Similar trends are not observed in other petroleum families. In each case a three-ring structure is preferred, and this recalls the presence of the tetrahydro- or hexahydrocarbazole nucleus in certain alkaloids (*e.g.*, aspidospermine (**33**). Again it seems likely that a preference for a given structure in petroleum is rooted in a similar preference for that structure in plants.

A detailed examination of the structural relationships between individual N,O compounds and their precursors in nature will be presented elsewhere.[24]

(24) G. C. Speers and E. V. Whitehead, "Crude Petroleum. Organic Geochemistry: Methods and Results," Springer-Verlag, New York, N. Y., in press.

Silyl–Proton Exchange Reactions

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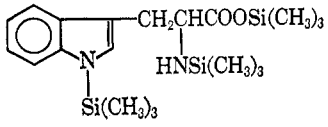
Organosilicon compounds are enjoying a rapidly growing appreciation among even those organic chemists and biochemists who are not otherwise particularly concerned with organometallic chemistry. This esteem arises from the fact that a large variety of organic and biologically important substances can readily—and reversibly—be converted into organosilyl derivatives with profoundly changed properties. The "silylation" of organic compounds—the replacement of protons from oxygen, nitrogen, and sulfur, to name the most common cases, by triorganosilyl (most often trimethylsilyl) groups—has the general effect of reducing hydrogen bonding between molecules and thus increasing volatility and solubility.

To illustrate the effect of silylation, the amino acid tryptophan is a high melting, moderately water soluble solid which is insoluble in most organic solvents and has a negligible vapor pressure; it therefore cannot be analyzed by gas–liquid partition chromatography. Its



tris(trimethylsilyl) derivative is a liquid which is miscible in all proportions with organic solvents such as benzene; it has a boiling point of 140° (0.2 mm) and is sufficiently thermally stable to allow analysis by glpc. On contact with water, the silyl groups are removed hydrolytically and tryptophan is regenerated.[1]

Silylation has become an important part of gas–liquid partition and thin-layer chromatographic analyses of materials such as carbohydrates, amino acids, Krebs cycle acids, and steroids. A recent review of this field revealed over 800 references to investigations of silylation and its application for analytical purposes.[2]

In synthetic applications, silylation of a molecule may increase its reactivity toward attacking reagents, either at the site of the newly introduced silyl substituent or in adjacent positions of the molecule, or the silyl group may serve as protection for sensitive functional groups during a synthesis. This actively growing field encompasses a wide spectrum of organic compounds and reactions.[3]

Methods of Silylation

Two general methods are available for silylations: reactions with chlorosilanes and a tertiary amine as acid acceptor, and exchange reactions with silicon–nitrogen compounds functioning as silyl donors. The classical chlorosilane method employs a very powerful reagent mixture; the removal of hydrochloric acid in the form of its amine salt provides sufficient driving force to displace practically any reactive hydrogen on a heteroatom by silyl. Separation problems stemming

$$RYH + (CH_3)_3SiCl + R'_3N \longrightarrow RYSi(CH_3)_3 + R'_3N\cdot HCl \quad (1)$$

from the formation of amine salts and the corrosive nature of the reagents are the drawbacks of this method.

Silylamines have long been used as alternative silylating agents. This silylation method is based on the relatively slow silyl–proton exchange between the silyl derivative of a low-boiling amine or ammonia[4] and mobile protons of the substrate. The reaction equilibria are shifted toward the product side by distillation of the amine. Although the exchange rates are enhanced

$$RYH + R'\underset{\displaystyle H}{\underset{|}{N}}Si(CH_3)_3 \rightleftharpoons RYSi(CH_3)_3 + R'NH_2 \quad (2)$$

by the addition of catalytic amounts of ammonium salts or chlorosilanes,[5] silylations by this method require typically several hours at reflux temperature.

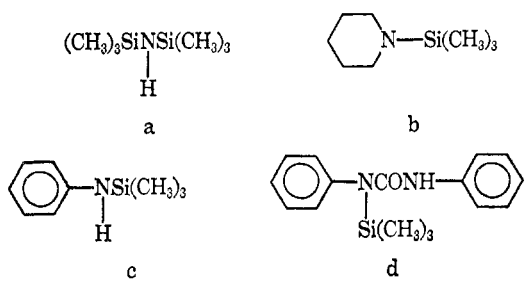
The most recent addition to the list of silylating agents is the class of silylamides[1,6,7] which combine the

(1) J. F. Klebe, H. Finkbeiner, and D. M. White, *J. Amer. Chem. Soc.*, **88**, 3390 (1966).
(2) A. E. Pierce, "Silylation of Organic Compounds," Pierce Chemical Co., Rockford, Ill., 1968.
(3) For reviews, see L. Birkofer and A. Ritter, *Angew. Chem.*, **77**, 414 (1965); K. Rühlmann, *Z. Chem.*, **5**, 130 (1965); J. F. Klebe, *Advan. Org. Chem.*, in press.
(4) O. Mjörne, *Kem. Tidskr.*, **62**, 120 (1950).
(5) R. Fessenden and D. F. Crowe, *J. Org. Chem.*, **26**, 4638 (1961).

advantage of much faster exchange rates with equilibrium positions which for many substrates are shifted so far to the product side that the removal of one of the reaction products from the equilibrium during the reaction is unnecessary.

$$RYH + R'CONHSi(CH_3)_3 \rightleftharpoons RYSi(CH_3)_3 + R'CONH_2 \quad (3)$$

The difference in performance between a number of silylating agents of the silylamine type and a silyl donor of the general class of silylamides is demonstrated by the following experiment.[8] Equimolar mixtures of *N,N'*-dimethylurea as the silyl acceptor and (a) hexamethyldisilazane, (b) *N*-trimethylsilylpiperidine, (c) *N*-trimethylsilylaniline, and (d) *N*-trimethylsilyl-*N,N'*-diphenylurea in acetonitrile were kept in closed containers, and the progress of the reaction was followed by glpc. The extent of *N*-trimethylsilyl-*N,N'*-dimethyl-



urea formation after 75 hr at room temperature was: (a) 0%, (b) 10%, (c) 3%. Mixture d, containing trimethylsilyldiphenylurea as the silyl donor, showed complete conversion to *N*-trimethylsilyldimethylurea after 1 min at room temperature.

The disparity of the results is caused by a combination of differences in rates and equilibrium constants. Dimethylurea is difficult to silylate, and the use of a silylamine for this purpose would require removal of amine by continuous distillation; it is obvious that trimethylsilyldiphenylurea is effective as a silylating agent without disturbance of the equilibrium.

Activation of the Si–N Bond by Carbonyl

Some observations during a study of silylureas several years ago first directed our attention to the unusually high mobilities of silyl groups in compounds containing the ≡SiN(CO–)– moiety.[9] Examination of the proton magnetic resonance spectra of a mixture of two urea derivatives, distinguished by their aromatic substituents and an *N*-trimethylsilyl group in one of the compounds, revealed that, in addition to the two ureas placed in the chloroform solution, there were two other compounds present, obviously formed by a silyl–proton exchange between the two original urea derivatives. The same mixture of four compounds could be obtained from either pair of reactants, and, more surprisingly,

$$C_6H_5NHCON(CH_3)_2 + p\text{-Tol-}\underset{\displaystyle Si(CH_3)_3}{\underset{|}{N}}CON(CH_3)_2 \rightleftharpoons C_6H_5\underset{\displaystyle Si(CH_3)_3}{\underset{|}{N}}CON(CH_3)_2 + p\text{-Tol-NHCON}(CH_3)_2 \quad (4)$$

equilibrium between the four compounds was reached within less than 1 min at room temperature.

The carbonyl group adjacent to nitrogen is primarily responsible for the high mobility of the silyl groups, as the subsequent investigation of many similar compounds has shown. However, the third substituent on nitrogen also has a significant influence on the reactivity of the Si–N bond; interaction of *N*-methyl-*N'*-phenylurea with its bis(trimethylsilyl) derivative in dimethyl sulfoxide solution led to the very rapid formation of two monosilylureas with the silyl groups in the N and N' positions, respectively. One of these subsequently rearranged into the other at a more than 100-fold slower rate (eq 5). The result can be explained by the rapid

$$\begin{array}{l} C_6H_5NCONC_6H_5 \\ \quad | \quad\quad | \\ (CH_3)_3Si \quad Si(CH_3)_3 \\ + \\ C_6H_5NCONCH_3 \\ \quad | \quad\quad | \\ \quad H \quad\quad H \end{array} \xrightarrow{\text{fast}} \begin{array}{l} C_6H_5NCONC_6H_5 \\ \quad | \quad\quad | \\ \quad H \quad Si(CH_3)_3 \\ + \quad\quad \downarrow \text{slow} \\ C_6H_5NCONCH_3 \\ \quad | \quad\quad | \\ (CH_3)_3Si \quad H \end{array} \quad (5)$$

exchange between substituents on the phenyl-bound nitrogens, followed by the slower rearrangement of the thermodynamically less stable *N*-silyl- into the *N'*-silylurea.

That it is indeed the silyl group in proximity of the phenyl rather than the one flanked by the methyl substituent that is being exchanged rapidly was shown by a similar experiment in which a stoichiometric amount of methanol was used as the silyl acceptor (eq 6).[10] Again

$$\begin{array}{l} C_6H_5NCONCH_3 \\ \quad | \quad\quad | \\ (CH_3)_3Si \quad Si(CH_3)_3 \end{array} \xrightarrow[-CH_3OSi(CH_3)_3]{CH_3OH}$$

$$\begin{array}{l} C_6H_5NCONCH_3 \\ \quad | \quad\quad | \\ \quad H \quad Si(CH_3)_3 \end{array} \xrightarrow{\text{slow}} \begin{array}{l} C_6H_5NCONCH_3 \\ \quad | \quad\quad | \\ (CH_3)_3Si \quad H \end{array} \quad (6)$$

the rearrangement proceeded at about $^1/_{1000}$th of the rate of the methanolysis. Rate measurements indicated that the rearrangement is an intermolecular process.

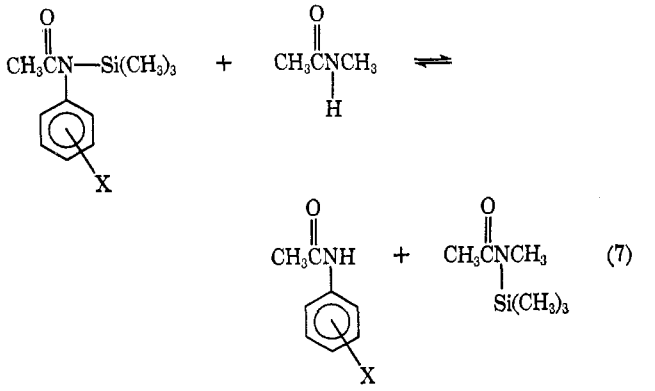
Substituent Effects

Comparisons of silylureas with silylamides showed both classes of compounds to possess comparable properties as silyl donors. In order to further explore the effect of substituents on the reactivity of the Si–N bond, we undertook to establish a scale of thermodynamic silylating power within a group of silyl-substituted anilides.

The equilibrium positions of a number of ring-sub-

(6) L. Birkofer, A. Ritter, and R. Bentz, *Chem. Ber.*, **97**, 2196 (1964).
(7) D. L. Stalling, C. W. Gehrke, and R. W. Zumwalt, *Biochem. Biophys. Res. Commun.*, **31**, 616 (1968).
(8) J. F. Klebe, *J. Amer. Chem. Soc.*, **86**, 3399 (1964).
(9) J. F. Klebe, J. B. Bush, Jr., and J. E. Lyons, *ibid.*, **86**, 4400 (1964).
(10) J. F. Klebe and J. B. Bush, Jr., First International Symposium on Organosilicon Chemistry, Prague, 1965; Conference Abstracts, p 328.

stituted silylacetanilides and one disilylamide in mixture with *N*-methylacetamide could be determined from the intensities of the well-resolved proton magnetic resonance signals of the four components in each mixture (eq 7).[10] Similarly, the rates of silyl–proton ex-

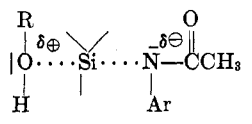


change of these compounds with ethanol or *tert*-butyl alcohol were determined, following the concentrations of the reaction partners with time by measurement of the areas of the respective acetyl signals (eq 8). The

$$\underset{\text{Si(CH}_3)_3}{\text{RNCOCH}_3} + \text{R'OH} \longrightarrow \underset{\text{H}}{\text{RNCOCH}_3} + \text{R'OSi(CH}_3)_3 \quad (8)$$

rate laws for the reactions with the alcohols were found to be first order in alcohol and in silylamide and rate constants were calculated employing a standard kinetic treatment. No indication of reversibility of the alcoholysis was detected. Table I contains the equilibrium constants for reaction 7 and the rate constants for reaction 8.

It is evident from the equilibrium constants in Table I that electron-withdrawing substituents on the aromatic ring increase the thermodynamic silylating power of silylanilides; the change in equilibrium position is paralleled by a considerable enhancement in the reaction rates with increasing electron withdrawal of the substituent. This is consistent with a substantial negative charge being placed on the amide nitrogen in the transition state of the alcoholysis. However, the surprisingly high rate of alcoholysis of tri-



methylsilyl-*N*-methylacetamide, which has a more basic amide nitrogen than the silylanilides, does not fit this picture, nor does it correlate with the fact that in bis(trimethylsilyl)-*N*-methyl-*N'*-phenylurea the silyl group adjacent to phenyl proves the more reactive one (reactions 5 and 6).

BSA as Silyl Donor

The large equilibrium constant of bis(trimethylsilyl)-acetamide in Table I signifies the superior silylating power of this compound which is probably caused by $(p\text{–}d)_\pi$ interaction of both silyl groups with the free electron pairs of the amide moiety, thereby destabilizing the silicon–heteroatom bond.

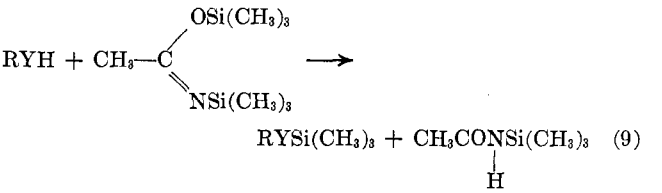
Table I

Trimethylsilyl derivative of	Equilibrium constant for reaction 7[a]	Rate constants for reaction 8[a] Alcohol	k, M sec $\times 10^5$
p-Methoxyacetanilide	0.12	Ethanol	164
p-Methylacetanilide	0.18	Ethanol	204
m-Methoxyacetanilide	0.24		
Acetanilide	0.24	Ethanol	310
		tert-Butyl alcohol	0.033
p-Chloroacetanilide	0.30		
m-Nitroacetanilide	0.37		
p-Nitroacetanilide	0.40	*tert*-Butyl alcohol	1.9
N-Methylacetamide		*tert*-Butyl alcohol	0.31
Bis(trimethylsilyl)-acetamide	51	*tert*-Butyl alcohol	0.032
		Ethanol	530

[a] In pyridine, 40.0°.

This ability to silylate even amides (which are strong silylating agents in their own right, as this discussion has shown) prompted us to test bis(trimethylsilyl)acetamide as a general silylating agent. The compound is readily prepared from acetamide and trimethylchlorosilane–triethylamine[11] (it is now commercially available), and the thermally reasonably stable, easy-to-handle liquid has been found very useful in the silylation of numerous compounds.

Table II shows a selection from various classes of silylated products prepared with bis(trimethylsilyl)-acetamide[1] and the conditions for complete conversion according to reaction 9.



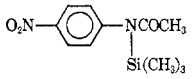
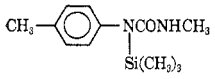
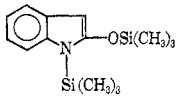
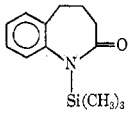
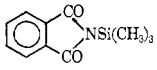
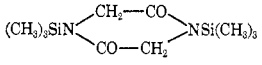
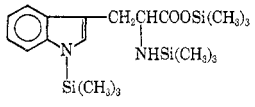
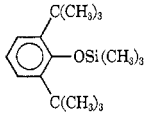
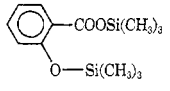
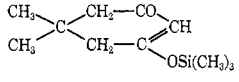
The second silyl group of the silylating agent can also be utilized for many substrates, but it is often preferable to use a full equivalent of the bissilylamide per exchangeable proton. The monosilylacetamide then formed has a boiling point of 45–47° (0.2 mm) and can easily be removed *in vacuo* whenever the vapor pressure of the silylated product is sufficiently low, leaving the product behind. The same advantages apply for silylations on a small scale for gas–liquid partition chromatography. After the desired separation or chemical operation has been performed, the silyl groups can readily be removed with water or alcohol; addition of a small amount of acid or base aids the hydrolysis of more stable silyl derivatives.

Optically Active Silicon by Asymmetric Synthesis

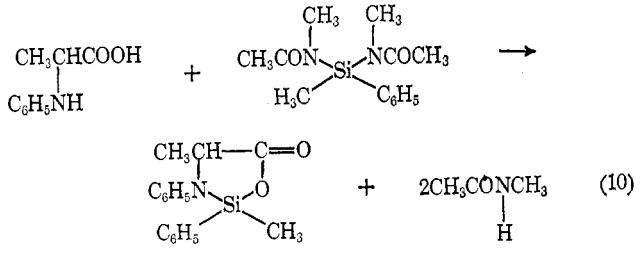
Silyl–proton exchange reactions are, of course, not restricted to organosilicon compounds with only one functional group; many cyclic and linear products have been obtained from dichloro- or diaminosilanes

(11) L. Birkofer, A. Ritter, and W. Giessler, *Angew. Chem.*, 75, 93 (1963).

Table II
Products of Silylation with Bis(trimethylsilyl)acetamide

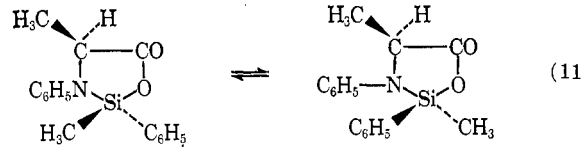
Compound	Silylation conditions
	In CH_3CN, 5 min, 80°
	In CH_3CN, 15 min, 30°
	In CH_3CN, 1 hr, 30°
	In CH_3CN, 1 hr, 80°
	In CH_3CN, 15 hr, room temperature
	In CH_3CN, 4 hr, 80°
	In CH_3CN, 2 hr, 30°
	In CH_3CN, 15 hr, 90°
	In $CHCl_3$, 10 min, 30°
	In benzene, 15 hr, 30°

with compounds containing reactive protons. An example is the formation of siloxazolidones from amino acids and bis(amidosilanes) (eq 10).[12] Starting with


(10)

(+)-*N*-phenylalanine, a mixture of the two diastereomeric siloxazolidones was formed within 15 min at room temperature. In solution, the diastereomers are in equilibrium with each other and are generally present in unequal amounts; the rearrangement of one into the other is catalyzed by bases such as amines or amides. This diastereomer interconversion is an example of a second-order asymmetric transformation.

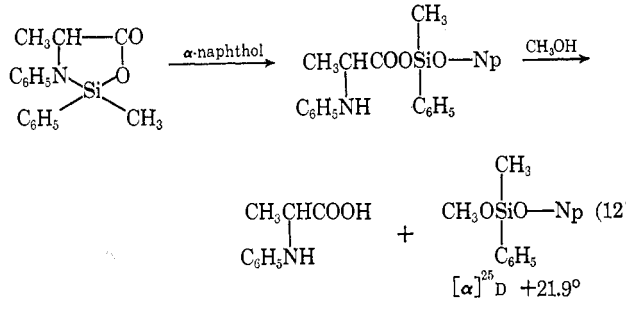
(12) J. F. Klebe and H. Finkbeiner, *J. Amer. Chem. Soc.*, **90**, 7255 (1968).


(11)

The rearrangement in the presence of *N*-methylacetamide is fast enough that upon crystallization of the predominant diastereomer the entire mixture is converted into this one compound, so that the reaction represents an asymmetric synthesis of an optically active silicon derivative. This process could be followed conveniently by proton magnetic resonance spectroscopy; Figure 1 shows the two alanine methyl doublets and the two Si-methyl singlets of the mixture and the single set of signals of the crystalline diastereomer which in the absence of a catalyst is moderately stable in solution.

The formation and relative stability of siloxazolidones depend critically upon the substituent on nitrogen. No cyclic product could be obtained from amino acids unsubstituted on nitrogen; *N*-methyl or *N*-isopropyl amino acids afforded the siloxazolidones in good yield, but no predominance of one diastereomer and no rearrangement was observed; however, the four *N*-phenyl-substituted amino acids investigated all showed the rearrangement of their cyclic derivative described above.

Both bonds to silicon in siloxazolidones are subject to cleavage by alcohols, but the Si–N bond is the more reactive one. By choice of a proper pair of hydroxylic reagents, it is possible to displace the amine group exclusively in a first step and then cleave the silyl ester bond with the second alcohol; the resulting asymmetric silane can be obtained in optically active form (eq 12). The intermediate naphthoxysilyl ester


(12)

racemizes very readily; racemization can be monitored by pmr since it involves formation of a second diastereomer, and the best conditions for maintaining optical purity can thus be determined by these simple means.

The Structure of Silylamides

The remarkable reactivity of the silicon–nitrogen bond in silylamides and related compounds may in part be simply explained by the ability of amide groups to accommodate a negative charge in the transition state of a displacement reaction, making them good leaving groups. However, not all observations, some

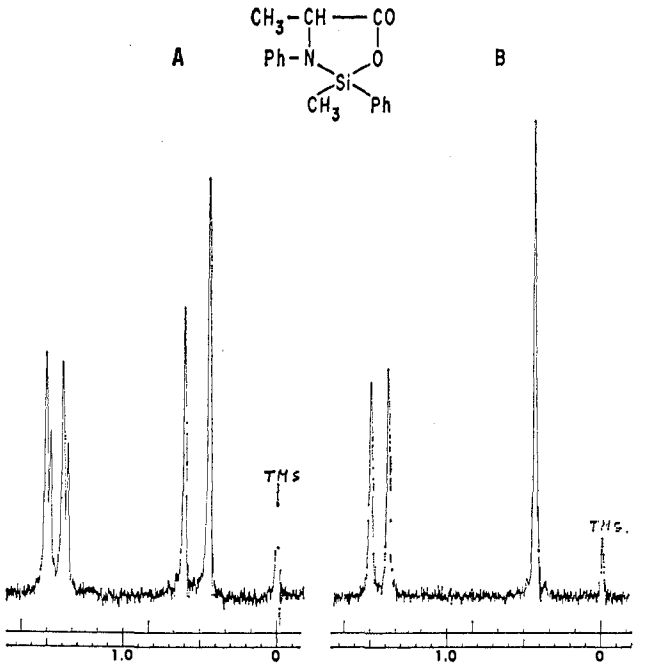
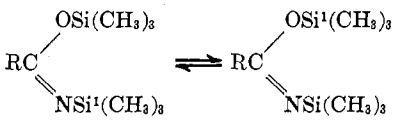


Figure 1. Pmr methyl signals of 2-(methylphenylsila)-3-phenyl-4-methyloxazolidone-5: (A) mixture of diastereomers; (B) stable diastereomer obtained by rearrangement during crystallization (15% in benzene).

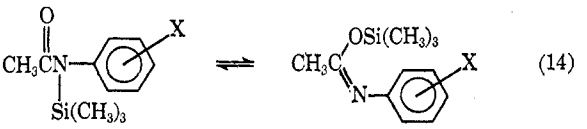
of which were described above, fit this explanation well, and a closer examination of the structure of silylamides is relevant in the hope of finding further clues to the reactivity of these compounds.

The *N*-silyl silylimidate structure of bis(trimethylsilyl)acetamide shown in eq 9 implies that the silyl group in silylamides is not necessarily bound to nitrogen. This structure was suggested on the basis of proton magnetic resonance spectra and was shown to apply to bissilylamides in general.[13] Moreover, temperature-dependent changes of these spectra indicated that the two silyl groups undergo a rapid intramolecular exchange (eq 13)


(13)

We have observed a similar phenomenon when we investigated the pmr spectra of the series of silylanilides shown in Table I. The trimethylsilyl signals of these compounds, which are sharp singlets at 40° and above, show exchange broadening when the temperature is lowered and separate into two signals which become sharp at about 0° or below. The two low-temperature signals are unequal in intensity; their ratio depends upon the substituent on the aromatic ring. We have interpreted this finding as an exchange of the trimethyl group between nitrogen and oxygen which is rapid at elevated temperatures but becomes slow on the nmr time scale at low temperatures, allowing the detection of the two species.

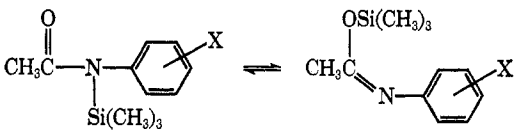
Figure 2 shows the temperature-dependent pmr


(14)

spectra of trimethylsilyl-*p*-methoxyacetanilide and of the analogous homodihydrocarbostyril derivative which exhibits the same behavior; unlike the silylanilides, this cyclic compound cannot rotate about the carbonyl–nitrogen bond, thus precluding an interpretation of this phenomenon as rotational isomerism. The dependence of the "silyl tautomer" ratio on the substituent also makes the latter interpretation unlikely. The equilibrium constants in Table III for eq 14 were

Table III

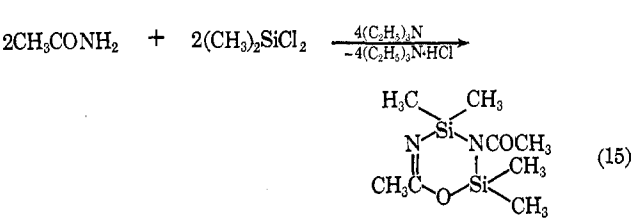
***N*-Silyl–*O*-Silyl Tautomerism—Equilibria**



X	K = (*O*-Si)/(*N*-Si) (pyridine, 0°)
p-CH_3O	0.17
p-CH_3	0.39 (0.95 in CCl_4)
m-CH_3O	0.98
H	0.82 (2.2 in CCl_4)
p-Cl	1.58 (1.29 in C_6H_5CN)
m-Cl	2.95
m-NO_2	9.5
p-NO_2	20

determined from the relative areas under the pmr signals; the data show that electron-withdrawing substituents favor strongly the *O*-silyl tautomer and *vice versa*. A plot of the logarithms of the equilibrium constants against the Hammet σ constants gives a satisfactory linear correlation with $\rho = +1.6$.

No silylureas or trimethylsilylamides were found showing this kind of silyl tautomerism, a fact which may be due to structural rigidity or could be caused by an even more rapid positional exchange, which could prevent the distinction of the tautomeric forms by pmr. However, an interesting class of cyclic silylamides can be synthesized from amides and dihalosilanes, containing *N*-silyl as well as *O*-silyl tautomeric structure elements (eq 15).[14] These disiloxadiazines are


(15)

structurally nonrigid just as the bissilylamides and the silylanilides, but in a more complex manner: their pmr spectra at temperatures below about 20° show that the acyl groups as well as the pairs of substituents on the silicon atoms are nonequivalent, as required

(13) J. Pump and E. G. Rochow, *Chem. Ber.*, **97**, 627 (1964).

(14) J. F. Klebe, *J. Amer. Chem. Soc.*, **90**, 5246 (1968).

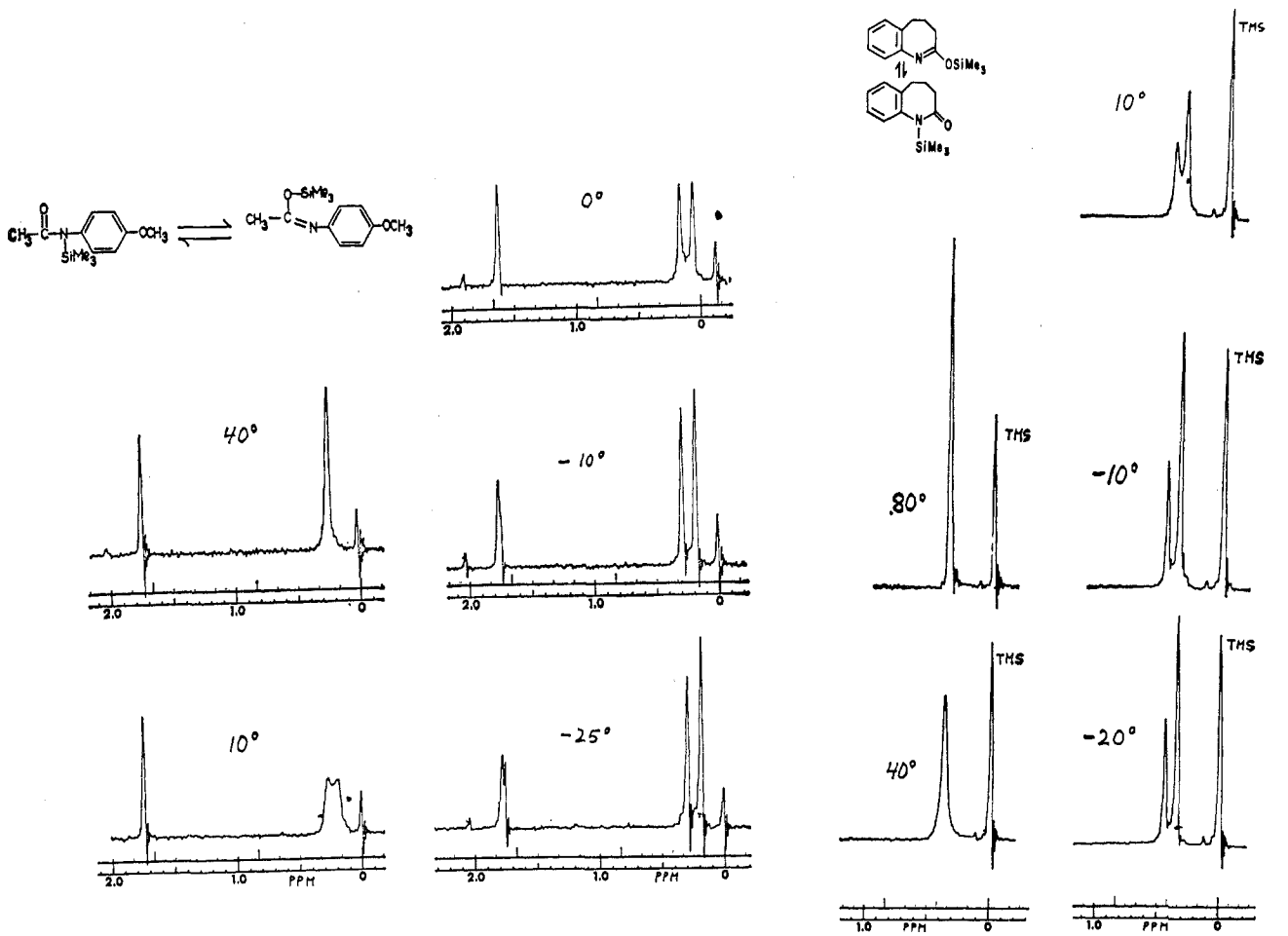
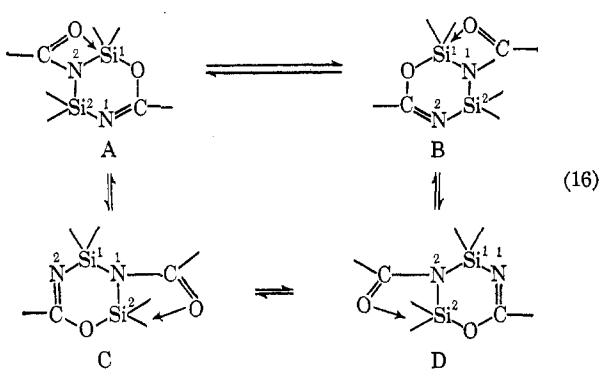


Figure 2. Pmr methyl signals of silyl tautomeric mixtures: (A, left) trimethylsilyl-*p*-methoxyacetanilide; (B, right) trimethylsilylhomodihydrocarbostyril (15% in pyridine).

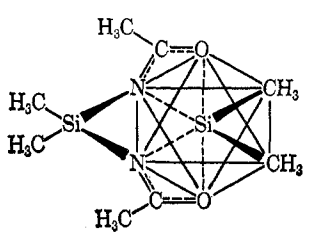
by the structural formulas. At temperatures of 20–45°, depending on the substituents on silicon and on the acyl carbon, the signals due to the acyl groups merge while the silyl protons remain nonequivalent up to a temperature some 60–80° higher, when the silyl groups also become equivalent. The original sets of signals reappear in successive steps upon lowering the temperature. The phenomenon is illustrated by Figure 3 for the methylmethoxysilyl compound in which the number of signals is doubled due to the presence of cis and trans isomers; only the methoxy signals are fully resolved.

The spectra can be interpreted by assuming that the exocyclic acyl group is drawn into the coordination sphere of one of the silicon atoms (Si^1), allowing a relatively facile bond-breaking and -forming process involving the two acyl groups. A rapid exchange A ⇌ B and C ⇌ D in eq 16 would lead to coalescence of the acyl proton signals at intermediate temperatures. Such an assumption would imply that the silicon atom involved in this exchange process has an expanded octet shell while Si^2 remains tetrahedral. Supply of more energy is required to break Si^1 out of its expanded octet configuration followed by rotation of the acyl groups and coordination with Si^2. This rearrangement depicted by A ⇌ C and B ⇌ D thus is accompanied by coalescence of the signals due to the silyl substituents at much higher temperatures.



(16)

Each phase of these rearrangments involves the bond cleavage and bond formation between silicon and two nitrogens as well as two oxygens, and it is tempting to propose a transition state with all of these atoms grouped around silicon in an octahedral configuration



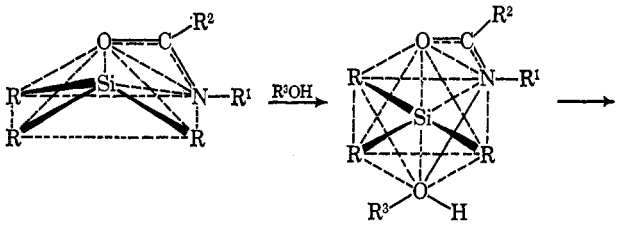
which illustrates persuasively the facile interchange between the two amide groups and the difference in the bonding situation of the two silicon atoms.

This representation can be valid only for a transition state but not a ground state, as shown by an X-ray diffraction study of a disiloxadiazine by other investigators,[15] who find that there is indeed an interaction of the exocyclic carbonyl with the silicon atom flanked by oxygen and nitrogen (Si^1 in A, eq 16), but no unusual interaction with the other nitrogen in the crystalline state.

On the Mechanism of Silyl–Proton Exchange

The incipiently pentacoordinate geometry of silicon in these cyclic silylamides demonstrated for the solid state encourages some speculative thoughts regarding the mechanism of silyl–proton exchange. It is generally accepted, mainly on the basis of Sommer's work,[16] that displacement reactions at silicon proceed *via* transition states in which the silicon atom undergoes a valency shell expansion. The activation energy of such a displacement reaction will be principally expended in the formation of the complex of the incoming group with the silane involving the octet shell expansion of the latter. The activation energy of the reaction may well be lower if the silane by virtue of a functional group is already in a state of valency shell expansion. The rapid hydrolysis of the Si–Cl bond in the hexacoordinate acetylacetonates $RSiA_2Cl$ may be a case in point[17] and so are perhaps the fast silyl–proton exchange reactions of silylamides.

The reactions of a silylamide with a proton donor may then be described in terms of transformation of the trigonal bipyramid or tetragonal pyramid ground state into an octahedral transition state incorporating the displacing group and subsequent separation into products (eq 17). In this picture, the



$$R^3OSiR_3 + R^2CONHR^1 \quad (17)$$

rapid silyl–proton exchange reactions of silylamides on the one hand and the much slower exchanges of silylamines on the other are analogous to the two silyl tautomerizations described for the disiloxadiazines: the low-temperature isomerization of the acetyl groups involving the expanded octet silicon in these cyclic compounds parallels the silylamide proton exchange, whereas the high-temperature coalescence which indicates the involvement of the tetrahedral silicon correlates with the displacement reaction of a silylamine.

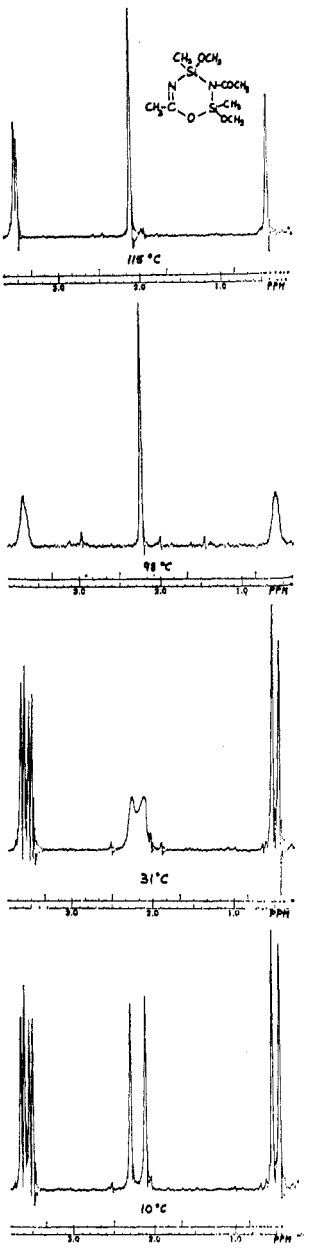


Figure 3. Temperature-dependent pmr spectra of 2,4-bis(methylmethoxysila)-3-acetyl-6-methyl-1,3,5-oxadiazine. Mixture of cis and trans isomers (10% in pyridine).

Very little quantitative information on the relative rates and equilibria of silylamine and silylamide reactions has yet appeared; particularly quantitative comparisons of different classes of such compounds are lacking, so that presently detailed considerations of the reaction mechanisms are no more than working hypotheses whose merits will have to await judgment in the light of future work.

(15) F. P. Boer and F. P. van Remoortere, *J. Amer. Chem. Soc.*, **92**, 801 (1970).
(16) L. H. Sommer, "Stereochemistry, Mechanism and Silicon," McGraw-Hill, New York, N. Y., 1965.
(17) R. West, *J. Amer. Chem. Soc.*, **80**, 3246 (1958).