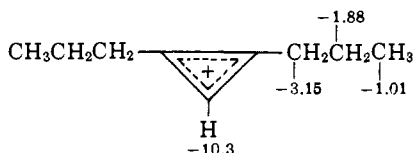H
|0.266
/C\
CH₂   CH₂
0.367   0.367

This treatment had taken into account the contribution of 1,3-π-interactions between the terminal centers. In contrast, the traditional resonance argument or the simple Hückel treatment of the two odd alternant terminal allyl cations would put the excess positive charge predominantly on the terminal carbon atoms.

The large experimentally observed deshielding effect of the >CH proton in the allyl cation and similarly that of the methyl protons in the 2-methylallyl cation indicate the strong contribution of 1,3-π-interactions.[6]

H   CH₃
| |
/C\   /C\
CH₂-+--CH₂   CH₂-+--CH₂

This suggestion is supported by observations of Breslow and co-workers[7] on the proton magnetic resonance shifts of the dipropylcyclopropenyl cation

                              -1.88
                              |
CH₃CH₂CH₂——⟨·+·⟩——CH₂CH₂CH₃
                          | |
                       -3.15   -1.01
                        H
                       -10.3

Katz and Gold[8] recently put forward strong evidence for 1,3-π-interactions in cyclobutenyl cations and demonstrated from the observed proton magnetic resonance shifts of these ions that the charge densities are about halfway between those in simple alkenyl cations and the fully symmetrical cyclopropenyl cations, where the charge density must be one-third of a unit charge on each ring carbon atom.

We are extending our investigations. to precursors which potentially should yield the cyclopropyl and cyclopropenyl cations in our carbonium ion formation method, and hope to report these data and their comparison with those of the allyl cations in a subsequent publication.

(7) R. Breslow, H. Hover, and H. W. Chang, J. Am. Chem. Soc., **84**, 3168 (1962); R. Breslow and H. Hover, ibid., **82**, 2644 (1960).

(8) T. J. Katz and E. H. Gold, ibid., **86**, 1600 (1964).

THE DOW CHEMICAL COMPANY   GEORGE A. OLAH
EASTERN RESEARCH LABORATORY   MELVIN B. COMISAROW
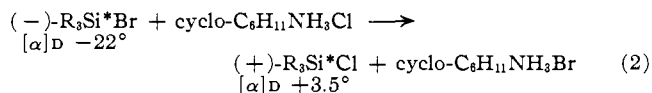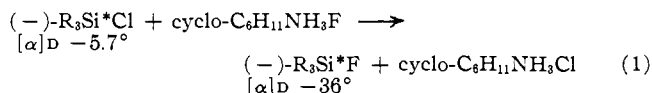FRAMINGHAM, MASSACHUSETTS   01702

Halide–Halide Exchange at Asymmetric Silicon

Sir:

We wish to report the first stereochemical studies of halide–halide exchange reactions at asymmetric silicon in optically active α-naphthylphenylmethylsilanes,[1] R_3Si^*X.
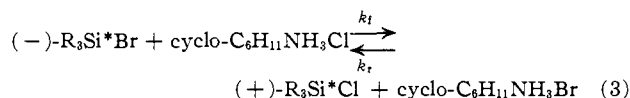
In the following reactions (1 and 2), which take place with predominant inversion of configuration, based on previous assignments of relative configuration,[1] the entering nucleophile is a stronger base and (for silicon) a better nucleophile than the leaving group, X. Both reactions were carried out in pure, dry chloroform.

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

(−)-R_3Si^*Cl + cyclo-$C_6H_{11}NH_3F$ ⟶
[α]D −5.7°
            (−)-R_3Si^*F + cyclo-$C_6H_{11}NH_3Cl$ (1)
            [α]D −36°

(−)-R_3Si^*Br + cyclo-$C_6H_{11}NH_3Cl$ ⟶
[α]D −22°
            (+)-R_3Si^*Cl + cyclo-$C_6H_{11}NH_3Br$ (2)
            [α]D +3.5°

Reaction 1 proceeds with at least 90% *inversion* of configuration. Reaction 2 proceeds with predominant *inversion* of configuration and a minimum stereospecificity of 80%.

For reaction 2 which was homogeneous (no solid salt present), infrared spectra showed that equimolar concentrations of R_3Si^*Br and cyclo-$C_6H_{11}NH_3Cl$ give a product which contains a maximum of 2% of R_3Si^*Br. Thus, for the equilibrium formulation

$$(-)\text{-}R_3Si^*Br + \text{cyclo-}C_6H_{11}NH_3Cl \underset{k_r}{\overset{k_f}{\rightleftharpoons}}$$
$$(+)\text{-}R_3Si^*Cl + \text{cyclo-}C_6H_{11}NH_3Br \quad (3)$$

it is possible to assign a minimum value for the equilibrium constant, which also provides the ratio $k_f/k_r \geq 2.4 \times 10^3$.

A linear plot of $1/C$ vs. time for reaction 2 during the first half-life was obtained from polarimetric rate data and gave the second-order rate constant for reaction 2 as $k_2 = 6.7$ l. min.$^{-1}$ mole^{-1}. In view of the above equilibrium formulation for k_f/k_r, this means that the second-order rate constant for the backward reaction in (3), k_r, has a maximum value of $k_2 \leq 2.8 \times 10^{-3}$ l. min.$^{-1}$ mole^{-1}.

In Table I are given the first- and second-order rate constants for the salt-induced racemization of R_3Si^*Cl by cyclohexylammonium chloride, bromide, and iodide. In each case the product was racemic *chlorosilane*, the racemizations were approximately first-order in added salt over the range from 0.04 to 0.09 M salt, and the rate law is rate = $k_2[R_3Si^*Cl][cyclo-C_6H_{11}NH_3X]$.

Two aspects of the data in Table I are noteworthy. First, k_2 (inversion) for racemization of R_3Si^*Cl by RNH_3Br exceeds the rate of displacement of Cl by Br by a factor of at least 15: $k_2(\text{inversion})/k_2(\text{displacement}) = (4.2 \times 10^{-2}/\leq 2.8 \times 10^{-3}) \geq 15$. Furthermore, the insensitivity of rate of racemization to variation in the halide ion component of the salt (less than a factor of four is involved) is also quite suggestive. Taken together the data suggest operation of mechanism[2] S_N1–Si for racemizations (1), (2), and (3) in Table I, which involves salt-promoted formation of siliconium ion pairs in the rate-controlling step.

TABLE I

RATE CONSTANT DATA FOR THE RACEMIZATION OF R_3Si^*Cl
(0.0872 M) AT 25.0° IN CHLOROFORM WITH
CYCLOHEXYLAMMONIUM SALTS (0.0872 M)

Reaction	Halide	k_1(rac.), min.$^{-1}$	k_2(rac.), l. min.$^{-1}$ mole^{-1}	k_2(inv.), l. min.$^{-1}$ mole^{-1}
1	Cl	1.2×10^{-2}	1.4×10^{-1}	6.9×10^{-2}
2	Br^c	7.2×10^{-3}	8.4×10^{-2}	4.2×10^{-2}
3	I^a	2.6×10^{-2}	3.0×10^{-1}	1.4×10^{-1}

^{a} The product is racemic chlorosilane.

(2) For a discussion of the meaning of symbol S_N1–Si and other examples of siliconium ion pair mechanisms, see L. H. Sommer, "Stereochemistry, Mechanism and Silicon," McGraw-Hill Book Co., New York, N. Y., in press.

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

$$R_3Si^*Cl + cyclo\text{-}C_6H_{11}NH_3Cl^{36} \rightleftharpoons$$
$$R_3Si^*Cl^{36} + cyclo\text{-}C_6H_{11}NH_3Cl$$
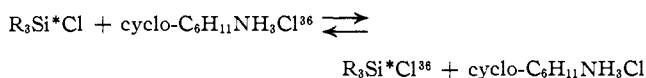
the rate of racemization and the rate of chloride–radiochloride exchange are the same within experimental error. Polarimetric and exchange rate data were obtained on the same reaction mixture and the agreement in duplicate runs was good. For run 1 $k(\text{rac.})/k(\text{ex.}) = 1.1 \pm 0.1$. For run 2, $k(\text{rac.})/k(\text{ex.}) = 1.0 \pm 0.1$. 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 SN2-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 $k(\text{rac.})/k(\text{ex.})$. 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 SN2-Si mechanism, the classical SN2 pattern might be observed,[5] *i.e.*, $k(\text{rac.})/k(\text{ex.}) = 2.0$. Indeed, it seems probable that an SN2-Si mechanism and perhaps also an ionization (SN1-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).

WHITMORE LABORATORY   L. H. SOMMER
THE PENNSYLVANIA STATE UNIVERSITY   F. O. STARK
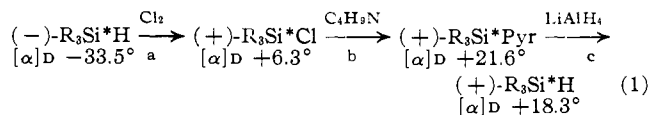UNIVERSITY PARK, PENNSYLVANIA   K. W. MICHAEL

RECEIVED OCTOBER 5, 1964

## 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.
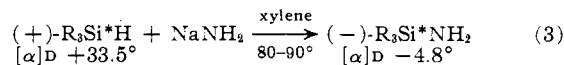
(+)-α-Naphthylphenylmethyl-(1-pyrrolidinyl)-silane (R_3Si^*Pyr) (*Anal.* Calcd.: C, 78.95; H, 7.89; N, 4.38. Found: C, 78.90; H, 7.72; N, 4.70) and (+)-N-isobutyl-α-naphthylphenylmethylsilylamine (R_3Si^*NHBu) (*Anal.* Calcd.: C, 78.44; H, 8.47; N, 4.36; Si, 8.74. Found: C, 78.67; H, 8.07; N, 4.44; Si, 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

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

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.

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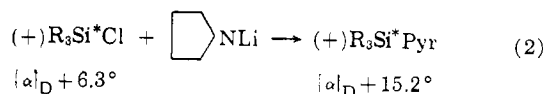
(−)-α-Naphthylphenylmethylsilylamine ($R_3Si^*NH_2$) (*Anal.* Calcd.: C, 77.52; H, 6.51; N, 5.32. Found: C, 77.67; H, 6.75; N, 5.29) was prepared by the reaction of powdered $NaNH_2$ with (+)-R_3Si^*H in xylene.

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

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°.