*, **86**, 3280 (1964); see also ref. 2.

(4) S. Winstein, S. Smith, and D. Darwish, *J. Am. Chem. Soc.*, **81**, 5511 (1959); S. Winstein, E. C. Friedrich, and S. Smith, *ibid.*, **86**, 305 (1964).

(5) Unfortunately, the use of polar solvents brings about solvent-induced racemization of R_3Si^*Cl (to be reported later) and larger concentrations of free chloride ion give rates too fast to measure by conventional polarimetric techniques.

(6) A. D. Allen and G. Modena, *J. Chem. Soc.*, 3671 (1957).

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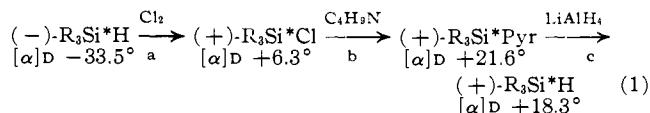
## Stereochemistry of Asymmetric Silicon. The Silicon–Nitrogen Bond

Sir:

Despite considerable interest in the chemistry of organosilicon amines and their derivatives[1] there 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 can be very useful from a fundamental standpoint, and we report below the first examples of such studies made with optically active compounds containing asymmetric silicon.
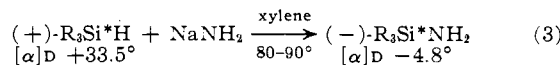
(+)-α-Naphthylphenylmethyl-(1-pyrrolidinyl)-silane (R_3Si^*Pyr) (*Anal.* Calcd.: C, 78.95; H, 7.89; N, 4.38. Found: C, 78.90; H, 7.72; N, 4.70) and (+)-N-isobutyl-α-naphthylphenylmethylsilylamine (R_3Si^*NHBu) (*Anal.* Calcd.: C, 78.44; H, 8.47; N, 4.36; Si, 8.74. Found: C, 78.67; H, 8.07; N, 4.44; Si, 8.84) were synthesized by addition of the amine to the chlorosilane[2] (+)-R_3Si^*Cl, in pentane solvent. Reduction of R_3Si^*Pyr with $LiAlH_4$ comprises the final step in the Walden cycle

$$(-)\text{-}R_3Si^*H \xrightarrow{Cl_2} (+)\text{-}R_3Si^*Cl \xrightarrow{C_4H_9N} (+)\text{-}R_3Si^*Pyr \xrightarrow{LiAlH_4}$$
$$[\alpha]_D -33.5°\ a \quad [\alpha]_D +6.3°\ b \quad [\alpha]_D +21.6°\ c$$
$$(+)\text{-}R_3Si^*H \quad (1)$$
$$[\alpha]_D +18.3°$$

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 alkoxy silanes,[2,3] the reasonable choice is inversion for 1b and retention for 1c. Furthermore, stereospecific reactions of R_3Si^*Cl with negatively charged strong nucleophiles proceed with inversion of configuration,[2–4] and thus reaction 2 is consistent with inversion for 1b.

$$(+)R_3Si^*Cl + \boxed{}NLi \rightarrow (+)R_3Si^*Pyr \quad (2)$$
$$[\alpha]_D +6.3° \qquad\qquad\qquad [\alpha]_D +15.2°$$
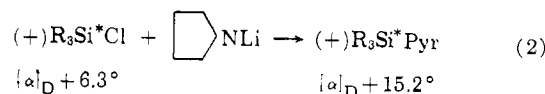
(−)-α-Naphthylphenylmethylsilylamine ($R_3Si^*NH_2$) (*Anal.* Calcd.: C, 77.52; H, 6.51; N, 5.32. Found: C, 77.67; H, 6.75; N, 5.29) was prepared by the reaction of powdered $NaNH_2$ with (+)-R_3Si^*H in xylene.

$$(+)\text{-}R_3Si^*H + NaNH_2 \xrightarrow[80\text{-}90°]{xylene} (-)\text{-}R_3Si^*NH_2 \quad (3)$$
$$[\alpha]_D +33.5° \qquad\qquad\qquad [\alpha]_D -4.8°$$

When R_3Si^*NHLi, prepared from *n*-butyllithium and (−)-$R_3Si^*NH_2$, was treated with (+)-R_3Si^*Cl, there was obtained (−)-1,3-di-α-naphthyl-1,3-diphenyl-1,3-dimethyldisilazane ($R_3Si^*NHSi^*R_3$) (*Anal.* Calcd.: C, 80.11; H, 6.13; N, 2.75. Found: C, 80.17; H, 6.24; N, 2.61). Use of (±)-$R_3Si^*NH_2$ gave disilazane[5]

(1) R. Fessenden and J. R. Fessenden, *Chem. Rev.*, **61**, 361 (1961); S. W. Jarvie and D. Lewis, *J. Chem. Soc.*, 4758 (1963); K. A. Andrianov, V. V. Astakhin, and B. P. Nikiforov, *Zh. Obshch. Khim.*, **34**, 914 (1964); W. Fink. *Ber.*, **97**, 1433 (1964); W. L. Lehn, *J. Am. Chem. Soc.*, **86**, 305 (1964); L. Tansjo, *Acta Chem. Scand.*, **18**, 456 (1964); U. Wannagat, P. Geymayer, and G. Schreiner, *Angew. Chem.*, **76**, 99 (1964).

(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, K. W. Michael, and W. D. Korte, *ibid.*, **85**, 3712 (1963); L. H. Sommer, P. G. Rodewald, and G. A. Parker, *Tetrahedron Letters*, **18**, 815 (1962).

(5) Work with the disilazane was carried out using material from this reaction. Since this is a 1:1 mixture of *meso-* and (−)-disilazane, the rotation of pure (−) isomer is −8.2°.

$$(-)\text{-}R_3Si^*NH_2 \xrightarrow[\ [\alpha]D\ -4.8°\ ]{n\text{-BuLi}} R_3Si^*NHLi \xrightarrow{(+)\text{-}R_3Si^*Cl}$$
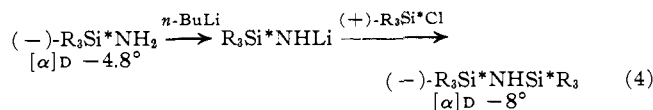
$$(-)\text{-}R_3Si^*NHSi^*R_3 \quad (4)$$
$$[\alpha]D\ -8°$$

having half the specific rotation obtained for the product in reaction 4. Assignment of an invertive

$$(\pm)\text{-}R_3Si^*NH_2 \xrightarrow[\ [\alpha]D\ 0°\ ]{n\text{-BuLi}} R_3Si^*NHLi \xrightarrow{(+)\text{-}R_3Si^*Cl}$$
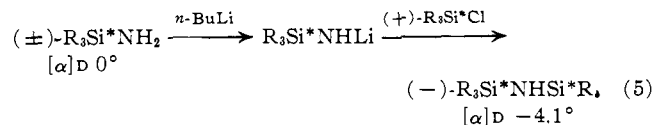
$$(-)\text{-}R_3Si^*NHSi^*R_4 \quad (5)$$
$$[\alpha]D\ -4.1°$$

path for the reactions of R_3Si^*Cl in (4) and (5) compels the conclusion that R_3Si^*Cl, $R_3Si^*NH_2$, and R_3Si^*-$NHSi^*R_3$ of the same sign of rotation also have the same configuration. Thus, reaction 3 must proceed with retention of configuration. It is interesting to note that reaction of R_3Si^*H and KOH_s to give R_3-Si^*OK also proceeds with retention.[6]

The above correlations of configuration together with specific rotations are summarized in Table I. The preceding configurational relationships receive
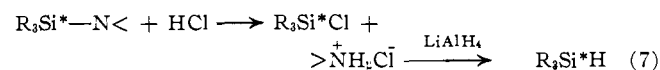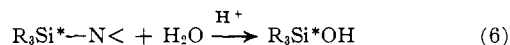
TABLE I

SILYLAMINES HAVING THE $(+)$-R_3Si^*H CONFIGURATION[a]

Compd.	$[\alpha]D$	Concn.[b]
$(+)$-R_3Si^*Pyr	$+21.6°$	1.3
$(+)$-R_3Si^*NHBu	$+5.1°$	3.6
$(-)$-$R_3Si^*NH_2$[c]	$-4.8°$	1.2
$(-)$-$R_3Si^*NHSiR_3$	$-8.2°$	4.4

[a] The absolute configuration of $(+)$-R_3Si^*H has been determined (ref. 2). [b] All rotations were taken in pentane. [c] M.p. 91.9–94.3° (uncor.).

additional support from the largely parallel stereochemistry exhibited in the reactions of all four Si–N compounds.

Stereochemical studies of the above compounds were carried out with dilute aqueous acid (eq. 6) and anhydrous HCl (eq. 7). Hydrolysis was achieved by dis-

$$R_3Si^*\!-\!N< + H_2O \xrightarrow{H^+} R_3Si^*OH \quad (6)$$

$$R_3Si^*\!-\!N< + HCl \longrightarrow R_3Si^*Cl +$$
$$>\!\overset{+}{N}H_2\overset{-}{Cl} \xrightarrow{LiAlH_4} R_3Si^*H \quad (7)$$

solving the appropriate Si–N compound in ethyl ether, and shaking with ~0.25 N hydrochloric acid for 0.5 to 2 min.[7] After washing and drying, the silanol[2] was isolated. Reaction with HCl was accomplished by allowing the HCl to bubble into a solution of the silylamine in pentane. Reaction seemed to occur as rapidly as HCl was added. The product was usually worked up by reducing the chlorosilane to R_3Si^*H with $LiAlH_4$ (cf. ref. 2); however, in several reactions the chlorosilane was isolated to check the products and rotation. Stereochemical results are given in Table II and are based on present and previous[2] correlations of configuration.

All new compounds and products of reactions had the anticipated infrared spectra.[8] In addition, the proton magnetic resonance spectrum of $R_3Si^*NHSi^*R_3$ agreed with the structure proposed.

Full discussion of mechanistic implications of the above stereochemical results is deferred to a later full

(6) L. H. Sommer, et al., J. Am. Chem. Soc., **83**, 2210 (1961).
(7) The disilazane did not hydrolyze under these conditions.
(8) A. L. Smith, Spectrochim. Acta, **16**, 87 (1960); R. Fessenden, J. Org. Chem., **25**, 2191 (1960).

TABLE II

REACTION OF SILYLAMINES WITH HCl AND H_2O

Reactant	Reagent	Product	Stereospecificity[a]
$(+)$-R_3Si^*Pyr	H_2O	$(-)$-R_3Si^*OH	76% inversion
$(+)$-R_3Si^*NHBu	H_2O	$(-)$-R_3Si^*OH	95% inversion
$(+)$-$R_3Si^*NH_2$	H_2O	$(+)$-R_3Si^*OH	96% inversion
$(+)$-R_3Si^*Pyr	HCl	$(-)$-R_3Si^*H	52% retention[b]
$(+)$-R_3Si^*NHBu	HCl	$(+)$-R_3Si^*H	80% inversion[b]
$(+)$-$R_3Si^*NH_2$	HCl	$(-)$-R_3Si^*H	91% inversion[b]
$(+)$-$R_3Si^*NHSiR_3$	HCl	$(-)$-R_3Si^*H	96% inversion[b]

[a] A stereospecificity of, say, 90%, means that the product was 80% optically pure (20% racemic), if optically pure reactant was used. [b] Stereospecificity for the reaction of HCl with the Si–N compound, assuming the $LiAlH_4$ reaction to be 100% inversion.[2]

article, but it may be noted here that predominant inversion of configuration for acid-catalyzed hydrolysis of Si–N probably reflects predominant operation of an S_N2–Si mechanism[9,10] involving displacement of a good leaving group formed by partial or complete protonation of the nitrogen-containing functional group. Although the reactions with hydrogen chloride in a nonpolar solvent provide circumstances which would appear to be favorable for operation of a quasi-cyclic four-center S_Ni–Si mechanism,[3,9,10] the finding of slight retention in one case and predominant inversion in the other three shows again that S_N2–Si is an exceedingly common mechanism path for silicon centers.

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

(9) L. H. Sommer, G. A. Parker, and C. L. Frye, J. Am. Chem. Soc., **86**, 3280 (1964).
(10) L. H. Sommer, "Stereochemistry, Mechanism and Silicon," McGraw-Hill Book Co., Inc., New York, N. Y., in press.

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Chemiluminescent and Thermochemiluminescent Lophine Hydroperoxide

Sir:

The lophyl radical (2,4,5-triphenylimidazyl radical),[1] generated by solution of its piezochromic dimer[1b] and a 3% hydrogen peroxide solution, have been found to give rise to a 59% yield[2] of lophyl hydroperoxide, Ia, m.p. 110° with effervescence, then solidification and subsequent melting at 225–265° (Anal. Found: C, 77.0; H, 5.0; N, 8.1). Compound Ia can also be prepared in 68% yield by modifying the procedure of Dufraisse,[3] i.e., irradiating a chloroform solution of lophine in the presence of methylene blue and oxygen at 18°. The hydroperoxide is presumably the material which Dufraisse obtained in low yield in the absence of a photosensitizer and to which he assigned the endoperoxide structure II.[4]

Structure Ia is now assigned on the basis of spectral studies, analogous peroxide syntheses, and chemical

(1) (a) T. Hayashi and K. Maeda, Bull. Chem. Soc. Japan, **33**, 565 (1960); (b) D. M. White and J. Sonnenberg, Abstracts, 144th National Meeting of the American Chemical Society, Los Angeles, Calif., April, 1963, p. 55M.
(2) Based on the stoichiometry: $(C_{21}H_{15}N_2)_2 + H_2O_2 \rightarrow Ia + C_{21}H_{16}N_2$ (lophine).
(3) C. Dufraisse, A. Étienne, and J. Martel, Compt. rend., **244**, 970 (1957).
(4) The ultraviolet absorption of Ia at 283 mμ (ϵ 1.58 × 10^4) is not consistent with structure II since model compounds such as 2,4,5-triphenylimidazoline and N-benzylbenzaldimine only absorb strongly at 250 mμ and lower.