densations of the ketone catalyzed by the boron trifluoride complex. Vpc examination of the ether concentrate from the above reaction at 195°, flow rate 60 ml/min, showed 64% of the seven-membered ketone and 36% of the six (relative areas) at 12.2 and 8.4 min retention time, respectively. A small amount of the eight-membered ketone was also present.

The above ketone mixture was reduced under Wolff-Kishner conditions with 0.19 g of potassium hydroxide, 0.19 ml of hydrazine hydrate, and 1.9 ml of diethylene glycol for 1 hr at 145° followed by a 4 hr reflux at 195-200°. The reaction was worked up with 15 ml of water followed by extraction with ether. Vpc examination of the concentrated ether extracts showed no starting ketones but two new major peaks in relative amounts similar to those for the ketone mixture at shorter retention times, 69% of I-7 (3.0 min) and 31% of I-6 (1.8 min). (A small amount of I-8 (4.6 min) was also present.) Collection by vpc at 180° gave *ca.* 20 mg of I-6 and *ca.* 45 mg of I-7. The mass spectra of I-6 and I-7 gave correct parent ion peaks and fragmentation patterns: *m/e* 140 and 83 for I-6 and 154 and 97 for I-7.

Anal. Calcd for $C_{11}H_{22}$: C, 85.63; H, 14.37. Found: C, 85.78; H, 14.56.

***t*-Butylcyclooctane (I-8), *t*-Butylcyclononane (I-9), and *t*-Butylcyclodecane (I-10).** These hydrocarbons were prepared according to the following route as a mixture and separated in the last stage by vpc. 5-*t*-Butylcyclooctanone was obtained from 5-*t*-butylcyclooctanol[11] by a Brown chromic acid oxidation.[18] The alcohol, 1.14 g (6.2 mmol), was oxidized with 1.4 g of sodium dichromate, 1.0 ml of concentrated sulfuric acid, and 6 ml of water at room temperature for 2.5 hr. Vpc examination of the concentrated ether extracts at 165°, flow rate 60 ml/min, showed no alcohol and a new peak identical with that of a known sample of *t*-butylcyclooctanone[19] at a shorter retention time.

After several attempts at ring expansion, the above mixture was dried over molecular sieves to remove water and ethanol and concentrated to *ca.* 30 ml in ether. Diazomethane from 204 mmol of N-nitrosomethylurea was added to the ketone mixture and 0.5 ml of boron trifluoride–etherate complex (added immediately prior to diazomethane addition; see above). The reaction was vigorous giving large precipitation of polymethylene. Vpc analysis at 215°, flow rate 100 ml/min, gave the following relative areas of ketones: I-8, 43%; I-9, 31%; and I-10, 26% (two peaks slightly resolved, *ca.* 50:50). Some higher homologs were indicated by vpc but were not analyzed for. This mixture of ketones was concentrated by distillation and subjected directly to Wolff-Kishner reduction with 0.82 ml of hydrazine hydrate, 0.82 g of potassium hydroxide, and 3.2 ml of diethylene glycol at 143-145° for 2 hr followed by reflux at 195° for 6 hr. To the cool reaction mixture was added 25 ml of water and the reaction worked up as before. Vpc examination of the concentrated reaction mixture at 215°, flow rate 100 ml/min, showed no peaks corresponding to unreacted starting material at 3.8, 12.3, and 18.2 min and three new peaks at 1.9, 2.9, and 4.2 min for I-8, I-9, and I-10, respectively. Collection of these peaks on the same column at 180° gave 89.5 mg of I-8, 66.9 mg of I-9, and 48.2 mg of I-10. A small amount of a higher homolog believed to be the eleven-membered ring hydrocarbon was also collected. The mass spectra of I-8, I-9, and I-10 gave correct parent ion peaks and fragmentation patterns: *m/e* 168 and 111 (I-8), 182 and 125 (I-9), and 196 and 139 (I-10).

Anal. Calcd for C_nH_{2n}: C, 85.63; H, 14.37. Found for I-8: C, 85.59; H, 14.28. Found for I-9: C, 85.70; H, 14.38. Found for I-10: C, 85.66; H, 14.41.

***t*-Butylcyclooctane (I-8) (Alternate Preparation).** To 0.3 g (1.63 mmol) of 5-*t*-butylcyclooctanol[11] in 5 ml of dry pyridine was added 0.40 g (2.20 mmol) of *p*-toluenesulfonyl chloride and the solution was allowed to stand at 0° for 24 hr. Following the usual work-up, the ether was evaporated and 10 ml of tetrahydrofuran was added. The solution was added dropwise to a slurry of 0.70 g (18.5 mmol) of lithium aluminum hydride in 15 ml of THF and the mixture was refluxed for 47 hr. To the cool solution was added 35 ml of 6 *N* hydrochloric acid followed by 10 ml of petroleum ether (bp 40-60°). The ether phase was separated, washed with water, and dried over magnesium sulfate. After concentration under reduced pressure, the *t*-butylcyclooctane was collected by vpc on a 10-ft Silicone GE SF-96 column (30% on Chromosorb P, HMDS, 60-80 mesh) at 180°. The nmr spectrum of this compound (10% in carbon disulfide) was identical with that obtained as reduced starting material in the preparation of the *t*-butylcycloalkanes I-8, I-9, and I-10 given above.

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[18] H. C. Brown and C. P. Garg, *J. Amer. Chem. Soc.*, **83**, 2952 (1961).

[19] Similarly prepared from *t*-butylcyclooctanol by M. St. Jacques, Ph.D. Thesis, University of California at Los Angeles, Los Angeles, Calif., 1967, p 244: ir 1700 cm^{-1} (lit.[11] bp 113-115° (7 mm)); n^{26}D 1.4714.

Disilaoxadiazines. Silyl Tautomerism in Cyclic Silylamides Involving Expanded-Octet Silicon

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Contribution from the General Electric Research and Development Center, Schenectady, New York. *Received February 19, 1968*

Abstract: 2,4-Disila-1,3,5-oxadiazine derivatives have been prepared by reaction of dimethyl-, methylphenyl-, methylmethoxy-, and diphenyldichlorosilane with acetamide and/or benzamide. The new six-membered heterocycles contain two silyl and two amide groups, one of the latter in imino ether form. Protonic reagents displace two molecules of amide from silicon in successive steps. The disilaoxadiazines undergo reversible intramolecular rearrangements at two temperature levels. At 20-50°, depending on the nature of the substituents, amide and imino ether moieties interconvert at a rate causing coalescence of their respective nmr signals. A temperature increase of 50-80° leads to coalescence of signals due to substituents on silicon. The phenomena suggest coordination of the amide moieties with one of the silicon atoms in an expanded shell, the other silicon being tetracoordinated. At higher temperatures, the silicon moieties interconvert reversibly.

The structure of silylamides has been a subject of controversy for a number of years. Probing of the alternatives—N-silylamide or O-silylimino ether—by chemical means is unsuitable because tautomerizations of intermediates and products are likely to occur, leaving the issue to spectroscopic arguments. Evidence cited in favor of the N-silylated amide form is based primarily on infrared spectra,[1] whereas ultraviolet absorption data of aromatic silylamides have been interpreted as evidence for O-silylated enol struc-

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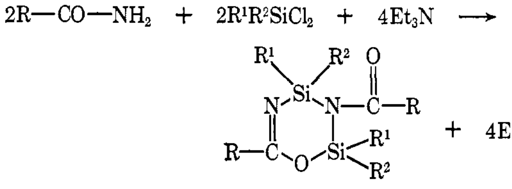
[1] W. Giessler, Inaugural Dissertation, Universität Köln, Germany, 1963.

tures.[2] Proton magnetic resonance investigations have provided further information about two families of compounds in the class of silylamides. Silyl groups in bistrimethylsilyl-substituted amides undergo a rapid intramolecular exchange presumably between oxygen and nitrogen; thus, N-silylsilylimidate structures have been suggested for these compounds.[3] A temperature-dependent intramolecular silyl group exchange in trimethylsilyl-substituted anilides leads to equilibrium mixtures of amide and imino ether forms whose relative amounts depend on the nature of substituents on the aromatic ring.[4] Both findings indicated a structural mobility at least in certain silylamides which had not been suspected earlier.

Silylamides and the related silylureas have recently gained importance as silyl donor reagents because of their high reactivity toward protonic compounds.[5–8] The carbonyl group is apparently primarily responsible for the increased silyl donor activity of silylamides as compared with the related class of silylamines; however, no straightforward relationship between the basicity of the parent nitrogen compound and the reactivity of the silylated derivative has been detected.[9] The present paper describes experiments bearing on structure and reactivity of silylamides.

Results

Our recent study of silaoxazolidones[10] made synthetic use of bis(N-methylacetamido)methylphenylsilane. The preparation of this silylamide from methylphenyldichlorosilane and N-methylacetamide was straightforward, while attempts to synthesize the analogous compound from acetamide led to mixtures whose compositions depended on reaction conditions and the nature of the solvent. A closer examination of the reaction of dichlorosilanes with N-unsubstituted amides has now shown that under suitable reaction conditions, both amide protons are displaced by silyl groups and good yields of 2,4-disila-1,3,5-oxadiazine derivatives can be obtained. This new six-membered heterocycle contains two silicon moieties and two amide groups, one of them in the imino ether form



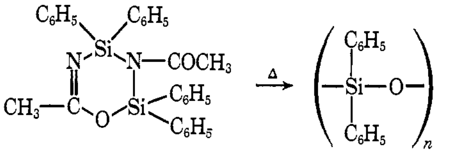
$2R-CO-NH_2 + 2R^1R^2SiCl_2 + 4Et_3N \longrightarrow$ + $4Et_3N{\cdot}HCl$ (1)

1

1a, R, R^1, R^2 = CH_3
b, R, R^1 = CH_3; R^2 = C_6H_5
c, R = CH_3; R^1, R^2 = C_6H_5
d, R, R^1 = C_6H_5; R^2 = CH_3
e, R = C_6H_5; R^1, R^2 = CH_3
f, R, R^1 = CH_3; R^2 = OCH_3

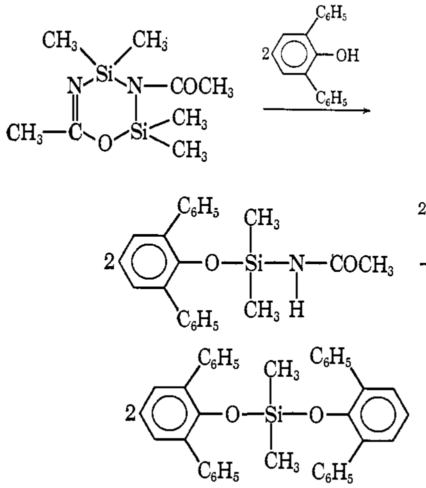
The reaction was found to be general for a variety of amides and dichlorosilanes. Elemental analyses and molecular weight determinations are in agreement with structure **1**. The products are colorless solids which are readily soluble in hydrocarbons and other solvents. *cis* and *trans* isomers are formed in equal amounts when R^1 and R^2 are different; in one case (**1f**) one of the isomers could be separated from the mixture by crystallization.

Linear and cyclic siloxanes are among the by-products of disilaoxadiazine formation, particularly when the reactions are run at elevated temperatures. Nitrile is eliminated and siloxanes are formed, when disilaoxadiazines are heated neat or in solution (eq 2). This decomposition is pronounced with aromatic substituents on silicon while the analogous methyl-substituted compounds are much more stable.



+ CH_3CN (2)

Compounds with reactive protons like alcohols or water displace amide from **1** in often strongly exothermic reactions. In suitable cases, the cleavage reaction can be shown to proceed in two steps, *e.g.*, with 2,6-diphenylphenol.



+ $2CH_3CONH_2$ (3)

The infrared spectra of the disilaoxadiazines **1a–f** show two strong absorptions at 1610–1635 and at 1660–1685 cm^{-1}, presumably due to the C=O and C=N stretching vibrations, the absorption at higher frequency being somewhat larger in all cases. While a definite assignment of the two bands cannot be made presently, they nevertheless appear to be characteristic for this ring system; the infrared spectra of linear silylamides, linear and cyclic silylureas and silylimides generally show single broad absorptions between 1600 and 1750 cm^{-1}.

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(2) E. Frainnet, A. Bazouin, and R. Calas, *C. R. Acad. Sci., Paris*, **257**, 1304 (1963).

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

(4) J. F. Klebe and J. B. Bush, Jr., International Congress on Organosilicon Chemistry, Prague, 1965.

(5) L. Birkofer, A. Ritter, and F. Bentz, *Chem. Ber.*, **97**, 2196 (1964).

(6) J. F. Klebe, J. B. Bush, Jr., and J. E. Lyons, *J. Amer. Chem. Soc.*, **86**, 4400 (1964).

(7) J. F. Klebe, *ibid.*, **86**, 3399 (1964).

(8) J. F. Klebe, H. Finkbeiner, and D. M. White, *ibid.*, **88**, 3390 (1966).

(9) The silyl donor strength and the rate of silyl proton exchange with silyl acceptor molecules increases in a series of ring-substituted trimethylsilylanilides with increasing electron withdrawal of the substituent. However, trimethylsilyl-N-methylacetamide equals the silyl donor strength and exceeds the exchange rates of the trimethylsilylanilides despite the higher basicity of the former amide.[4] A qualitative comparison of N-trimethylsilylphthalimide and N-trimethylsilylsuccinimide with a number of trimethylsilylamides in our laboratory has shown that the former react much slower with methanol than the latter.

(10) J. F. Klebe and H. Finkbeiner, *J. Amer. Chem. Soc.*, **88**, 4740 (1966).

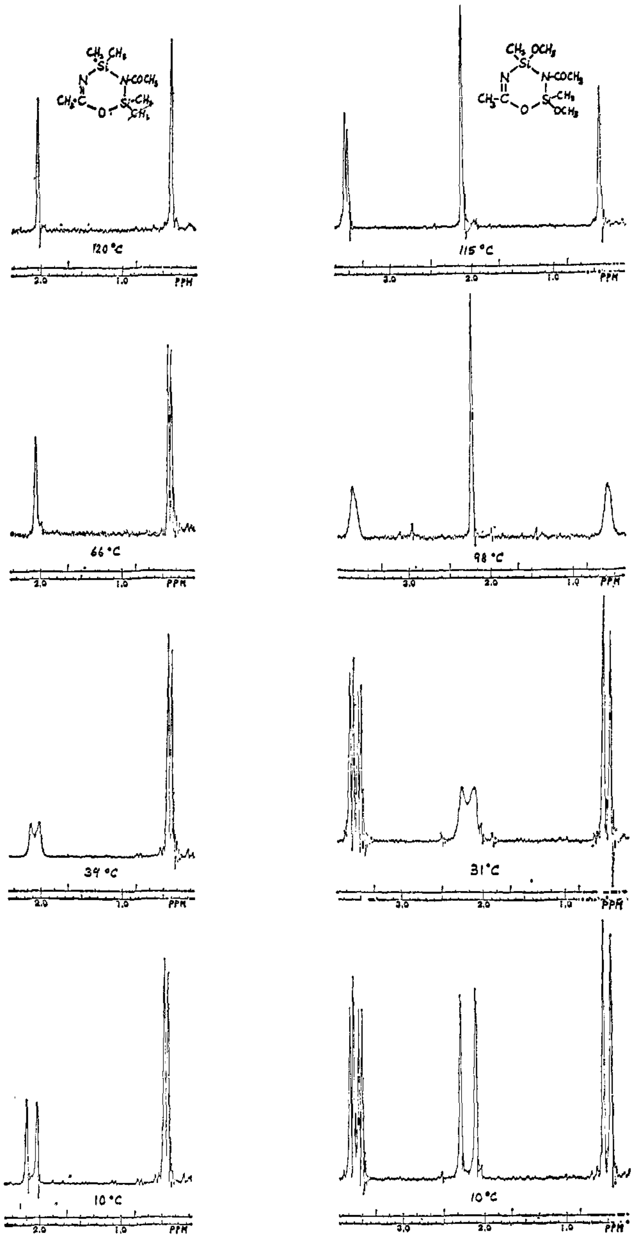


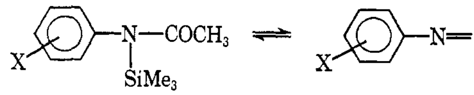
Figure 1. Temperature-dependent nmr spectra of disilaoxadiazines **1a** and **1f** in benzonitrile and pyridine solution, respectively.

The proposed disilaoxadiazine structure is strongly supported by the proton magnetic resonance spectra. As required for structure **1**, each of the substituents R, R^1, and R^2 produces two signals in suitable solvents at low temperatures; this number is doubled because of *cis–trans* isomerism if R^1 and R^2 are different, and in some cases, the four signals are clearly resolved. The signals due to aromatic protons are complicated and not amenable to simple analysis. If the temperature is raised, the lines of the amide protons (R) broaden in a manner typical for exchange processes until at a temperature T_{c1} the lines coalesce to a single signal. At this temperature, the signals of the substituents on silicon (R^1, R^2) are unchanged in shape, giving no indication for an exchange process involving the silicon moieties. However, a further temperature increase causes line widening of the silicon substituent signals and finally, at the temperature T_{c2}, collapse of these signals. If R^1 and R^2 are different, the four low-temperature lines coalesce at T_{c2} into two signals of the respective *cis* and *trans* forms. All signals are broad at the coalescence temperatures and sharpen upon temperature increase; separation into the original pairs of lines is observed when the temperature is lowered, showing the processes to be reversible. The difference in coalescence temperatures of the acetyl methyl and the silicon methyl signals is not due to a larger low-temperature shift difference of the latter signals. Figure 1 shows the nmr spectra of the disilaoxadiazines **1a** and **1f** over a temperature range covering the exchange phenomena. The coalescence temperatures are somewhat solvent dependent; values of T_{c1} and T_{c2} measured on 15% chlorobenzene solutions are listed in Table I along with other physical data of the disilaoxadiazines.

The line separations of the groups R as well as R^1 and R^2 below the coalescence temperatures were found to increase with decreasing temperature down to below −50° although the line widths remained constant over a wide temperature interval below the coalescence temperatures, indicating very slow exchange. This inconstancy of the peak separations hampered the calculation of activation energies for the exchange processes by conventional methods. Accurate measurements of initial line broadening for the purpose of rate determinations have not yet been undertaken.

Discussion

The phenomena described above require reversible isomerizations which can best be rationalized by a process analogous to the keto–enol tautomerism. We have called a temperature-dependent reversible isomerization involving trimethylsilyl-substituted anilides "N–O silyl tautomerism."[4] In that case, the exchange rates of trimethylsilyl groups between O and N become sufficiently low at low temperature (0–20°), so that silylamide and silylimino ether structures in equilibrium mixtures can be distinguished by nmr.



A related phenomenon is the temperature-dependent intramolecular exchange of trimethylsilyl groups in N-silylsilylimidates shown by Pump and Rochow.[3]

$$R{-}C\begin{matrix}\nearrow O{-}SiMe_3\\ \searrow N{-}Si^1Me_3\end{matrix} \rightleftharpoons R{-}C\begin{matrix}\nearrow O{-}Si^1Me_3\\ \searrow N{-}SiMe_3\end{matrix}$$

The temperature-dependent spectral changes of the disilaoxadiazines described above can be explained by reversible rearrangements between the "silyltautomeric" forms A–D in solution (see Figure 2). At the temperature T_{c1}, the interconversion between A and B and between C and D proceeding with the rate r_1 becomes fast enough to make the amide moieties indistinguishable by nmr, resulting in coalescence of the respective signals. The silicon atoms have not changed their environment during this tautomerization, hence their substituent signals remain separate. When the temperature is raised to T_{c2}, the rate r_2 for the tautomerization between A and C (B and D) becomes fast enough to lead to coalescence of the silicon substituent signals.

Table I. Disilaoxadiazines 1

No.	R	R^1	R^2	Method of Preparation^a	Yield %	M.P. °C	T_{c1}^{b} °C	T_{c2}^{b} °C	$\delta\omega$^{b} cps, 10°C CH_3-CO	CH_3-Si	Calculated, % C	H	N	Si	Found, % C	H	N	Si	Molecular Weight Calculated	Found
1a	CH_3	CH_3	CH_3	A	80	44-46	21	108	2	7	41.7	7.9	12.2	24.4	42.0	7.6	12.5	25.1	230	230^c
1b	CH_3	CH_3	C_6H_5	B(A)	70(55)	108-113^d	45	95	19	12	60.7	6.2	7.9	15.8	61.0	6.3	8.0	16.5	354	358
1c	CH_3	C_6H_5	C_6H_5	B	60	140-145 (decomp.)	20	---	20 (-33°)	--	70.3	5.5	5.9	11.7	70.4	5.3	6.0	12.2	478	(e)
1d	C_6H_5	C_6H_5	CH_3	B	46	116-122^d	--	58	--	28	70.3	5.5	5.9	11.7	70.0	5.7	5.7	12.2	478	(e)
1e	C_6H_5	CH_3	CH_3	B	55	127-128	--	73	--	17	61.0	6.2	7.9	15.8	61.1	6.1	7.9	16.2	354	354^c
1f	CH_3	CH_3	OCH_3	B	65	45-48^f	32	96	7	8	36.6	6.9	10.7	21.4	37.0	6.7	10.7	22.3	262	262

(a) See Experimental Section

(b) 15% in PhCl. The accuracy is about ±1°. The separations between the CH_3CO signals and the CH_3-Si signals, respectively, are given for a temperature at which all peaks have reached their ultimate line width. Values of $\delta\omega$ increased down to the lowest accessible temperature, -50°C.

(c) Molecular ion peak of mass spectrum.

(d) Mixture of isomers

(e) No satisfactory determinations could be obtained because of the thermal and hydrolytical instability of the compound.

(f) About 95% enriched in one isomer. The 1:1 mixture of the cis- and trans-isomer is a liquid at room temperature.

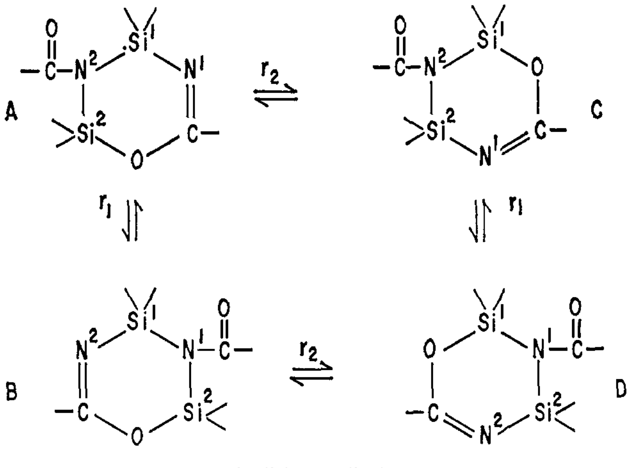


Figure 2. Silyl tautomeric disilaoxadiazine structures.

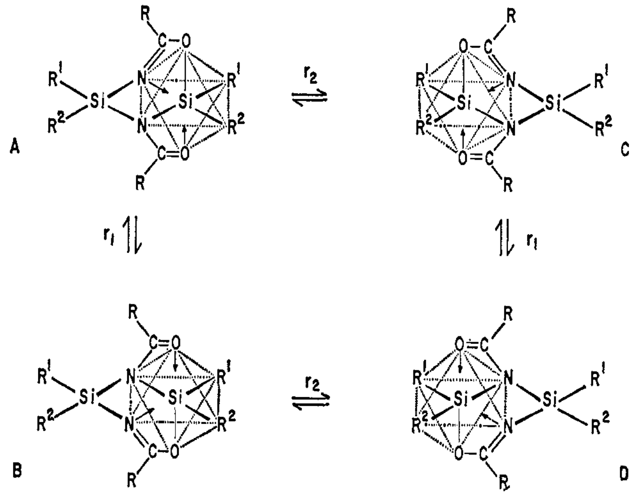


Figure 3. Rearrangements between silyl tautomeric disilaoxadiazine structures. Fast rates, r_1, result in low coalescence temperatures for R; more extensive change of geometry governed by slower rates, r_2, leads to higher coalescence temperatures for R^1 and R^2.

As can readily be seen, the tautomerizations governed by r_1 and r_2 both involve the breaking and the making of one Si-N and one Si-O bond; it is difficult to deduce from this representation that the energy requirements for the two processes should be different.

However, in the light of the well-authenticated ability of silicon to expand its coordination number to five or six[11] by utilizing its 3d orbitals when it is bonded to electronegative elements like the halogens, nitrogen, or oxygen, the representation shown in Figure 3 appears attractive as a description of the disilaoxadiazine tautomerism. Both amide groups are now located within the octahedral coordination sphere of one of the silicon atoms while the second silicon has the normal tetrahedral configuration. Very little change of geometry seems necessary for the interconversion between A and B (C and D) at the "fast" rate r_1. A greater amount of

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(11) (a) F. G. A. Stone and D. Seyferth, *J. Inorg. Nucl. Chem.*, **1**, 112 (1955). (b) L. H. Sommer, "Stereochemistry, Mechanism and Silicon," McGraw-Hill Book Co., Inc., New York, N. Y., 1965. (c) C. L. Frye, G. E. Vogel, and J. A. Hall, *J. Amer. Chem. Soc.*, **83**, 996 (1961). (d) C. L. Frye, *ibid.*, **86**, 3170 (1964). (e) C. L. Frye, G. A. Vincent, and G. L. Hauschildt, *ibid.*, **88**, 2727 (1966). (f) R. West, *ibid.*, **80**, 3246 (1958). (g) S. K. Dhar, V. Doron, and S. Kirschner, *ibid.*, **80**, 753 (1958).

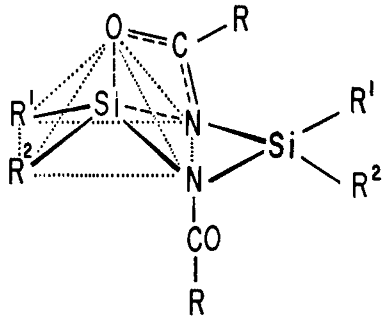
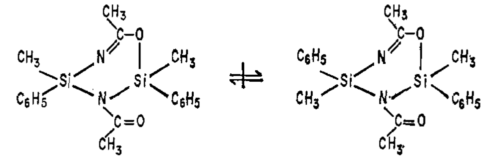


Figure 4. Pentacoordinate silicone ground state of a disilaoxadiazine.



Ib (cis) Ib (trans)

Figure 5. *cis-* and *trans*-disilaoxadiazines do not interconvert during silyl tautomer rearrangements.

energy should be required to break Si^1 out of its octahedral configuration and allow Si^2 to assume the higher coordination, which is formally accomplished by a 180° rotation of both carbonyl groups around the C–N bonds. This latter process represents the interconversions A $\rightleftharpoons$ C and B $\rightleftharpoons$ D at the observed "slow" rate r_2. This representation involves somewhat compressed bond angles; however, a N–Si–O angle in the order of 90° does not seem unduly small for extracoordinate silicon.[11d] The hexacoordinate configuration may represent a transition state rather than the molecule in the ground state for which a tetragonal pyramide with pentacoordinate silicon also appears possible,[12] which would leave freedom of rotation for the acyl group (Figure 4).

The substituents R^1 and R^2 retain their relative positions during these tautomerizations as shown by the collapse of the four CH_3O–Si signals of **1f** to two signals at T_{c2}, which do not further coalesce (Figure 1). The corresponding CH_3–Si and CH_3–CO signals of **1f** are unresolved. Likewise, the four partially resolved low-temperature signals due to CH_3–CO of **1b** coalesce at T_{c1} to two signals, which do not change upon further temperature increase suggesting that an isomerization **1b** (*cis*) $\rightleftharpoons$ **1b** (*trans*) does not occur (Figure 5).

The concept of valency shell expansion of silicon in disilaoxadiazines may well apply also to linear silylamides and provide an explanation for their high reactivity toward protonic reagents. Sommer has suggested the coordination of a nucleophilic group into a vacant d orbital of silicon as the first step in the rapid hydrolysis of halosilanes.[13] West reports the "instantaneous" hydrolysis of the Si–Cl bond in the hexacoordinate acetyl acetonates $RSiA_2Cl$ by water.[11f] If valency shell expansion of silicon is indeed a general principle for the transition state of displacement reactions on silicon, it is attractive to correlate the high reactivity of silylamides with structures in which the silicon atom has already expanded its shell and is "set up" for the displacement, *e.g.*, in the reaction of a silylamide with an alcohol starting out with the pentacoordinate tetragonal pyramide leading up to an octahedral transition state with little change of the molecular geometry (Figure 6). The ground state of the less reactive silylamines presumably has tetrahedral coordination; the slower displacement rates of these compounds may then have a parallel in the "slow" tautomerization rates r_2 of the disilaoxadiazines.

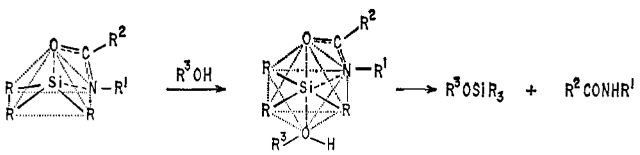


Figure 6. Displacement of amide from pentacoordinate silicon in silylamides.

Experimental Section

Commercial dimethyldichlorosilane and methylphenyldichlorosilane were found sufficiently pure by nmr for direct use. Diphenyldichlorosilane was distilled. Methylmethoxydichlorosilane was prepared from methyltrichlorosilane and methanol according to known procedures.[14] Reagent grade benzene and acetonitrile were used for the syntheses. Benzene and hexane used for recrystallizations were dried with LAH. Anhydrous acetonitrile were prepared by removing water as a ternary azeotrop with benzene. Triethylamine was purified by distillation.

Two procedures were used for the synthesis of disilaoxadiazines, examples of which are given below. Table I shows data pertinent to preparation and analysis of the compounds.

All nmr spectra were taken on a Varian A-60 spectrometer equipped with a variable-temperature probe. The temperature of samples was determined by measuring the separation of methyl and hydroxyl signals of a precalibrated methanol sample in a capillary mounted coaxially in the same tube.[15] Temperatures above magnet temperature were measured in the same fashion using ethylene glycol.

Cyclobis(acetamidodimethylsilane).[16] **Procedure A.** Dimethyldichlorosilane, 13 g, was slowly added under anhydrous conditions to the stirred suspension of 6 g of acetamide in 25 g of triethylamine and 150 cc of dry benzene. The temperature rose to about 35° during the dropwise addition; triethylamine hydrochloride precipitated immediately. The stirring was continued for about 2 hr after the addition was complete. The hydrochloride was then filtered off under a blanket of dry nitrogen and the filtrate was concentrated *in vacuo*. The residue crystallized on standing; nmr showed the product essentially free of by-products. The material was purified by sublimation at 40° (0.1 mm), mp 44–46°. In another experiment, the dimethyldichlorosilane was added to the other components at reflux temperature with essentially the same results.

Cyclobis(acetamidodiphenylsilane). Procedure B. To the ice-cooled, stirred mixture of 25 g of diphenyldichlorosilane and 6 g of acetamide in 150 cc of dry acetonitrile was slowly added, under anhydrous conditions, 25 g of triethylamine within a period of about 30 min. Stirring was continued for 2 hr without external cooling. The precipitate of triethylamine hydrochloride was then filtered off under a blanket of dry nitrogen and the filtrate was concentrated *in vacuo*. The solid residue was recrystallized from acetonitrile to

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(12) Trigonal bipyramidal structures are more generally accepted for pentacoordinate silicon, but the energy difference between the trigonal bipyramide and the tetragonal pyramide is considered very small; E. L. Muetterties and R. A. Schunn, *Quart. Rev.* (London), **20**, 245 (1966).

(13) L. H. Sommer and O. F. Bennet, *J. Amer. Chem. Soc.*, **79**, 1008 (1957).

(14) K. A. Andrianov and V. V. Astakhin, *Zh. Obshch. Khim.*, **29**, 3754 (1959); *Chem. Abstr.*, **54**, 19460 (1960).

(15) C. H. Sederholm, paper presented at the Sixth Experimental NMR Conference, Pittsburgh, Pa., Feb 1965.

(16) The lengthy systematic name is 2,4-bis(methylphenylsila)-3-acetyl-6-methyl-1,3,5-oxadiazine [IUPAC 1957 Rules, *J. Amer. Chem. Soc.*, **82**, 5567 (1960)].

yield 60% of the theoretical amount of the cyclic silylamide, mp 140–145° dec. The major by-products were bis(acetamido)diphenylsilane and cyclic diphenylsiloxanes. These by-products predominated when procedure A was used or when the reaction was run without external cooling.

Dimethylbis(2,6-diphenylphenoxy)silane. A solution of 115 mg (0.5 mmol) of cyclobis(acetamidodimethylsilane) and 500 mg (2 mmol) of 2,6-diphenylphenol in 2 cc of dry pyridine was prepared. The nmr spectrum of the solution after 30 min at room temperature showed no indication of the original signals (acetyl absorptions at δ 2.12 and 2.16 ppm; CH_3–Si absorptions at 0.46 and 0.52 ppm); instead, two new signals had arisen at 1.64 and −0.03 ppm (upfield of TMS), respectively, presumably due to dimethyl(2,6-diphenylphenoxy)acetamidosilane. These signals disappeared on heating at 100° overnight and two new absorptions formed at 2.03 ppm (acetamide) and −1.05 ppm. On cooling, colorless crystals formed, mp 156–157° after recrystallization from benzene–ethanol. The compound in deuteriochloroform solution has a CH_3–Si signal 79 cps upfield of tetramethylsilane.

Anal. Calcd for $C_{38}H_{32}O_2Si$: C, 83.1; H, 5.9; Si, 5.1; mol wt, 549. Found: C, 83.4; H, 6.2; Si, 5.2; mol wt, 536.

Acknowledgment. The author is indebted to Dr. J. B. Bush, Jr., for many helpful discussions.

General Methods of Synthesis of Indole Alkaloids. VII. Syntheses of *dl*-Dihydrogambirtannine and Aspidosperma–Strychnos Alkaloid Models[1,2]

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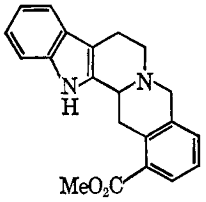
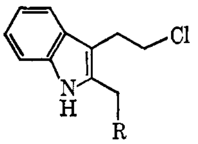
Received March 28, 1968

Abstract: The synthesis of dimethyl isoquinoline-4,5-dicarboxylate and its four-step conversion into the indole alkaloid dihydrogambirtannine are reported. The preparation of methyl 3-(β-chloroethyl)-2-indoleacetate, its N-alkylation of several β-acylpyridines, and hydrogenation of the salts are described. The use of the resultant 2-piperideines and related 2-methylindole compounds in a study of the rarely observed β-indole cyclization process and the synthesis of Aspidosperma and Strychnos alkaloid models are portrayed.

In continuation of our studies of the synthesis of indole alkaloids by the scheme of hydrogenation and cyclization of 1-alkyl-3-acylpyridinium salts[2] syntheses of dihydrogambirtannine (I) and of tetracyclic models of the Aspidosperma and Strychnos alkaloids were undertaken. This exercise was devised principally to determine whether the synthesis scheme was applicable to the 4-acylisoquinoline area and to β-indole cyclization, all cyclizations heretofore having been of the α-indole type.

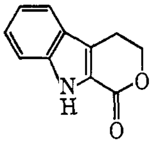


I

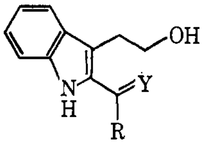


IIa, R = CN
b, R = CO_2Me

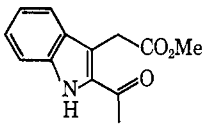
The latter problem required the preparation of methyl 3-(β-chloroethyl)-2-indoleacetate (IIb) which was accomplished by two routes of synthesis. One, reminiscent of the mode of preparation of 2-indoleacetic ester,[3] involved the following reaction sequence: (a) treatment of lactone III[4] with dimethylamine, (b) lithium aluminum hydride reduction of the resultant amide IVa, (c) methylation of the amine IVb, (d) cyanide displacement of the salt IVc, and (e) treatment of the resultant nitrile IVd with methanolic hydrochloric acid. A second route involved (a) lithium aluminum hydride reduction of methyl 2-acetyl-3-indoleacetate (V),[5,6] (b) manganese dioxide oxidation of the diol IVe, (c) Willgerodt rearrangement of the ketone IVf, (d) consecutive treatments of the hydroxyamide IVg with acetic anhydride, phosphorus oxychloride and aqueous base, and (e), as before, exposure of the resultant hydroxynitrile IVd to methanolic hydrochloric acid.



III



IVa, R = NMe_2; Y = O
b, R = NMe_2; Y = H_2
c, R = N^+Me_3; Y = H_2
d, R = CN; Y = H_2
e, R = Me; Y = HOH
f, R = Me; Y = O
g, R = $CONH_2$; Y = H_2



V

Dihydrogambirtannine (I). This alkaloid is one of several yohimboid constituents of the tanning material gambir, isolated from *Uncaria gambier* Roxb.,[7,8] as

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(1) This work was supported by the U. S. Department of Health, Education and Welfare (grant GM-11571).

(2) Part VI: E. Wenkert, K. G. Dave, R. G. Lewis, and P. W. Sprague, *J. Am. Chem. Soc.*, **89**, 6741 (1967).

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