THE CHEMISTRY OF SILICON-NITROGEN COMPOUNDS

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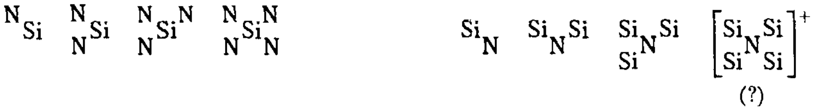
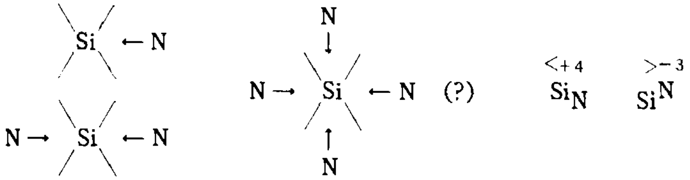
I. Introduction

Silicon and nitrogen, because of their positions in the periodic system, can combine in a variety of ways. Thus it can be shown that, in principle, four nitrogen atoms may be bound to one of silicon, or three silicon atoms to one of nitrogen, and that a fourfold silyl-substituted ammonium ion is possible. Addition compounds should exist in which one, two, or even four tertiary amine molecules are linked to a silicon halide molecule by using the vacant 3*d* orbitals of silicon and the free pair of electrons on the nitrogen atom of the tertiary amine. Furthermore, compounds of higher molecular weight with —SiN— units in chains or as members of rings must be possible, and compounds with oxidation states other than +4 for silicon or −3 for nitrogen should also be obtainable.

It is astonishing that these abundant possibilities have been so little used in preparative and synthetic chemistry until recently, in spite of the fact the first SiN compounds were prepared 150 years ago. Only in the last 20 years since organohalosilanes, the most important starting materials



SiNSi SiNSiNSi $Si(NSi)_n$ $(—SiN—)_n$



for preparing silicon-nitrogen compounds, became available in unlimited amounts from the silicone industry, has the chemistry of Si—N compounds undergone any considerable development. Up to the present some 600 publications have appeared in this field. Until 1960 the chief emphasis was on the synthesis of substances containing a range of units from SiN to SiN_4. More recently the exhaustive silyl substitution of NH_3 and of NH_2 groups and the preparation of Si—N compounds with oxidation states other than +4 for silicon and −3 for nitrogen have become more prominent.

In this article a short review will first be given of some general problems associated with the Si—N bond; selected topics from the more recent developments will then be described in detail. Other reviews on SiN compounds have appeared elsewhere (*33, 37a, 39, 93, 96*). The system of nomenclature and abbreviations used for organic substituents, which have proved particularly suitable for blocking residual Si and N valencies because of their low reactivity, is based on that used in Gmelin's *Handbuch der anorganischen Chemie*, Silicon C (Organosilicon Compounds) (cf. Table II). Frequent use has been made of abbreviated formulations for structural units, which show the arrangement of the SiN groups in the structure. In this case only the symbols for adjacent elements are given, e.g.

Formula:	$(CH_3)_2Si[NHC(CH_3)_3]_2$;	$[(CH_3O)_3Si]_2N—SiCl_2CH{=}CH_2$
Abbreviated formula:	$me_2Si(NH^tbu)_2$	
	or	
	$me_2Si(NHCme_3)_2$;	$[(meO)_3Si]_2N—SiCl_2vi$
Structural unit:	$\begin{matrix} & N \\ Si & \\ & N \end{matrix}$	$\begin{matrix} Si & & Si \\ & N & \\ & Si & \end{matrix}$

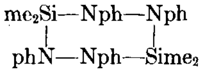
The basic units in the nomenclature of SiN compounds are SiH_4 and NH_3; $H_3Si—NH_2$ can then be designated as silylamine or as aminosilane. The inherently logical term "silazane" is not to be recommended since the term silazane has, unfortunately, been used indiscriminately for chain and ring compounds. Thus, for example, the trisilylamine sometimes has wrongly been called trisilazane. In cases of doubt it is advisable to base the nomenclature on hydrocarbon chains and to designate the replacement of CH_2 with SiH_2 by the prefix sila and that with —NH— by aza.

SiN = silylamine
NSi = aminosilane
SiNSi = bis(silyl)amine
NSiN = bis(amino)silane

$Si\underset{Si}{N}Si$ = tris(silyl)amine

$N\underset{N}{\overset{}{Si}}N$ = tetrakis(amino)silane

$Si(NSi)_n$ = polysilazane, (n = 1) disilazane
(n = 2) trisilazane, etc.
$(—NSi—)_n$ = cyclosilazane, (n = 3) cyclotrisilazane
(n = 4) cyclotetrasilazane
$me_3SiNHCH_2COOH$ = trimethylsilylaminoacetic acid
or
= 3-aza-4-sila-4,4-dimethylvaleric acid



= 1,1,4,4-tetramethyl-2,3,5,6-tetraphenyl-1,4-disila-2,3,5,6-tetrazacyclohexane

II. Preparation and Properties of the Si—N Bond

Only in the rarest cases are redox reactions used in the preparation of Si—N bonds. The general method almost always involves substitution or condensation reactions involving reactants with the appropriate oxidation state of Si or N already established. Thus elementary silicon reacts with N_2 or NH_3 only at temperatures above 1200°, when Si_3N_4 results (*11*, *51*), and the interaction of elementary nitrogen and silicon tetrachloride is possible only in a glow discharge. A complex mixture of reaction products results (*38*, *105*).

The most common way of establishing a bond between Si and N is by the reaction of ⩾SiCl with an >NH group. The generally accepted view of the mechanism is that the following steps are involved:

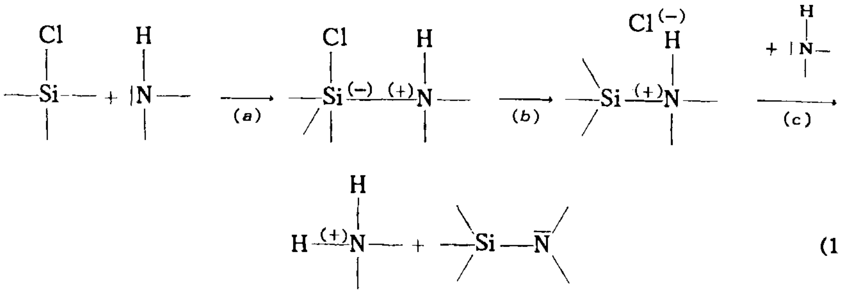
(1) Addition of the amino group to the chlorosilane by interaction of a free electron pair of N with a vacant 3*d* orbital of Si. Nitrogen then has an ammonium structure with Si in a 5-coordinated state and has a formal negative charge (Reaction 1*a*).

(2) Cleavage of the Cl, initially bonded covalently, as a chloride ion (Reaction 1*b*); a silyl-substituted ammonium salt is left.

(3) The strongly basic amine taken initially removes a proton from this silyl-substituted ammonium salt (Reaction 1*c*).

(4) The Si—N compound formed establishes a mesomeric equilibrium and forms a d_π—p_π double bond between the Si and N atoms (Reaction 2).

Primary and secondary amines react rapidly via Reactions 1*a* and 1*b*. Tertiary amines interact only with silanes such as $RSiCl_3$ or $SiCl_4$, which are extensively halogenated; reaction is restricted, however, to the primary



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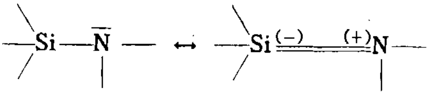
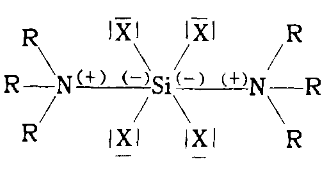
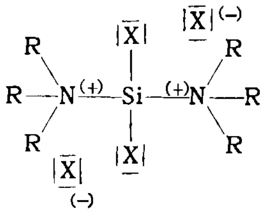


(2)

addition. A second NR_3 molecule is often added. The addition of four NR_3 molecules is known with certainty only in the case of SiI_4py_4 (py = pyridine) (*99*, *140*, *167*). With ureas or acid amides, addition ratios as high as 1:6 and 1:10 are observed (*50*, *123*, *140*). Although more than 50 publications have appeared which deal with addition compounds between silicon halides and amines, it has not yet been possible to prove conclusively whether the structure of these addition compounds is of type A, with coordinate links in a monomolecular structure, or of type B, with ionized halide



(A)

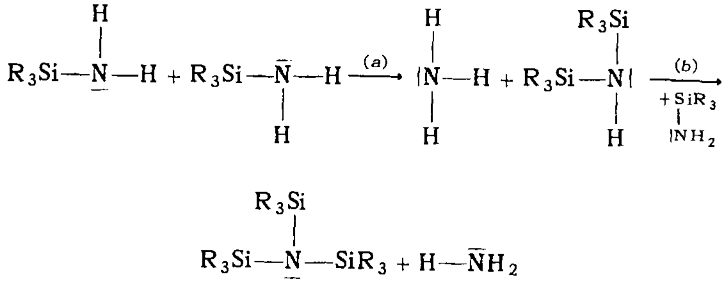


(B)

(*7*, *8*, *62*, *100*, *121*, *122*). Since the addition compounds are extremely sensitive to moisture and tertiary amines are very difficult to obtain in an anhydrous state, the majority of publications on this class of compound may well contain incorrect observations: even the presence of small quantities of water in solvents suffices to precipitate mixtures of silicic acids and ammonium halides, which in most cases cannot be distinguished analytically from the addition compounds being sought. It would be a rewarding task to bring some light to this confused section of silicon-nitrogen chemistry by the use of unexceptionable experimental procedures and modern methods of elucidating structure.

In many cases, such as that of the carbonic acid amides $RCONH_2$, the amine base is too weak to bring about step 1*c* in the reaction scheme. In such cases the addition of tertiary amines to remove protons has been found to be a very useful way of promoting silylation (*15*, *18*, *31*, *113*).

If the reactions are carried out with secondary amines, R_2NH, Reaction 1 is terminated at the 1*c* stage. The same is true in most cases for primary amines. With ammonia as the starting material, subsequent multiple condensation reactions take place, leading to two- or even threefold silyl substitution of the ammonia.



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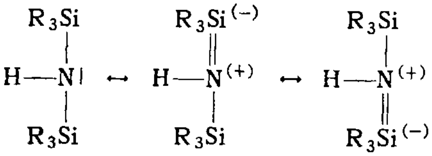

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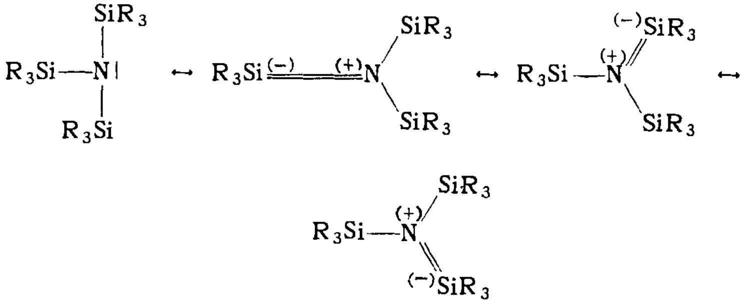


(5)

The extent of these subsequent condensation reactions depends on how far the electron pair of the N atoms in the limiting mesomeric forms shown in Reaction 2 or 4 is available for further addition reactions or is blocked by d_π—p_π bonding. It is also dependent on steric factors due to the R substituents on the silicon atom. Thus the chlorosilane $RSiH_2Cl$ reacts with ammonia successively to form the tris(silyl)amines; $RSi(me_2)Cl$ below

50° goes to bis(silyl)amines and $RSi(et)_2Cl$ only to silylamines (if R is not H). With the alkoxychlorosilanes $(RO)_3SiCl$, condensation to the bis(silyl)-amines occurs more readily than with alkylchlorosilanes.

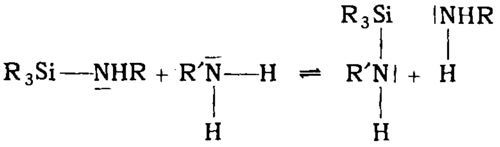
$$3RSiH_2Cl + 4NH_3 \rightarrow [RSiH_2]_3N + 3NH_4Cl \qquad (R = H,me,SiH_3) \tag{6}$$

$$2RSi(me)_2Cl + 3NH_3 \rightarrow [RSi(me)_2]_2NH + 2NH_4Cl \qquad (R = me,et,CH_2Cl) \tag{7}$$

$$RSi(et)_2Cl + 2NH_3 \rightarrow RSi(et)_2NH_2 + NH_4Cl \qquad (R = me,et) \tag{8}$$

$$2(RO)_3SiCl + 3NH_3 \rightarrow [(RO)_3Si]_2NH + 2NH_4Cl \qquad (R = me,et,pr) \tag{9}$$

Condensation by Reaction 3*a* to a doubly silyl-substituted amine may often be brought about by increasing the temperature or, better, by using an acid catalyst such as NH_4Br or $(NH_4)_2SO_4$, though even under the most drastic reaction conditions the formation of the threefold silyl-substituted amine is not observed. Exchange reactions of amines in Si-N compounds proceed in the same way: the readily volatile amine RNH_2 is distilled off from the equilibrium mixture and thus dislodged from the silyl group (*87*, *90*):



$$R_3Si{-}\underline{N}HR + \underset{\displaystyle H}{\underset{|}{R'\bar{N}}}{-}H \rightleftharpoons \underset{\displaystyle H}{\underset{|}{\overset{\displaystyle R_3Si}{\overset{|}{R'N|}}}} + \overset{\displaystyle |NHR}{\overset{|}{H}} \tag{10}$$

The behavior of $\equiv$Si—Br or $\equiv$Si—I groups is like that of $\equiv$Si—Cl groups, though they have hardly been used at all in preparative work. On the other hand, $\equiv$Si—F or $\equiv$Si—H are often found to react only with metallated amines (*25*, *49*). Hydrogen has a higher electronegativity than Si (2.1 as against 1.8) and therefore behaves like a halogen when bonded to silicon.

$$ph_3SiF + Li + ph_2NH \rightarrow ph_3SiNph_2 + LiF + \tfrac{1}{2}H_2 \tag{11}$$

$$ph_3SiH + LiNme_2 \rightarrow ph_3SiNme_2 + LiH \tag{12}$$

Attachment of a pseudohalogen through nitrogen to a silicon atom may be effected by splitting off a metal halide:

$$\equiv Si{-}Cl + Me^+X^- \rightarrow \equiv Si{-}X + Me^+Cl^- \tag{13}$$

where Me = Li, Na, K, NH_4, Ag, Pb; X = —NCO, —NCS, —NNN, —NCN—, —NC (?).

Other reactions, as for example the transformation of $\equiv$Si—O— to $\equiv$Si—N$=$, are of much less importance. "Silyl esters" of inorganic acids react readily with ammonia (*134*, *145*). The Si—O—C_6H_5 bond is cleaved by $NaN(SiR_3)_2$, $LiNR_2$, or $NaNH_2$ (*164*) while, under more drastic conditions, $\equiv$Si—O—Si$\equiv$ is cleaved by $NaNH_2$ (*63*). Nucleophilic cleavage of $\equiv$Si—C$\equiv$ by $NaNH_2$ may also sometimes occur (*55*). Alkali silyl compounds can condense with amines, with elimination of alkali hydride (*182*), or may be added across the double bond in —N=N— or C=N— (*181*):

$$2me_3SiOClO_3 + 3NH_3 \rightarrow (me_3Si)_2NH + 2NH_4ClO_4 \tag{14}$$

$$me_3SiOph + LiNet_2 \rightarrow me_3SiNet_2 + LiOph \tag{15}$$

$$2me_3SiOSi(me)_3 + 2NaNH_2 \rightarrow (me_3Si)_2NH + 2me_3SiONa + NH_3 \tag{16}$$

$$2phCHClSi(me)_3 + 2NaNH_2 \rightarrow phCHCHph + 2NaCl + (me_3Si)_2NH + NH_3 \tag{17}$$

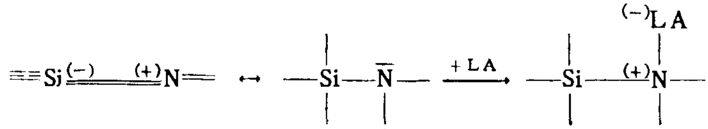
$$ph_3SiLi + HNme_2 \rightarrow ph_3SiNme_2 + LiH \tag{18}$$

$$ph_3SiK + ph_2C{=}Nph \rightarrow ph_2CK{-}(ph_3Si)Nph \tag{19}$$

Formation of a d_π—p_π bond (*30*) is especially characteristic of the Si-N bond. In the bond between N and Si the combined effect of atomic radii, electronegativity difference, bond polarity, and tendency to donate electrons is clearly an optimum compared with the bond between silicon and all other elements, leading to extensive overlapping of the *p* orbitals of the free electron pair of N with the unoccupied *d* orbitals of Si. The tetrahedral configuration of the Si atom is scarcely changed in this process, for electron diffraction and X-ray studies on SiN compounds show only minor deviations from the tetrahedral angle (110 ± 5°). The nitrogen bond angle, on the other hand, undergoes considerable widening compared with that for the sp^3 and sp^2 configurations; it is in the range 130–135° in $me_3SiNHme$, $(me_3Si)_2NH$, and $[{-}(me_3Si)N{-}Si(me)_2{-}]_2$ (*75*, *109*, *174*). It amounts to 119.6 ± 1° in the planar NSi_3 unit of tris(silyl)amine, $N(SiH_3)_3$ (*56*), and presumably also in other isolated NSi_3 structures (*52*). The three angles for the N atom in $[{-}(me_3Si)N{-}Si(me)_2{-}]_2$ have been found to be 91.7°, 135.4°, and 132.8° for a planar arrangement of the Si_3N unit (*174*). In H_3SiNCS and H_3SiNCO the SiNC angle is 180° (*35*, *36*, *64*). For the variable results of N angle determinations in the cyclosilazanes, see Section VI. The results so far obtained are so few and confusing that definite conclusions can hardly be drawn.

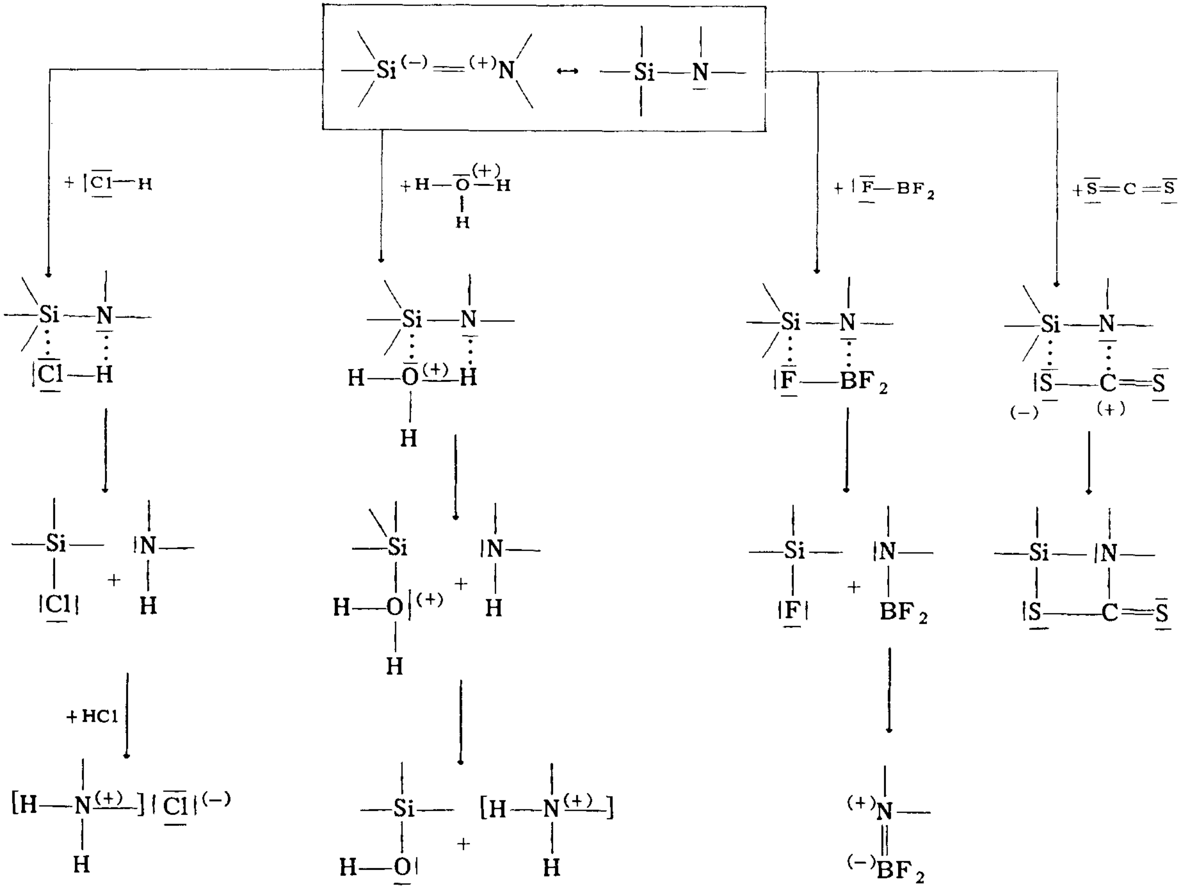
The position regarding bond distances is clearer. Compared with the calculated (*p*—*p*) single bond in Si—N calculated from the sum of the covalent radii (variously assessed as 1.87 or 1.80 Å) and a (p_π—p_π) double bond in =Si=N— (1.62 Å), an interatomic distance of 1.73 ± 0.01 Å has been found for a series of SiN compounds such as $me_3SiNHme$, $N(SiH_3)_3$, H_3SiNCS, and $[{-}(me_3Si)N{-}Si(me)_2{-}]_2$. This indicates a structure $\equiv Si^{(-)}{=}^{(+)}N{=}$. From spectroscopic data the force constant of the SiN bond is seen to be substantially increased. It lies in the region of 4.0 mdynes/Å, compared with 3.26 mdynes/Å for a single SiN bond, and shows that the shortening of the distance does not arise from the contribution of polar structures (*34, 75, 76, 78*). The calculated bond order of 1.26 for $N(SiH_3)_3$ and of 1.18 for $(me_3Si)_2NH$ shows that the free electron pair on nitrogen is not fully absorbed in the *d* orbitals of Si. For the mesomeric equilibria shown in Reactions 4 and 5 the canonical forms with a SiN single bond have considerable weight. With complete transfer of the electron pair from nitrogen, bond orders of 1.33 or 1.50 would occur (*75, 76*). The Si—N dissociation energy derived from spectroscopic data is 77 kcal/mole for $(me_3Si)_2NH$ and 82 kcal/mole for $N(SiH_3)_3$; the Si—N bond energy from calorimetric measurements is 83.3 kcal/mole for me_3SiNet_2 (*26, 75, 76*). Formation of d_π—p_π bonds also accounts for the relatively low dipole moments of SiN compounds (*28, 116*). In the infrared and Raman spectra of SiN compounds, among which structures containing SiNSi, ${}^{Si}_{Si}N^{Si}$, and $(\text{—SiN—})_n$ units have been most studied, the characteristic antisymmetrical Si—N(Si) stretching frequency lies in the region 900–1000 cm^{-1}, and the symmetrical stretching frequency for the same group is at 400–600 cm^{-1}. Increasing use has recently been made of NMR spectra in determining the constitution of SiN compounds (*37, 86, 108*).

The strongly developed d_π—p_π double bond component of the SiN bond is reflected in the chemical behavior of these compounds. The silicon atom is protected to a major extent against nucleophilic attack. Thus the majority of SiN compounds are insensitive to hydrolysis, provided a pH value of 8 is not exceeded. Tris(silyl)amines may be heated for long periods with concentrated alkali without decomposition; they sublime unchanged into the condenser (*52, 147, 156a*). SiN compounds react more readily with Lewis acids (LA), which withdraw the electron pair of the N atom from the d_π—p_π bond with the Si atom:

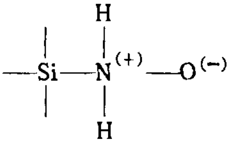


$$=\mathrm{Si}\overset{(-)\qquad(+)}{=\!=\!=\!=}\mathrm{N}= \;\leftrightarrow\; -\underset{|}{\overset{|}{\mathrm{Si}}}-\underset{|}{\bar{\mathrm{N}}}- \xrightarrow{+\mathrm{LA}} -\underset{|}{\overset{|}{\mathrm{Si}}}-\underset{|}{\overset{\overset{(-)}{\mathrm{LA}}}{\overset{|}{{}^{(+)}\mathrm{N}}}}- \qquad (20)$$

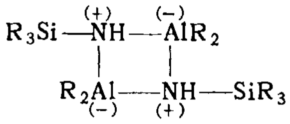
Elements of the third main group of the periodic system are particularly suitable for this purpose. By varying the substituents one is able to influence the stability of the newly formed addition compounds and also to examine the base strength of the SiN compounds. The compounds used include B_2H_6, BR_3, BF_3, Al_2Cl_6, $Al(me)_3$, $Ga(me)_3$. One typical example of the sequence of basicities, taken from a large number of investigations, is: $me_3N > me_2N(SiH_3) > meN(SiH_3)_2 > N(SiH_3)_3 < O(SiH_3)_2 < FSiH_3$ (*95*). Addition products of Lewis acids and SiN compounds often dissociate below room temperature and are also sensitive to moisture since the Si atoms are no longer protected. Pronounced sensitivity of an SiN compound to mois-

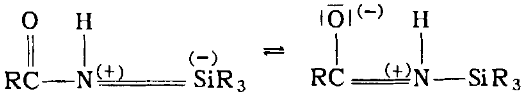

+ HCl
+ H—O—H
+ F—BF2
+ S=C=S
+ HCl

ture is always indicative of a silylammonium structure, in which the d_π—p_π bond has disappeared or is very weak (*119, 153, 154*).



$$-\overset{|}{\underset{|}{Si}}-\overset{H}{\underset{H}{N^{(+)}}}-O^{(-)}$$





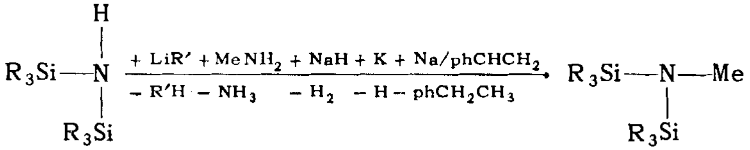
$$RC(=O)-\overset{H}{N}{}^{(+)}=\overset{(-)}{Si}R_3 \rightleftharpoons RC(-|\overline{O}|^{(-)})={}^{(+)}\overset{H}{N}-SiR_3$$

Alkyl and silyl halides prove in general to be too weak as Lewis acids to convert SiN compounds into substituted ammonium derivatives such as $[(H_3Si)_4N]^+X^-$ or $[(H_3Si)_3Nme]^+X^-$ (*136*).

If a four-center mechanism with combined electrophilic and nucleophilic attack on the SiN bond is involved, cleavage of the bond will occur very readily, as for example in its reaction with aqueous acids, hydrogen chloride in benzene, or nonmetallic halides (e.g., see *20*). These reactions have been used not only in detecting SiN bonds but also very extensively in preparative synthesis.

III. Silyl-Substituted Alkali Metal Amides

Alkali bis(silyl)amides were discovered only very recently, but they have become most interesting groups of inorganic reagents because of their convenient physical properties and surprising versatility. They are produced by metallation of bis(silyl)amines (*120, 146, 149, 156, 164a*), but not by silylation of alkali amides (*170a*). Suitable metallating agents are the organic alkali metal compounds, alkali amides, and alkali hydrides. Even the alkali metals themselves will serve, though only in special cases and then preferably in solution in liquid ammonia or in suspension in styrene or a naphthalene-tetrahydrofuran mixture (*52, 107, 163*):



$$R_3Si-\overset{H}{\underset{R_3Si}{N}} \xrightarrow[-R'H\ -NH_3\ \ -H_2\ \ -H-phCH_2CH_3]{+LiR'\ +MeNH_2\ +NaH+K+Na/phCHCH_2} R_3Si-\underset{R_3Si}{N}-Me \qquad (21)$$

(where R′ = pr, bu, ph; Me = Na, K).

Metallation with $NaNH_2$ in benzene suspensions is particularly simple and quantitative. In the case of bis(alkoxysilyl)amines $[(RO)_3Si]_2NH$, which have become readily available (*23*), the organolithium compounds are not suitable as reagents as they cleave the Si—O bonds. Controlled metallation in the homogeneous phase may be brought about in this case by double decomposition, as for example (*156a*):

$$(me_3Si)_2NLi + [(meO)_3Si]_2NH \rightarrow (me_3Si)_2NH + [(meO)_3Si]_2NLi \qquad (22)$$

The same is true for metallation of cyclosilazanes such as $(—R_2Si—NH—)_3$, where the separate NH groups are metallated stepwise. Metallation of the last NH group occurs as a rule only under more drastic conditions (*43, 163, 169*).

The analogous metallation of NH_2 or NH groups with subsequent silylation has led to a number of Si—N compounds not accessible by other routes (*147, 148, 150*).

$$et_3SiNH_2 \rightarrow et_3SiNHMe \rightarrow et_3SiNHSiR_3 \qquad (23)$$

$$R_3SiNHNHSiR'_3 \rightarrow R_3SiNHNLiSiR'_3 \rightarrow R_3SiNHN(SiR'_3)(SiR''_3) \qquad (24)$$

$$ph_2NH \rightarrow ph_2NMe \rightarrow ph_2NSiR_3 \qquad (25)$$

Alkali bis(silyl)amides have previously been formulated as intermediates in complicated reactions, without having been isolated, e.g., in the reaction of et_3SiH with KNH_2 (*74*), of me_3SiCH_2ph with KNH_2 (*54*), or of $(me_3Si)_2NH$ with Na and me_3SiCl in styrene (*52*).

Metallation of bis(silyl)amines is possible not only with alkali metals but also by way of magnesium and aluminum derivatives. Particularly well-formed crystals are obtained with the Grignard reagent in the following reaction (*155*):

$$R_2Mg{\cdot}X_2Mg + 2(me_3Si)_2NH + n\,Oet_2 \rightarrow 2RH + [(me_3Si)_2N]_2Mg{\cdot}X_2Mg{\cdot}(Oet_2)_2{\cdot}(n—2)Oet_2 \qquad (26)$$

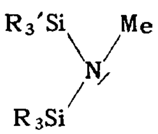
(where R = me, et, pr; X = Cl, Br, I; $n = 2$ for Cl and Br, $= 4$ for I). Lithium aluminum hydride yields hexakis(trimethylsilyl)aluminum triamide, which melts at about 230°C and in which the PMR spectrum shows all the 54 H atoms to be equivalent (*107*).

$$4(me_3Si)_2NH + LiAlH_4 \rightarrow 4H_2 + [(me_3Si)_2N]_3Al + (me_3Si)_2NLi \qquad (27)$$

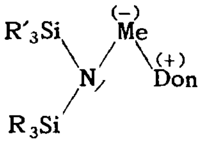
The alkali bis(silyl)amides prepared up to the present are shown in Table I; all are solids except $(me_3Si)(et_3Si)NLi$. They may be recrystallized (or where their solubility characteristics are unsuitable, dissolved and reprecipitated) from hydrocarbons in well-formed but relatively soft colorless crystals. They have definite melting points and may be distilled in vacuum without decomposition, though there is a marked tendency to sublime at a little above the melting point. As a rule they are stable in air, though some turn yellow or brown under the influence of oxygen, particularly when in solution. It is best therefore to carry out the preparations and

TABLE I
ALKALI BIS(SILYL)AMIDES AND THEIR ADDUCTS

Group I



Group II



(Don = donor molecule)

No.	Me	R$_3$Si	R'$_3$Si	Donor	B.P.	Torr	M.P.	Reference
Group I								
1	Li	me$_3$Si			115°	1	70–72°	(*146, 149*)
2	Li	me$_3$Si	et$_3$Si		162–164°	2	—	(*149*)
3	Na	me$_3$Si			204°	2	183°	(*149, 168*)
4	Na	me$_5$Si$_2$					58–62°	(*157*)
5	Na	(meO)$_3$Si					182–184°	(*156*)
6	Na	(etO)$_3$Si					104°	(*156a*)
7	Na	(^{i}prO)$_3$Si					204–206°	(*156a*)
8	Na	me$_2$(etO)Si					97°	(*162a*)
9	Na	me(meO)$_2$Si					171–172°	(*162a*)
10	Na	vi(meO)$_2$Si					184°	(*162a*)
11	Na	me(^{i}prO)viSi					70°	(*162a*)
12	K	(meO)$_3$Si					202°	(*120*)
Group II								
1	Li	me$_3$Si		1 Oet$_2$			95–110° (decomp)	(*149*)
2	Li	me$_3$Si		0.75 OC$_4$H$_8$O			200° (decomp)	(*149*)
3	Li	ph$_3$Si		1 Oet$_2$			380° (decomp)	(*149*)
4	Na	me$_3$Si		1 Oet$_2$			72–74°	(*149*)
5	Na	me$_3$Si		1 OC$_4$H$_8$			70–85° (decomp)	(*149*)
6	Na	me$_3$Si		0.5 OC$_4$H$_8$O			Charring	(*149*)
7	Na	me$_3$Si		1 py			150–160° (decomp)	(*149*)
8	K	me$_3$Si		2 OC$_4$H$_8$O			Charring	(*149*)

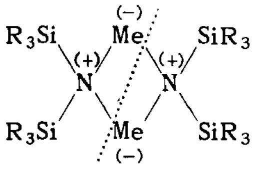
to work up the compounds in an inert atmosphere. The lithium derivatives decompose explosively when heated in a stream of oxygen or treated with concentrated nitric acid. All alkali silylamides burn with a somewhat smoky flame of the characteristic color of the alkali metal and with some of the luminosity due to SiO_2. Sodium bis(trimethylsilyl)amide, which represents an optimum as regards both stability and reactivity, may be stored in a well-sealed flask and, with rapid manipulation, may be removed with a spatula. Hydrolysis by atmospheric moisture is slow. In solution this occurs on adding water in a rapid first stage:

$$(R_3Si)_2NMe + HOH \rightarrow (R_3Si)_2NH + Me^+ + OH^- \tag{28}$$

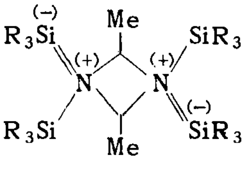
This is followed by slow conversion of the disilazane to the disiloxane. Acids bring about immediate decomposition to the ammonium ion (*149*):

$$(R_3Si)_2NMe + 2H_3O^+ \rightarrow (R_3Si)_2O + H_2O + Me^+ + NH_4^+ \tag{29}$$

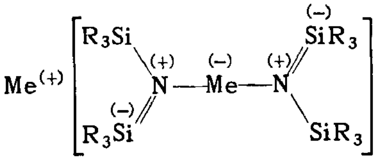
Alkali bis(silyl)amides dissolve readily, sometimes extremely readily, in nonpolar organic solvents such as benzene, toluene, and xylene, e.g., 140 gm $(me_3Si)_2NLi$ in 100 gm xylene at 30°. In these solutions they are present with few exceptions as dimers and show no conductivity. The ^7Li NMR spectrum shows only a single signal. Autocomplexes (C), such as are formed by the dimeric organolithium compounds are thus clearly excluded; the remaining structural possibilities are a bridge complex (A) and a three-center bond complex (B):



(A)



(B)



(C)

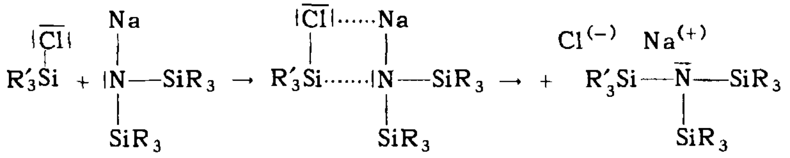
In reactions the dimeric complexes split off. The monomeric units show unusually strongly developed nucleophilic properties and support structure (A). On the other hand, spectroscopic data and the influence of substituents

(R) on the Si atom lead to the conclusion that the free electrons of N are more strongly drawn into the SiN bond than in the case of bis(silyl)amines. A full elucidation of the structures of these compounds (bond angles, bond distances, force constants, and electron distribution) would be valuable in view of their many reactions.

The alkali bis(silyl)amides are not only strongly nucleophilic but, because of the coordinative unsaturation of the alkali atoms which in this case apparently show a strong tendency towards covalency with a maximum coordination number of 2, are also electrophilic reagents. They readily add electron-pair donors such as diethyl ether, tetrahydrofuran, dioxane, and pyridine with, as a rule, one donor molecule per alkali metal atom. When this occurs the dimeric structure is broken down.

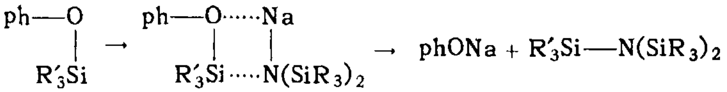
Alkali bis(silyl)amides exhibit a wealth of possible reactions which are certainly not fully explored at present. In explaining them it is simplest to represent the compounds by the monomeric formulas and to consider them as reacting by a four-center mechanism, when their nucleophilic and electrophilic properties are both operative and appear to induce analogous polar structures in the reaction partners.

Among the nonmetallic halides and all other halides which are not salt-like in structure, the reactions with halosilanes are the most clearly defined; as a rule it suffices to heat under reflux in a high-boiling hydrocarbon as solvent. Yields are high. Whereas previously amines substituted by three silyl groups were accessibly only when $RSiH_2$ units were available, over sixty tris(silyl)amines of the most varied types have now been made from alkali bis(silyl)amides by Reaction 30:



$$\mathrm{R'_3Si{-}Cl} + \mathrm{Na{-}N(SiR_3)_2} \rightarrow \mathrm{R'_3Si\cdots Cl\cdots Na\cdots N(SiR_3)_2} \rightarrow \mathrm{Cl^{(-)}\,Na^{(+)}} + \mathrm{R'_3Si{-}N(SiR_3)_2} \qquad (30)$$

Examples are given in Table II. Silyl phenolates (R_3Si—Oph) react analogously, whereas "silyl alcoholates" (R_3Si—Oalk) remain unattacked:



$$\mathrm{ph{-}O{-}SiR'_3} \rightarrow \mathrm{ph{-}O\cdots Na,\ R'_3Si\cdots N(SiR_3)_2} \rightarrow \mathrm{phONa} + \mathrm{R'_3Si{-}N(SiR_3)_2} \qquad (31)$$

The halides of other elements react similarly in so far as they possess free *p* or *d* orbitals: otherwise the reaction is more complicated (as with CCl_4 or $CHCl_3$). However, R_3SiCl is often split off in addition to NaCl. If a di- or trichloride is used, reaction can go in two ways for the same mole-

TABLE II

THE KNOWN TRIS(SILYL)AMINES[a,b]

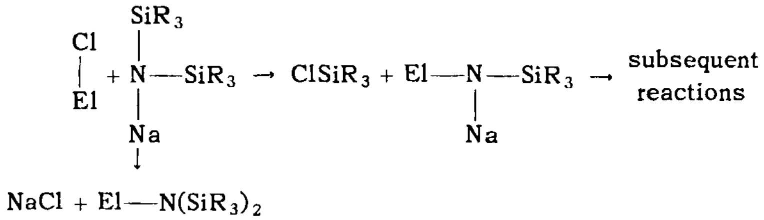
Type	Substituent[c]
$N(SiR_3)_3$	R = H, Cl, me, Ome, Oet, O^{i}pr
$N(SiR_2R')_3$	R = H; = Ome; = me
	R′ = me, SiH_3; = me, vi; = Oet
$N(SiRR'R'')_3$	R = me; R′ = vi; R″ = O^{i}pr
$N(SiR_3)(SiR'_3)(SiR''_3)$	R = me; R′ = et; R″ = pr
$(me_3Si)_2N\text{-}SiR_3$	R = H, F, Cl, Br, I, me, pr, Ome
$(me_3Si)_2N\text{-}SiRCl_2$	R = me, vi, pr, ch, ph
$(me_3Si)_2N\text{-}SiRX_2$	R = me, ph; = vi
	X = OH, Ome, NH_2; = Ome
$(me_3Si)_2N\text{-}Si(me)_2X$	X = $Si(me)_3$, NH_2, Net_2, $N[Si(me)_3]_2$, OH, Ome, Cl
$(me_3Si)_2N\text{-}SiRR'Cl$	R = ph; R′ = me, ph, NH_2
$[(RO)_3Si]_2N\text{-}SiR'Cl_2$	R = me; = et; = ^{i}pr
	R′ = pr, vi, Cl; = Cl; = me, vi, Cl
$(R_2R'Si)_2N\text{-}SiR''_3$	R = Ome; R′ = vi; R″ = me, Ome, Cl
	= et; = Ome, Cl
$(R_2R'Si)_2N\text{-}SiR''_2R'''$	R = Ome; R′ = me, vi; R″ = Cl; R‴ = me, vi
	= me; = Oet; = me; = Cl, Net_2
$(RR'R'')_2N\text{-}SiRR'R'''$	R = me; R′ = vi; R″ = O^{i}pr; R‴ = Cl, O^{i}pr

[a] References: *34a, 52, 102, 105, 136, 146, 147, 149, 151, 156, 156a, 157, 160, 162, 162a, 164, 165, 171.*

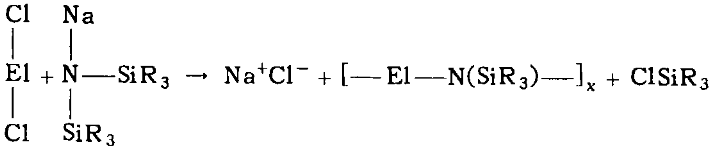
[b] Spring, 1963.

[c] Abbreviations: me = CH_3; et = C_2H_5; pr = $CH_2CH_2CH_3$; ^{i}pr = $CH(CH_3)_2$; ch = C_6H_{11} (cyclohexyl); vi = $CHCH_2$; ph = C_6H_5; py = NC_5H_5 (pyridine); dp = $N_2C_{10}H_8$ (α,α'-dipyridyl); alk = alkyl; ar = aryl; Me = univalent metal.

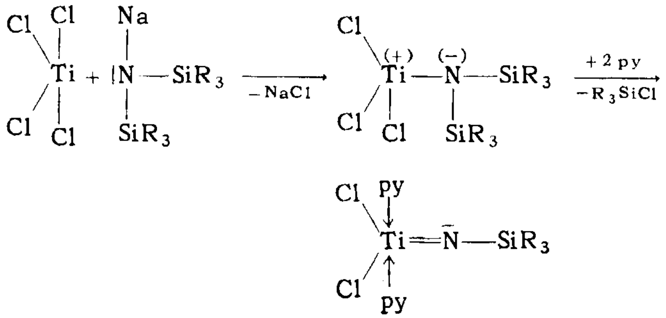
cule, leading to a polymeric structure or to formation of a double bond (Reactions 33 and 34):



$$\begin{array}{l}\underset{\mathrm{El}}{\overset{\mathrm{Cl}}{|}} + \underset{\underset{\mathrm{Na}}{|}}{\overset{\overset{\mathrm{SiR_3}}{|}}{\mathrm{N}}}\!-\!\mathrm{SiR_3} \rightarrow \mathrm{ClSiR_3} + \mathrm{El}-\underset{\underset{\mathrm{Na}}{|}}{\mathrm{N}}-\mathrm{SiR_3} \rightarrow \begin{array}{c}\text{subsequent}\\ \text{reactions}\end{array}\\ \qquad\downarrow\\ \mathrm{NaCl} + \mathrm{El}-\mathrm{N(SiR_3)_2}\end{array} \qquad (32)$$

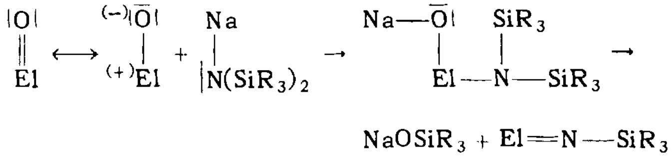


$$\underset{\underset{\mathrm{Cl}}{|}}{\overset{\overset{\mathrm{Cl}}{|}}{\mathrm{El}}} + \underset{\underset{\mathrm{SiR_3}}{|}}{\overset{\overset{\mathrm{Na}}{|}}{\mathrm{N}}}\!-\!\mathrm{SiR_3} \rightarrow \mathrm{Na^+Cl^-} + [-\mathrm{El}-\mathrm{N(SiR_3)}-]_x + \mathrm{ClSiR_3} \qquad (33)$$



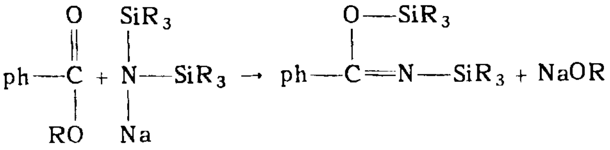
$$\mathrm{TiCl_4} + \mathrm{|N(Na)(SiR_3)-SiR_3} \xrightarrow[-\mathrm{NaCl}]{} \mathrm{Cl_3\overset{(+)}{Ti}-\overset{(-)}{N}(SiR_3)-SiR_3} \xrightarrow[-\mathrm{R_3SiCl}]{+2\,\mathrm{py}} \mathrm{Cl_2(py)_2Ti=\bar{N}-SiR_3} \qquad (34)$$

Doubly bonded oxygen is exchanged for silylamino groups:



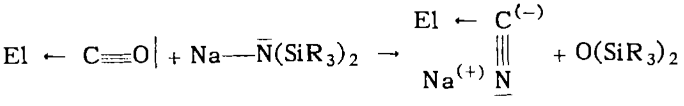
$$\mathrm{|O|{=}El} \longleftrightarrow \mathrm{{}^{(-)}|\bar{O}|-{}^{(+)}El} + \mathrm{Na-|N(SiR_3)_2} \rightarrow \mathrm{Na-\bar{O}|-El-N(SiR_3)-SiR_3} \rightarrow \mathrm{NaOSiR_3} + \mathrm{El{=}N-SiR_3} \qquad (35)$$

Ketones such as benzophenone, fluorenone, and benzoquinone may be transformed in this way into the analogous *N*-silyl-ketimines. From CO_2 or $COCl_2$, bis(silyl)carbodiimide results, while SO_2 or $SOCl_2$ yield the analogous diimide of quadrivalent sulfur. Benzoic esters, on the other hand, are transformed into *N*,*O*-bis(silyl)benzimidic acids:



$$\mathrm{ph-C(=O)-OR} + \mathrm{Na-N(SiR_3)-SiR_3} \rightarrow \mathrm{ph-C(O-SiR_3){=}N-SiR_3} + \mathrm{NaOR} \qquad (36)$$

Carbonyls are converted to the corresponding cyanides with loss of disiloxane:



$$\mathrm{El} \leftarrow \mathrm{C{\equiv}O|} + \mathrm{Na-\bar{N}(SiR_3)_2} \rightarrow \mathrm{El} \leftarrow \mathrm{C^{(-)}{\equiv}\underline{N}\;Na^{(+)}} + \mathrm{O(SiR_3)_2} \qquad (37)$$

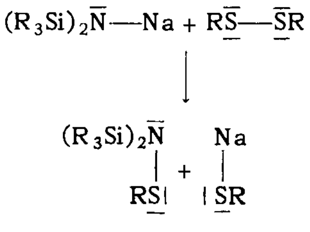
Carbon disulfide reacts essentially according to the equation:

$$\mathrm{CS_2} + \mathrm{NaN(SiR_3)_2} \rightarrow \mathrm{NaSCN} + \mathrm{S(SiR_3)_2} \qquad (38a)$$

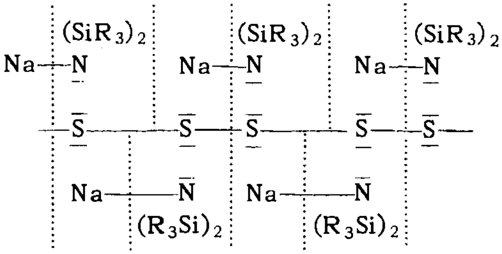
In addition, the following reaction takes place:

$$\mathrm{3CS_2} + \mathrm{4NaN(SiR_3)_2} \rightarrow \mathrm{2(R_3Si)_3N} + \mathrm{2NaSCN} + \mathrm{Na_2CS_3} + \mathrm{S(SiR_3)_2} \qquad (38b)$$

Sulfur chains are cleaved:



(39)



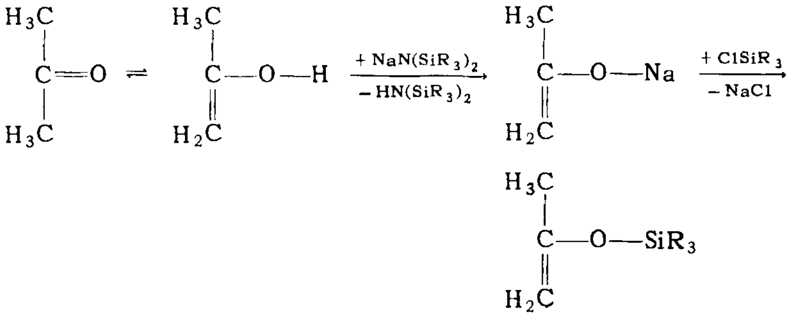
(40)

The S_8 ring with $NaN(SiR_3)_2$ in excess gives $(R_3Si)_2N—S—Na$, while with a deficit of the reagent derivatives such as $(R_3Si)_2N—SSS—Na$ are formed.

The metallating properties of sodium bis(trimethylsilyl)amide are particularly strongly developed in exchanges with "active" hydrogen atoms bonded to carbon:

$$NaN(SiR_3)_2 + H—C\equiv \rightarrow HN(SiR_3)_2 + Na^+[|C\equiv]^- \qquad (41)$$

Enolic structures in tautomeric equilibrium with ketones are easily fixed:



(42)

Sterically hindered Claisen or Stobbe condensations take place in good yield when using $NaN(SiR_3)_2$:

$$2me_2CHCOOR + NaN(SiR_3)_2 \rightarrow (R_3Si)_2NH + NaOR + me_2CHCOme_2COOR \qquad (43)$$

Acetonitrile is thrice metallated:

$$H_3C—C\equiv N \xrightarrow[-3\,HN(SiR_3)_2]{+3\,NaN(SiR_3)_2} Na_3[C=C=N] \xrightarrow[-3\,NaCl]{+3\,ClSiR_3}$$

$$(R_3Si)_2C=C=N—SiR_3 \qquad (44)$$

In Wittig reactions, $NaN(SiR_3)_2$ may also be used with advantage:

$$ph_2C=O + ph_3P + CH_3Br + NaN(SiR_3)_2$$
$$\rightarrow ph_2C=CH_2 + ph_3PO + NaBr + HN(SiR_3)_2 \qquad (45)$$

TABLE III

REVIEW OF THE REACTIONS OF SODIUM BIS(TRIMETHYLSILYL)AMIDE

$(me_3Si)_2NNa$

$+R_2Mg\cdot I_2Mg$	(155)	$[(me_3Si)_2N]_2Mg$
$+BCl_3$	(48a)	$[-(me_3Si)N-BCl-]_3$
$+SnCl_4$	(165)	$(me_3Si)_2N-SnCl_3$ $[(me_3Si)_2N]_2SnCl_2$ $[-(me_3Si)N-SnCl_2-]_x$
$+TiCl_4$	(24)	$(me_3Si)_2N-TiCl_3$
$+TiCl_4/py$	(24)	$(me_3SiN)Ti(py)_2Cl_2$
$+PCl_3$	(165)	$[-(me_3Si)N-PCl-]_x$
$+OPCl_3$	(168)	$[(me_3Si)_2N]_2POCl$ $[(me_3Si)_2N](me_3SiN)PO$
$+S_8$	(118)	$(me_3Si)_2N-SNa$
$+RSSR$	(117)	$(me_3Si)_2N-SR$
$+ClSSCl$	(151)	$[(me_3Si)_2N-S-]_2$
$+ClSCl$	(151)	$[(me_3Si)_2N]_2S$ $(me_3SiN)_2S$
$+SOCl_2$	(168)	$me_3Si-NSN-Si(me)_3$
$+SO_2$	(151)	$(me_3SiN)_2S$
$+Cl_2$	(179)	$(me_3Si)_2N-Cl$ $\downarrow$ $(me_3Si)_2N-NNN$
$+I_2$	(170a)	$(me_3Si)_2N-I$
$+El(\vert C\equiv O\vert)$	(168)	$Na[El(\vert C\equiv N\vert)]$
$+R_3SiCl$	(146, 147)	$(me_3Si)_2N-SiR_3$
$+R_2SiCl_2$	(147)	$(me_3Si)_2N-SiR_2Cl$ $[(me_3Si)_2N]_2SiR_2$
$+RSiCl_3$	(102, 160)	$(me_3Si)_2N-SiRCl_2$
$+XSiX_3$	(162)	$(me_3Si)_2N-SiX_3$
$+me_5Si_2Cl$	(157)	$(me_3Si)_2N-Si_2me_5$
$+R_3SiOph$	(164)	$(me_3Si)_2N-SiR_3$
$+RCH_2Cl$	(114)	$(me_3Si)_2N-CH_2R$
$+CCl_4$, $+CHCl_3$, $+CH_2Cl_2$	(165a)	lively reaction → complex products
$+COCl_2$	(106)	$me_3Si-NCN-Si(me)_3$
$+phCOCl$	(83)	$(me_3SiN)(me_3SiO)Cph$
$+ROCOCl$	(108a)	$(me_3SiN)_2(me_3SiO)COR$
$+BrCN$	(16)	$me_3Si-NCN-Si(me)_3$
$+CO_2$	(165a)	$me_3Si-NCN-Si(me)_3$
$+CS_2$	(165a)	$(me_3Si)_2S$ $(me_3Si)_3N$ Na_2CS_3
$+ph_2CO$	(82)	$me_3SiN=Cph_2$
$+me_2CO$	(85)	$(me_3SiO)Cme=CH_2$
$+phCOOR$	(83)	$(me_3SiN)(me_3SiO)Cph$
$+ph_2CO/ph_3P/meBr$	(85)	$ph_2C=CH_2$
$+me_2CHCOOR$	(85)	$me_2CHCOCme_2COOR$
$+CH_2(CN)_2$	(85a)	$me_3SiN=C=C=C=NSi(me)_3$

A summary of the most important reactions carried out to the present with sodium bis(trimethylsilyl)amide is given in Table III.

IV. Silicon-Nitrogen Compounds with Nitrogen in a Higher Oxidation State Than —3

The versatility of nitrogen in its compounds depends in large measure on the existence of a range of oxidation states between -3 and $+5$. In its combination with silicon, systems are known in which N has an oxidation state of -2, as in the derivatives of hydrazine, H_2NNH_2; of -1, as in derivatives of hydroxylamine, H_2NOH, or diimine, HN=NH (diazene); and $-1/3$, as in derivatives of hydrazoic acid, HN_3:

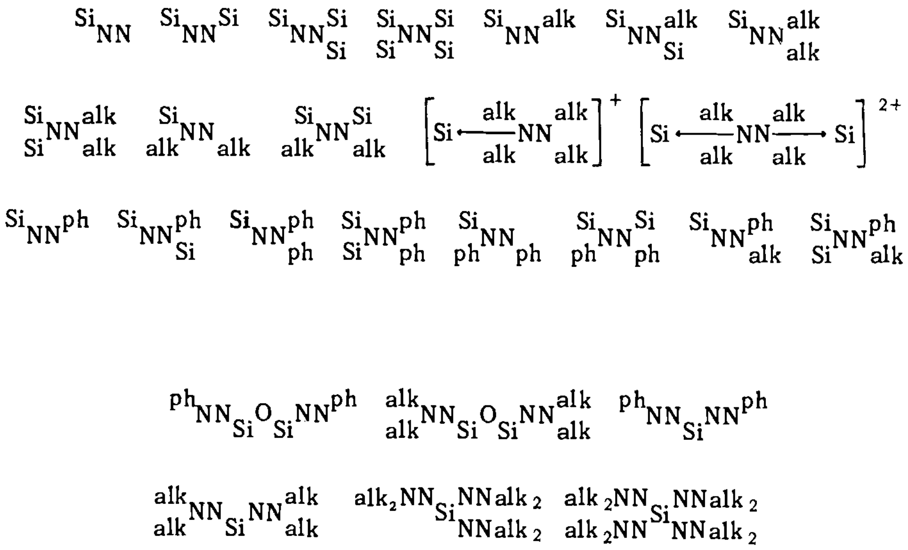
$$\geqslant\mathrm{Si{-}\underset{|}{N}{-}N}< \qquad \geqslant\mathrm{Si{-}\underset{|}{N}{-}O{-}} \qquad \geqslant\mathrm{Si{-}N{=}N{-}} \qquad \geqslant\mathrm{Si{-}N{=}N{=}N}$$

On the other hand, compounds where N has an oxidation state of $+1$ or $+3$, as in $\geqslant$Si—N=O or $\geqslant\mathrm{Si{-}NO_2}$, have not yet been prepared.

A. Silicon-Hydrazine Compounds

1. *Survey*

The preparative objectives of replacing H atoms in H_2NNH_2 by Si atoms and the halogen atoms in $\mathrm{Si(hal)_4}$ by hydrazino groups have been largely realized. The following structural units have so far been synthesized with H, alk ($=C_nH_{2n+1}$; n=1–3), or ph ($=C_6H_5$) attached to Si and H on the N atoms (in all cases where alk or ph is not so shown).



$$\mathrm{{}^{Si}NN} \quad \mathrm{{}^{Si}NN^{Si}} \quad \mathrm{{}^{Si}NN^{Si}_{Si}} \quad \mathrm{{}^{Si}_{Si}NN^{Si}_{Si}} \quad \mathrm{{}^{Si}NN^{alk}} \quad \mathrm{{}^{Si}NN^{alk}_{Si}} \quad \mathrm{{}^{Si}NN^{alk}_{alk}}$$

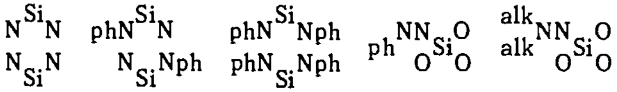
$$\mathrm{{}^{Si}_{Si}NN^{alk}_{alk}} \quad \mathrm{{}^{Si}_{alk}NN_{alk}} \quad \mathrm{{}^{Si}_{alk}NN^{Si}_{alk}} \quad \left[\mathrm{Si}\leftarrow\mathrm{{}^{alk}_{alk}NN^{alk}_{alk}}\right]^{+} \quad \left[\mathrm{Si}\leftarrow\mathrm{{}^{alk}_{alk}NN^{alk}_{alk}}\rightarrow\mathrm{Si}\right]^{2+}$$

$$\mathrm{{}^{Si}NN^{ph}} \quad \mathrm{{}^{Si}NN^{ph}_{Si}} \quad \mathrm{{}^{Si}NN^{ph}_{ph}} \quad \mathrm{{}^{Si}_{Si}NN^{ph}_{ph}} \quad \mathrm{{}^{Si}_{ph}NN_{ph}} \quad \mathrm{{}^{Si}_{ph}NN^{Si}_{ph}} \quad \mathrm{{}^{Si}NN^{ph}_{alk}} \quad \mathrm{{}^{Si}_{Si}NN^{ph}_{alk}}$$

$$\mathrm{{}^{ph}NN_{Si}{}^{O}{}_{Si}NN^{ph}} \quad \mathrm{{}^{alk}_{alk}NN_{Si}{}^{O}{}_{Si}NN^{alk}_{alk}} \quad \mathrm{{}^{ph}NN_{Si}NN^{ph}}$$

$$\mathrm{{}^{alk}_{alk}NN_{Si}NN^{alk}_{alk}} \quad \begin{matrix}\mathrm{alk_2NN} & & \mathrm{NNalk_2}\\ & \mathrm{Si} & \\ & & \mathrm{NNalk_2}\end{matrix} \quad \begin{matrix}\mathrm{alk_2NN} & & \mathrm{NNalk_2}\\ & \mathrm{Si} & \\ \mathrm{alk_2NN} & & \mathrm{NNalk_2}\end{matrix}$$

continued



$$\begin{matrix} N^{Si}N \\ N_{Si}N \end{matrix} \quad \begin{matrix} phN^{Si}N \\ N_{Si}Nph \end{matrix} \quad \begin{matrix} phN^{Si}Nph \\ phN_{Si}Nph \end{matrix} \quad {}_{ph}\begin{matrix} NN_{Si}O \\ O^{Si}O \end{matrix} \quad \begin{matrix} {}^{alk}NN_{Si}O \\ {}_{alk}O^{Si}O \end{matrix}$$

Synthesis of the following missing members of this systematic series should only be a matter of time:

$$ {}^{Si}_{alk}NN^{alk}_{alk} \qquad {}^{Si}_{Si}NN^{alk}_{Si} \qquad {}^{Si}_{ph}NN^{ph}_{ph} \qquad {}^{Si}_{Si}NN^{ph}_{Si} $$

For the following it seems likely that new preparative methods will have to be found:

$$ {}^{Si}_{alk}NN \qquad {}^{Si}_{ph}NN \qquad {}^{Si}_{Si}NN \qquad {}^{Si}_{Si}NN^{alk} \qquad {}^{Si}_{Si}NN^{ph} $$

So far only one representative Si derivative has been discovered (*4*) for the hydrazinium(1+) and (2+) ions, $[N_2H_5]^+$ and $[N_2H_6]^{2+}$; silicon halides seem to show little tendency to add to hydrazine.

A series of silyl derivatives of the acid hydrazides has been prepared, particularly from hydrazides of carbonic acid (*153*) and, in one case, also of phosphoric acid (*9*). The compounds with the structural units shown below [PO denotes —P(=O); CO denotes —C(=O)—] are difficult to obtain in the pure state and are very sensitive to hydrolysis:

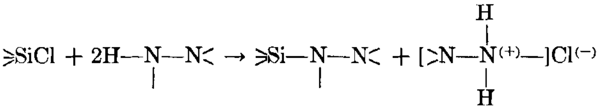
$$ {}^{Si}NN^{CO} \quad {}_{ph}NN^{CO}_{Si} \quad {}^{Si}NN^{CO}_{Si} \quad {}^{alk}_{ph}NN^{CO}_{Si} \quad {}^{Si}_{ph}NN^{CO}_{Si} \quad {}^{OC}_{Si}NN^{CO}_{Si} \quad {}^{SC}_{Si}NN^{CS}_{Si} \quad {}^{Si}NN^{PO} $$

Silyl derivatives of organolithium hydrazides have been prepared many times but actually isolated only in the case of ${}^{me_3Si}_{H}NN^{ph}_{Li}$ (*152*). Normally they are converted, without isolation, into multiply substituted silyl hydrazines. In almost all known silicon-hydrazine compounds, the residual silicon valencies are saturated with hydrogen atoms or organic groups; in only a few cases is silicon simultaneously bonded to oxygen (*101*, *143*, *166*).

2. Preparation of Silyl Hydrazines

The methods used are essentially the same as for amines.

a. Reactions of Hydrazine with Halogenosilanes. In inert organic solvents or in the gas phase (*19*) these reactions occur exothermally, half of the hydrazine being fixed as hydrochloride:



$$ \geqslant SiCl + 2H\text{—}\underset{|}{N}\text{—}N\lessdot \rightarrow\ \geqslant Si\text{—}\underset{|}{N}\text{—}N\lessdot + [\gtrdot N\text{—}\overset{H}{\underset{H}{N^{(+)}}}\text{—}]Cl^{(-)} \qquad (46)$$

In that way only *one* Si group can be bonded to one N atom of the hydrazine. Methyl groups on the same N atom do not interfere with the substitution, though a free NH_2 group will be substituted first (*65*, *144*):

$$\text{meNH—NH}_2 \rightarrow \text{meNH—NHSiR}_3 \rightarrow \text{R}_3\text{SiNme—NHSiR}_3 \qquad (47)$$

Phenyl groups, like silyl groups (except SiH_3), allow no further silyl substitution on the same N atom. Primary silyl hydrazines with R = me, et, or pr cannot be isolated as they immediately undergo further condensation to symmetrical bis(silyl)hydrazines with elimination of hydrazine (*19, 141, 142*):

$$\text{R}_3\text{SiNHNH}_2 + \text{H}_2\text{NNSiR}_3 \rightarrow \text{R}_3\text{SiNHNHSiR}_3 + \text{H}_2\text{NNH}_2 \qquad (48)$$

For the readily isolated $\text{ph}_3\text{SiNHNH}_2$ this condensation occurs under more drastic conditions (*142*). The use of mixtures of chlorosilanes such as $\text{me}_3\text{SiCl}/\text{et}_3\text{SiCl}$ with hydrazine leads to a mixture of $\text{me}_3\text{SiNHNHSime}_3$, $\text{me}_3\text{SiNHNHSiet}_3$, and $\text{et}_3\text{SiNHNHSiet}_3$ in statistical proportions (*142*). Hydrazine is converted by H_3SiI directly into the fourfold silyl-substituted derivative $(H_3Si)_2NN(SiH_3)_2$ (*3*). It has not so far been possible to prepare other fourfold silyl-substituted hydrazines, probably because of steric hindrance by the bulky alk_3Si groups. Dihalogenosilanes react with terminally substituted hydrazines to form compounds of Class IVb (*101, 129, 143*).

$$\text{R}_2\text{SiCl}_2 \rightarrow \text{R}_2\text{Si(NHNR}'_2)_2 \qquad (49)$$

With hydrazine itself, six-membered rings, $[\text{—R}_2\text{SiNHNH}]_2$, are formed together with polymers in which the structural unit $\text{—R}_2\text{SiNHNH—}$ predominates (*19, 101, 141*). In condensations of silyl hydrazines according to the scheme: $2|\overset{\text{Si}}{\diagup}\text{NN}\langle| \rightarrow \overset{\text{Si}}{\diagup}\text{NN}\overset{\text{Si}}{\diagdown} + {>}\text{NN}{<}$, the tendency for reaction to occur has been defined qualitatively as:

$\text{me}_3\text{SiNHNH}_2$ (strong) > $\text{me}_3\text{SiNHNHme}$ (weak) > $\text{me}_3\text{SiNHNme}_2$ (very small);

$\text{R}_2\text{Si(NH}_2)_2 < \text{R}_2\text{Si(NHNH}_2)_2 > \text{R}_3\text{SiNHNH}_2$; $\text{alk}_2\text{Si(NHNHR)}_2 < \text{alk}_2\text{Si(NHNH}_2)_2 > \text{ar}_2\text{Si(NHNH}_2)_2$

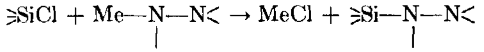
(*101, 144*).

b. Reaction of Hydrazines with Silylamines. This reaction occurs according to the equation:

$$2\text{RNHNH}_2 + (\text{me}_3\text{Si})_2\text{NH} \rightarrow 2\text{RNHNHSi(me)}_3 + \text{NH}_3 \quad (\text{R} = \text{H,ph}) \qquad (50)$$

in satisfactory yield only in presence of small quantities of $(NH_4)_2SO_4$ as catalyst (*40, 130*). Since $(\text{me}_3\text{Si})_2\text{NH}$ must first be prepared from me_3SiCl, the reaction using method (*b*) is more expensive than when (*a*) is used. It can be employed, however, with advantage for valuable hydrazines, since the loss due to forming the hydrazine hydrochloride is eliminated. Silylation with $(\text{me}_3\text{Si})_2\text{NH}$ or me_3SiNHme has also been carried out with varying success for $(\text{phO})_2\text{PO(NHNH}_2)$ and $\text{NH}_2\text{CONHNH}_2$ (*9, 153*).

c. Reaction of Metallated Hydrazines with Halogenosilanes. The reaction according to the equation



$$\geqslant SiCl + Me-\underset{|}{N}-N< \rightarrow MeCl + \geqslant Si-\underset{|}{N}-N< \qquad (51)$$

leads to silyl substitution also on such N atoms as already carry a silyl or phenyl group (*146, 148, 152*):

$$R_2NNHSiR_3 \rightarrow R_2NN(Li)SiR_3 \rightarrow R_2NN(SiR_3)_2 \qquad (52)$$

$$phNHNHSiR_3 \rightarrow phN(Li)NHSiR_3 \rightarrow phN(SiR_3)NHSiR_3 \qquad (53)$$

$$et_3SiNHNHSi(me_3) \rightarrow et_3SiN(Li)NHSi(me)_3 \rightarrow et_3SiN(me_3Si)NHSi(me)_3 \qquad (54)$$

Metallation takes place for phNH—N< more readily than for R_3SiNH—N<, and for et_3SiNH—N< more readily than for me_3SiNH—N<. Alkyl lithiums and aryl lithiums (prLi, buLi, phLi) are particularly suitable as metallating agents for hydrazine derivatives; $NaNH_2$ in benzene suspension, which is effective for metallating silylamines, causes cleavage of the N—N bond. Further silyl substitution may be brought about most readily by adding the solution of the metallated silyl hydrazine dropwise to the halosilane in question. Reaction of hydrazines doubly metallated in the *N,N′* positions, which may be prepared by e.g., addition of Li to azobenzene, with dihalosilanes R_2SiCl_2 gives mainly six-membered rings (*47, 101*):

$$phNNph \rightarrow phN(Li)N(Li)ph \rightarrow [-R_2SiNphNph-]_2 \qquad (55)$$

Metallation of phenylhydrazine to $phN(Li)NH_2$ and subsequent reaction with trialkylchlorosilanes leads, not to *N*-phenyl-*N*-trialkylsilyl hydrazine, but to *N,N′* isomers, presumably according to the equation:

$$phN(Li)NH_2 + alk_3SiCl \rightarrow phN(Li)NHSi(alk)_3 + HCl \rightarrow phNHNHSi(alk)_3 + LiCl \qquad (56)$$

d. Addition of Triorganosilyl Alkalis to Azobenzene or Azoxybenzene. The addition and subsequent careful hydrolysis take place according to the equations (*48, 181*):

$$ph_3SiK + phN{=}Nph \rightarrow ph_3SiNph-NKph \rightarrow ph_3SiNphNHph \qquad (57)$$

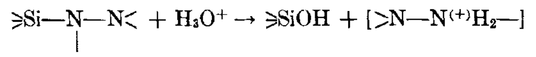
$$HOH + 2ph_3SiLi + phN(O)Nph \rightarrow ph_3SiOLi + ph_3SiNph-NHph + LiOH \qquad (58)$$

Reduction of azoxybenzene and addition of ph_3SiLi to the intermediate phNNph occur simultaneously, leading to the silyl hydrazines IVa/34 and IVa/35.

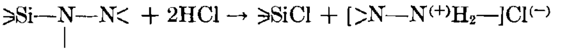
3. Properties of Silyl Hydrazines

The majority of the known silyl hydrazines are colorless mobile liquids, which sometimes smell like camphor or the silyl-free hydrazine. They may be distilled readily in vacuum and are not sensitive to heat; explosive decompositions have never been observed. Silylation as a rule raises the boiling point very little [b.p./12mm of $phNHNH_2$, 120°; of $phNHNHSi(me)_3$, 117°; of $phN(me_3Si)—NHSi(me)_3$, 123°]; there is clearly a balance between the increase in the mass of the molecule and the decrease in the tendency to association due to the breaking of hydrogen bridges between —NH— units. Melting points of trialkylsilyl hydrazines are usually very low, below −100°. Triphenylsilyl hydrazines, on the other hand, are solid white substances at room temperature.

Most silyl hydrazines of Class IVa are readily soluble in the usual organic solvents and are not particularly sensitive to moisture. They are, however, readily cleaved solvolytically by acids or by hydrogen chloride in ether:



$$\geqslant Si—\underset{|}{N}—N< + H_3O^+ \rightarrow \geqslant SiOH + [>N—N^{(+)}H_2—] \qquad (59)$$



$$\geqslant Si—\underset{|}{N}—N< + 2HCl \rightarrow \geqslant SiCl + [>N—N^{(+)}H_2—]Cl^{(-)} \qquad (60)$$

They inflame with concentrated HNO_3 and explode with fuming HNO_3; $(H_3Si)_2NN(SiH_3)_2$ oxidizes explosively on exposure to air. All other silyl hydrazines burn with a luminous white smoky flame. Chloranil oxidizes $me_3SiNHNHSi(me)_3$ in a vigorous reaction to N_2 and $me_3SiSi(me)_3$ (*19*); $et_3SiNHNHph$ and $pr_3SiNHNHph$ are colored deep blue by exposure to atmospheric oxygen (*144*, *158*).

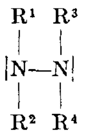
Substances of types IVb and IVd are particularly sensitive to protolysis. Even traces of water transform the bis(hydrazino)silanes IVb/8 and IVb/9 into the hydrazinodisiloxanes IVc/1 and IVc/2. The polysildiazanes $(—me_2Si—NHNH—)_x$ corresponding with the polysilazanes, which are viscous oils or glassy products of molecular weight ca. 3000 formed by reaction of me_2SiCl_2 with N_2H_4, show chain cleavage due to hydrolysis and oxidation, even during careful preparation (*101*). A number of compounds of type IVd also cannot be obtained in a pure state.

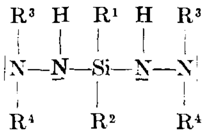
Silyl hydrazines have reducing properties. When a Si—H bond is present, as in $RSiH(NHNR_2)_2$ (IVb/1), they may have very strong reducing properties, e.g., they will convert Cu^{2+} to Cu in the cold, $[Ag(NH_3)_2]^+$ to Ag, and Hg^{2+} to Hg_2^{2+} and Hg. There is a parallel increase in reactivity with hydroxyl groups: IVa/11 is decomposed by alkalis to H_2, $H_2SiO_4^{2-}$, and N_2H_4, and IVb/1 reacts explosively with water or alcohols (*3*, *129*).

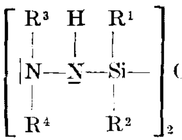
Silyl hydrazines with H atoms still linked to N react with phenyl isocyanate and as a rule only one phNCO is added per N atom:

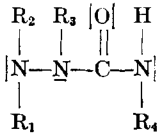
$$\geqslant Si—NH—NH_2 \rightarrow \geqslant Si—N(CONHph)—NH(CONHph) \qquad (61)$$

TABLE IV
SILICON-HYDRAZINE COMPOUNDS(IV)


IVa


IVb


IVc


IVd

No.	R^1	R^2	R^3	R^4	M.P.	B.P.	Torr	n_D	°C	D_4	°C	Prep. Eqn.	Reference
Group IVa													
1	H	H	H	ph$_3$Si	92°	—	—	—	—	—	—	(46)	*(141, 142)*
2	me$_3$Si	H	H	me$_3$Si	—	153–154°	732	1.4177	26	—	—	(50)	*(19, 40)*
					−137°	69–70°	40	1.4268	22	0.8165	21	(46)	*(141, 142)*
3	et$_3$Si	H	H	me$_3$Si	−126°	122°	40	1.4422	17	0.8418	22	(46)	*(141, 142)*
4	et$_3$Si	H	H	et$_3$Si	−123°	161–162°	40	1.4560	20	0.8595	23	(46)	*(19, 142)*
5	pr$_3$Si	H	H	pr$_3$Si	−105°	189–190°	20	1.4562	24	0.8480	21	(46)	*(141, 142)*
6	ph$_3$Si	H	H	ph$_3$Si	+140°	—	—	—	—	—	—	(48)	*(141, 142)*
7	me$_3$Si	me$_3$Si	H	me$_3$Si	—	89°	13	1.4442	20	0.8460	24	(51)	*(146, 148)*
8	et$_3$Si	me$_3$Si	H	me$_3$Si	—	126°	9	1.4612	20	0.8723	24	(51)	*(146, 148)*
9	et$_3$Si	et$_3$Si	H	me$_3$Si	−91°	142–145°	3	1.4739	20	0.8950	22	(51)	*(148)*
10	et$_3$Si	me$_3$Si	H	et$_3$Si	−87°	164°	3	1.4764	20	0.8918	21	(51)	*(146, 148)*
11	H$_3$Si	H$_3$Si	H$_3$Si	H$_3$Si^a	−24°	109.5°	760	—		0.83	20	(46)	*(3)*
12	me$_3$Si	H	H	me		96–97°	760	—		—	—	(47)	*(144)*
13	me$_3$Si	H	me	me$_3$Si		73–75°	40	1.3820	19	0.7708	19	(47)	*(141, 144)*
14	me$_3$Si	H	me	me		100°	760	1.4018	22	0.7659	20	(46)	*(130, 144)*
15	et$_3$Si	H	me	me		55–56°	8	1.4348	20	0.8202	20	(46)	*(128)*
16	pr$_3$Si	H	me	me		87–89°	7	1.4405	20	0.8209	20	(46)	*(128)*
17	(^{i}prO)$_3$Si	H	me	me		45–49°	1	1.3980	20	0.9003	20	(51)	*(166)*

18	me_3Si	H	et	et		144–145°	760	1.4195	20	0.7948	20	(46)	*(128)*
19	et_3Si	H	et	et		85–87°	11	1.4441	20	0.8340	20	(46)	*(128)*
19a	et_2HSi	H	et	et		79–81°	20	1.4341	20	0.8194	20	(50)	*(130)*
20	pr_3Si	H	et	et		114–115°	10	1.4471	20	0.8301	20	(46)	*(128)*
21	me_3Si	me_3Si	me	me		67°	12	1.4390	20	0.8431	19	(51)	*(146, 148)*
22	me_3Si	me	me	H		61–63°	260	1.3818	20	—	—	(46)	*(144)*
23	me_2SiCl	me	me	me_2SiCl		43–46°	10^{-4}	—	—	—	—	(46)	*(19)*
24	me_3Si	H	H	ph	21°	114°	10	1.5254	20	0.9574	26	(46) (50) (56)	*(144, 152)* *(19, 40)*
25	me_3Si	H	H	$^{p}meC_6H_4$		118°	9	1.5174	20	0.9407	20	(56)	*(152)*
26	et_3Si	H	H	ph		129–130°	1	1.5210	20	—	—	(46) (56)	*(144, 152)*
27	pr_3Si	H	H	ph		145.5°	1	1.4918	20	—	—	(46) (56)	*(144, 152)*
28	ph_3Si	H	H	ph	82°	—	—	—	—	—	—	(46)	*(144)*
29	$(^{i}prO)_3Si$	H	H	ph	—	104°	1	1.4493	20	0.9692	20	(51)	*(166)*
30	me_3Si	H	ph	me_3Si	1°	123°	10	1.5060	20	0.9277	25	(51)	*(152)*
31	me_3Si	H	ph	ph	57–60°	135–138°	1	—	—	—	—	(51)	*(148)*
32	me_3Si	me_3Si	ph	ph	—	124–126°	2	1.5720	20	—	—	(51)	*(148)*
33	me_3Si	ph	H	ph	55°	138°	1	—	—	—	—	(51)	*(146, 152)*
34	ph_3Si	ph	H	ph	140–141°							(57) (58)	*(48, 181)*
35	$meSi(ph)_2$	ph	H	ph	119–120°							(58)	*(48)*
36	ph_3Si	ph	ph_3Si	ph	265–266°							(57)	*(181)*
37	me_3Si	H	et	ph		113°	10	1.5152	20	0.9329	24	(62)	*(148)*
38	me_3Si	H	ph	$phCH_2$	−33°	113°	0.5	1.5645	20	1.0032	20	(62)	*(152)*
39	me_3Si	H	ph	me_3C		95–97°	0.5	1.5108	20	—	—	(62)	*(152)*
40	me_3Si	me_3Si	et	ph		100°	2	1.5155	20	0.9356	26	(51)	*(148)*
Group IVb													
1	H	me	me	me		45°	10	1.4348	20	0.8676	20	(49)	*(129)*
2	H	me	et	et		103°	19	1.4440	20	0.8636	20	(49)	*(129)*
3	H	et	me	me		75°	22	1.4392	20	0.8645	20	(49)	*(129)*
3a	H	et	et	et		103°	7	1.4481	20	0.8646	20	(50)	*(130)*

TABLE IV (*Continued*)

No.	R^1	R^2	R^3	R^4	M.P.	B.P.	Torr	n_D	°C	D_4	°C	Prep. Eqn.	Reference
3b	Cl	et	et	et		111°	4	1.4580	20	0.9611	20	(50)	*(130)*
4	me	me	me	me		62°	22	1.4298	20	0.8504	20	(49)	*(129)*
5	me	me	et	et		105°	14	1.4419	20	0.8594	20	(49)	*(129)*
6	et	et	me	me		85°	12	1.4415	20	0.8648	20	(49)	*(129)*
7	et	et	et	et		130°	14	1.4530	20	0.8673	20	(49)	*(129)*
8	ph	ph	me	me	42–43°	191–193°	10	—	—	—	—	(49)	*(101, 143)*
9	ph	ph	H	ph	105–115°	—	—	—	—	—	—	(49)	*(101, 143)*
10	$meSi(NHNet_2)_3$					130–131°	6	1.4529	20	0.8935	20	(50)	*(130)*
11	$etSi(NHNet_2)_3$					134–135°	5.5	1.4578	20	0.8961	20	(50)	*(130)*
12	$Si(NHNet_2)_4$					153–155°	5.5	1.4587	20	0.9009	20	(50)	*(130)*
Group IVc													
1	ph	ph	me	me	146–148°	—	—	—	—	—	—	—	*(101, 143)*
2	ph	ph	H	ph	157–158°	—	—	—	—	—	—	—	*(101, 143)*
Group IVd													
1	H	H	H	me_3Si	80–95°							(61)	*(153)*
2	me_3Si	H	H	me_3Si^b	—							(50)	*(153)*
3	me_3Si	H	me_3Si	me_3Si	110°							(61)	*(153)*
4	H	ph	me_3Si	ph	ca. 37°							(61)	*(153)*
5	me_3Si	ph	me_3Si	ph	oil							(61)	*(153)*
6	et	ph	me_3Si	ph	ca. 5°							(61)	*(153)*
7	$[phNH\text{-}CO\text{-}N(me_3Si)\text{-}]_2$				ca. 60°							(61)	*(153)*
8	$[phNH\text{-}CS\text{-}N(me_3Si)\text{-}]_2$				214–216°							(61)	*(153)*
9	$me_3Si\text{-}NHNH\text{-}PO(Oph)_2$				53–54°							(50)	*(9)*

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[a] Heat of vaporization 8.19 kcal/mole, Trouton's constant 21.4.

[b] Sublimes at 100–110°/1–2 Torr.

The resulting silyl semicarbazides and silyl-substituted hydrazinodicarbonic anilides of substances of type IVd hydrolyze readily. This allows a differentiation, for example, between the isomers $R_3SiNph—NH_2$ and $R_3SiNH—NHph$. The first will give phNHNHCONHph by phNCO addition and hydrolysis and the second HN(CONHph)—Nph(CONHph). In this way it has been possible to elucidate the position of ph or R_3Si on *N* or *N′* in a series of bis(silyl) or phenylsilyl hydrazines (*19*, *153*).

N-Lithium-*N*-phenyl-*N′*-trimethylsilyl hydrazine, $phNLi—NHSi(me)_3 \cdot Oet_2$, separates from ether in large colorless crystals which immediately turn blue in air and may inflame. Here and in all other cases where the LiCl formed in the metallation reactions (Section IV,A,*2*,*c*) contains some undecomposed lithiumsilyl hydrazide, it is necessary to anticipate ignition during filtration or centrifugation if air is admitted. The lithiumsilyl hydrazides react not only with halosilanes but also with organic halides (*152*).

$$phN(Li)NHSi(me)_3 + XR \rightarrow LiX + phNR—NHSi(me)_3 \qquad (62)$$

(where R = et, me_3C, $phCH_2$). Oxidation with Br_2 or I_2 leads to the deep blue silyldiazenes $R_3Si—N{=}N—R$ (*158*). The properties of SiN rings with SiNN structural units are dealt with in Section VI.

Little is known of the physical properties and detailed structures of the silyl hydrazines apart from the usual determinations of melting point, boiling point, density, refractive index, and molecular refraction. Infrared and Raman measurements on $(H_3Si)_2NN(SiH_3)_2$ and $(D_3Si)_2NN(SiD_3)_2$ have shown a staggered D_{2d} configuration and not a planar framework Si_2NNSi_2. The ν_{as} SiN(Si) vibrational frequencies lie at 1026–1013 cm^{-1} and are unusually high (*5*).

In the Si hydrazine compounds the free electron pair on N is considerably involved in $p_\pi—d_\pi$ bonding, as in other SiN compounds. No quantitative study has yet been made of the basicity of these compounds or of reactions with strong Lewis acids.

B. SILICON-HYDROXYLAMINE COMPOUNDS

Hydroxylamine, H_2NOH, does *not* react with trialkylchlorosilanes in a manner analogous to hydrazine, N_2H_4, in spite of the structural relationship. It might be expected that a monosilyl-substituted derivative $R_3Si(NHOH)$ would first be formed and that this would lose hydroxylamine and condense to bis(silyl)hydroxylamine, $R_3SiNHOSiR_3$, which after metallation could be transformed into a tris(silyl)hydroxylamine, $(R_3Si)_2NO(SiR_3)$. The exothermic reaction

$$2H_2NOH + R_3SiCl \rightarrow R_3Si(NH_2O) + [H_3NOH]Cl \qquad (63)$$

(where R = me, et, ph; and ether suspension is at 0°) stops, however, at the stage shown, even when the proportions of reactants are varied, giving a simple silyl-substituted hydroxylamine (*154*, *186*). Infrared and NMR studies show that of the three possible isomeric structures (*a*) $\mathrm{H_2N{-}O{-}SiR_3}$, (*b*) $\mathrm{R_3Si{-}NH{-}OH}$, and (*c*) $\mathrm{R_3Si{-}N^{(+)}H_2{-}O^{(-)}}$, (*c*) is the most probable (*154*).

The trialkylsilyl hydroxylamines are colorless liquids which are miscible with the usual organic solvents, can be stored in ampoules without decomposition, and do not decompose when heated to their boiling points. The case for structure (*c*) is supported by their sensitivity to hydrolysis (no stabilization of the SiN bond by the $p_\pi{-}d_\pi$ component) and by the reactions with phNCO (*154*), $\mathrm{CH_2CO}$ and $\mathrm{CH_2CHCOOR'}$ (*186*). These lead to the corresponding doubly substituted hydroxylamine derivatives via the silylated derivatives $\mathrm{(phNHCO)N(SiR_3)O(CONHph)}$, $\mathrm{(CH_3CO)N(SiR_3)O(COCH_3)}$, and $\mathrm{(R'OCOCH_2CH_2)N(SiR_3)O(CH_2CH_2COOR')}$ after hydrolytic cleavage of the silyl group. Hydrogen chloride in benzene brings about cleavage to $\mathrm{R_3SiCl}$ and $\mathrm{[H_3NOH]Cl}$. The hydrolyzates reduce $\mathrm{[Ag(NH_3)_2]^+}$ and give a positive benzhydroxamic acid reaction.

C. SILICON DIAZENES

Trialkylsilyl groups when bonded to an N atom behave like aromatic organic groups in many cases. In spite of many attempts, silicon compounds of the type $\mathrm{R_3Si{-}N{=}N{-}SiR_3}$, analogous to the organic azo compounds $\mathrm{ar{-}N{=}N{-}ar}$, have not yet been isolated. Even the mixed diazenes $\mathrm{R_3Si{-}N{=}N{-}ar}$ are markedly unstable, although they are formed from the analogous hydrazines $\mathrm{R_3Si{-}NH{-}NH{-}ar}$ on exposure to air and are recognized by a deep blue color on the surface (*144*). They may be obtained in yields up to 30% by the reaction below, after a complicated processing of the reaction mixture (*158*):

$$\mathrm{R_3Si{-}NLi{-}NLi{-}ar + X_2 \rightarrow R_3Si{-}N{=}N{-}ar + 2LiX} \tag{64}$$

(where X = Br, I; R = me, et, pr; ar = ph, $p{-}\mathrm{C_6H_4(CH_3)}$; at $< -30°$ in ether).

A less useful reaction is:

$$\mathrm{R_3Si{-}NH{-}N(Li)ph + \tfrac{1}{2}O_2 \rightarrow R_3Si{-}N{=}N{-}ph + LiOH} \tag{65}$$

The trialkylsilylaryl diazenes VI/1–4 cannot be obtained pure in spite of repeated distillation. They are always contaminated by 10–60% of trialkylsilylaryl amines formed in the secondary reaction

$$\mathrm{R_3Si{-}NH{-}NLi{-}ar + \tfrac{1}{2}X_2 \rightarrow R_3Si{-}NH{-}ar + LiX + \tfrac{1}{2}N_2} \tag{66}$$

Studies of the ESR, NMR, ultraviolet, infrared, and Raman spectra lead to the conclusion that they are diazenes and not hydrazyl radicals,

$R_3Si—NH—\dot{N}—ar$ (*84*). The deep blue compounds show strong absorption at 575–585 mμ and at 275 mμ in the ultraviolet. They are quite stable thermally and may be stored for years in sealed ampoules; there is only slight decomposition to N_2 and $arSiR_3$ on distillation. The most stable and easiest to prepare in a pure state is tripropylsilylphenyldiazene, VI/3.

The compounds are, however, uncommonly sensitive to the solvolytic reagents. Ether or benzene solutions of $me_3SiNNph$ are decolorized on standing for a few days. Solvolytic cleavage occurs as follows:

$$2R_3Si—N{=}N—ph + 2R'H \rightarrow phNHNHph + N_2 + 2R'SiR_3 \qquad (67)$$

(where R = me, pr; R′ = OH, Ome, Cl, phCOO).

A secondary decomposition reaction is:

$$R_3Si—N{=}N—ar + R'H \rightarrow arH + N_2 + R_3SiR' \qquad (68)$$

Hydrogenation with hydrogen over a palladium catalyst sometimes leads quantitatively to $R_3SiNHNHar$ (R = pr, ar = ph) with formation sometimes of up to 50% of $R_3SiNHar + \frac{1}{2}N_2$ (R = me, ar = ph) (*159*).

D. Silicon Azides

Since the earlier preparation (1954) of silicon tetraazide $Si(N_3)_4$ (*175*), this type of compound has been studied in more detail only recently after it had been established that most compounds of this group did not possess the extraordinarily explosive character of organic azides, but had a fairly high thermal stability. Derivatives with 1, 2, 3, and 4 azido groups on one Si atom are known; other substituents on Si are H, me, ph, and Cl:

$$NNN_{Si} \qquad NNN_{Si}NNN \qquad \begin{matrix}NNN & & NNN\\ & Si & \\ NNN & & \end{matrix} \qquad \begin{matrix}NNN & & NNN\\ & Si & \\ NNN & & NNN\end{matrix}$$

Silyl azides may be prepared by the following methods:

a. Cleavage of a Si-N Bond with Hydrazoic Acid. Cleavage occurs according to the equation:

$$\geqslant Si—N< + 2HNNN \rightarrow \geqslant Si—NNN + [>N^{(+)}H_2]N_3^{(-)} \qquad (69)$$

Dibutyl ether is a suitable solvent. The compounds $(H_3Si)_3N$, $(H_3Si)_2Net$ (*36*), and $(me_3Si)_2NH$ (*17*) have been decomposed in this way. Liberation of H_2 from SiH and HN_3 is not observed, not even with SiH_4 (*175*).

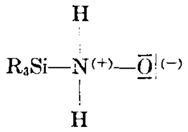
b. Reaction of Halosilanes with Alkali Azides. Reaction is according to the equation:

$$\geqslant Si—Cl + MeNNN \rightarrow \geqslant Si—NNN + MeCl \qquad (70)$$

These reactions are favored by catalytic quantities of Al_2Cl_6, $LiAlH_4$, or AlH_3 (*175*) and occur within 1–3 days in high yield at room temperature

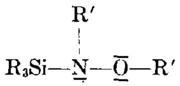
TABLE V

SILICON-HYDROXYLAMINE COMPOUNDS(V), SILICON DIAZINES(VI), AND SILICON AZIDES(VII)



$R_3Si{-}\overset{H}{\underset{H}{N^{(+)}}}{-}\underline{\bar{O}}|^{(-)}$

Va

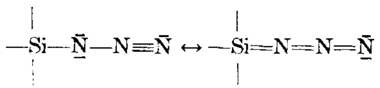


$R_3Si{-}\overset{R'}{\underline{N}}{-}\underline{\bar{O}}{-}R'$

Vb

$R_3Si{-}\bar{N}{=}\bar{N}{-}R'$

VI



$-\overset{|}{\underset{|}{Si}}-\underline{\bar{N}}-N{\equiv}\bar{N} \leftrightarrow -\overset{|}{\underset{|}{Si}}{=}N{=}N{=}\underline{\bar{N}}$

VII

No.	Compound	M.P.	B.P.	Torr	n_D	°C	D_4	°C	Prep. Eqn.	Ref.
Group V (R′ = phNHCO—)										
1	$\mathrm{me_3SiNH_2O}^a$	−77°	100°	760	1.4051	20	0.8572	20	(63)	(*154, 186*)
2	$\mathrm{et_3SiNH_2O}^a$	−65°	172°	760	1.4392	20	0.8876	20	(63)	(*154*)
3	$\mathrm{ph_3SiNH_2O}$	59°							(63)	(*154*)
4	$\mathrm{me_3SiN(R')O(R')}$	128–138°							(B)	(*154*)
5	$\mathrm{et_3SiN(R')O(R')}$	79–81°							(B)	(*154*)
Group VI^b										
1	$\mathrm{me_3SiNNph}$	(−72°	78°	6	1.5190	20	0.9304	29)	(64)	(*158*)
2	$\mathrm{et_3SiNNph}$		(106°	8	1.5140	20)			(64)	(*158*)
3	$\mathrm{pr_3SiNNph}$		(130°	4	1.5065	20	0.9061	24)	(64)	(*158*)
4	$\mathrm{me_3SiNNC_6H_4{}^p me}$		(108°	7	1.5225	20)			(64)	(*158*)
Group VII										
1	$\mathrm{H_3SiNNN}$	−81.8°	~28°	760					(69)	(*36*)
2	$\mathrm{me_3SiNNN}^a$	−95°	87–96°	760					(69) (70) (Dd)	(*17, 27, 138*)
3	$\mathrm{meCl_2SiNNN}$	—	100.5°	760					(70)	(*137*)
4	$\mathrm{me_2phSiNNN}$	—	70°	0.15					(70)	(*173*)
5	$\mathrm{ph_3SiNNN}$	81°	—	—					(70)	(*173, 178*)

6	$me_2Si(NNN)_2$	144.3°	760			(70) (71)	(*138*)
7	$meClSi(NNN)_2$	47°	20			(70)	(*137, 138a*)
8	$ph_2Si(NNN)_2$	85–90°	10^{-3}	1.5887	20	(70)	(*138a, 177*)
9	$meSi(NNN)_3$	~70–73°	20			(70)	(*137, 138a*)
10	$phSi(NNN)_3$	63°	0.01			(71)	(*137*)
11	$Si(NNN)_4$	Crystalline				(70)	(*175*)
12	$(me_3Si)_2NNNN$	40–42°	11			(D)	(*179*)

---

[a] Vapor pressure curve (log P Torr): V/1 $-2011/T + 8{,}265$; $V/2$ $-2499/T + 8{,}500$; VII/2 $-1915/T + 8{,}102$. Heat of vaporization (kcal/mole): V/1, 9.2; V/2, 11.42. Trouton's Constant: V/1, 24.6; V/2, 25.7.

[b] VI/1 contaminated with 25% $me_3SiNHph$; VI/2 with 60% $et_3SiNHph$; VI/3 with 10% $pr_3SiNHph$; VI/4 with ca. 50% $me_3SiNHC_6H_4CH_3$.

in pyridine, tetrahydrofuran, benzene, or at 230–250° in $ZnCl_2/KCl$ salt melts (*138*).

c. Exchange Reactions on Si Atoms. Exchange occurs according to the equation

$$R-\overset{|}{\underset{|}{Si}}-NNN + R'-\overset{|}{\underset{|}{Si}}-Cl \rightarrow R'\overset{|}{\underset{|}{Si}}-NNN + R-\overset{|}{\underset{|}{Si}}-Cl \qquad (71)$$

in presence of Al_2Cl_6 and under reflux quantitatively between me_3SiNNN and me_2SiCl_2, as well as with $phSiCl_3$ (*137*, *138*).

d. Thermal Decomposition of Tetrazoles. Thermal decomposition of 1-trimethyl-silylamino-3-trimethylsilyltetrazole leads, among other products, to me_3SiNNN and $me_3SiNCNSi(me)_3$ (*17*).

Silicon azides with one or two azido groups are thermally stable up to 300°. As a rule they decompose slowly from 500° with loss of nitrogen. They are not sensitive to shock and explode only when ignited. Pyrolysis of me_3SiNNN or decomposition in the light from a mercury arc leads to H_2, N_2, CH_4, C_2H_6, C_2H_4, C_2H_2, HCN, HN_3, NH_4N_3, and nonvolatile polymers (*27*). Nitrogen is split off in ultraviolet light even at room temperature. In contrast to the compounds VII/2–8, H_3SiNNN decomposes slowly on storage with evolution of SiH_4 (*36*). The compounds ph_3SiNNN and $ph_2Si(NNN)_2$ react with triphenylphosphine in boiling ether with loss of N_2 and formation of the stable compounds $ph_3Si{-}N{=}Pph_3$, m.p. 211–213°, and $ph_3P{=}N{-}Si(ph)_2{-}N{=}Pph_3$, m.p. 190–191° (*177*). Phenyltriazidosilane, $phSi(NNN)_3$, may be distilled at 63° in high vacuum without decomposition; $meSi(NNN)_3$ and $Si(NNN)_4$, on the other hand, detonate (*137*, *175*). All silicon azides are sensitive to hydrolysis.

The infrared spectrum of silicon azides shows a characteristic ν_s NNN frequency at 1290–1325 cm^{-1}; SiN vibrations have not been recorded. From the microwave spectrum an angular structure for H_3SiNNN has been unexpectedly deduced (*36*); $p_\pi{-}d_\pi$ bonding between Si and N must therefore be either absent or only weakly developed. The thermal stability of mono- and bis(azido)silanes has been attributed to resonance between structures such as:

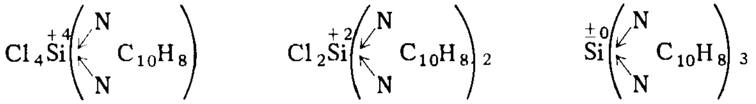
$$\underline{\bar{N}}{=}N{=}\bar{N}{-}SiR_2{-}\bar{N}{=}N{=}\underline{\bar{N}} \leftrightarrow \bar{N}{\equiv}N{-}\underline{\bar{N}}{-}SiR_2{-}\underline{\bar{N}}{-}N{\equiv}\bar{N}$$
$$\leftrightarrow \bar{N}{\equiv}N{-}\bar{N}{=}SiR_2{=}\bar{N}{-}N{\equiv}\bar{N} \leftrightarrow \underline{\bar{N}}{=}N{=}N{=}SiR_2{=}N{=}N{=}\underline{\bar{N}}$$

Reaction of lithium azide with bis(trimethylsilyl)chloramine (tetrahydrofuran, 20°, 2 days, high yield) gives bis(trimethylsilyl)azidoamine, $(me_3Si)_2N{-}NNN$, a colorless liquid, b.p. 40–42°, which decomposes above 150° with evolution of nitrogen (*179*). It is the first stable inorganic compound to be prepared with four adjacent N atoms. The structure proposed is that of a tetrazadiene $(me_3Si)_2N{=}\bar{N}{-}\bar{N}{=}\underline{\bar{N}}$; from the readiness of silyl migration and the stability of the compound, $me_3Si{-}\bar{N}{=}\bar{N}{-}\bar{N}{=}\bar{N}{-}Si(me)_3$ should also be considered as a possible structure.

V. Silicon-Nitrogen Compounds with Silicon in a Lower Oxidation State Than +4

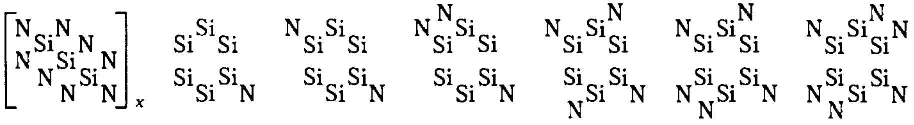
A. GENERAL SURVEY

Silicon-nitrogen compounds with the Si atom in a lower oxidation state than +4 have been isolated by reducing complexes formed by silicon halides with α,α′-dipyridyl or as disilanyl derivatives. All other known compounds of this class have more complex structures: in the case of Si^{2+} each Si atom is linked to two others to form chain or ring structures; for Si^{1+} the Si atom is surrounded by three others to form ring structures of high molecular weight:

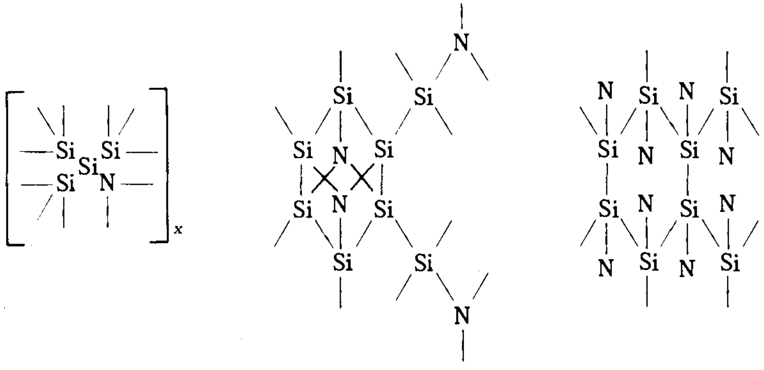


α,α′-Dipyridyl complexes

Disilanyl structures (with $\overset{+3}{\mathrm{Si}}$—$\overset{+3}{\mathrm{Si}}$ bonds)



Polysilane(+2) *chains and aminosiloxenes* (with Si—$\overset{+2}{\mathrm{Si}}$—Si bonds)



Polysilane(+1) *rings*

(N and Si are atoms saturated by H, R, or O; —N— and $\mathrm{Si}\leqslant$ are atoms bonded to further Si atoms.)

B. α,α'-DIPYRIDYL COMPLEXES OF Si(0) AND Si(+2)

When the white addition product of $SiCl_4$ with α,α'-dipyridyl (dp) (*170*) is reduced with two equivalents of dilithium dipyridyl in tetrahydrofuran, dark green crystals of silicon(II) dichloride-2-α,α'-dipyridyl separate from the deep green solution (*60*):

$$SiCl_4(N_2C_{10}H_8) + Li_2N_2C_{10}H_8 \rightarrow 2LiCl + SiCl_2(N_2C_{10}H_8)_2 \qquad (72)$$

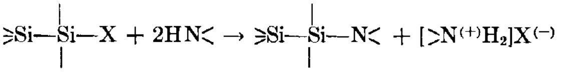
With 2 $Li_2 \cdot dp$ the violet solution yields black crystals of silicon(0)-3-α,α'-dipyridyl:

$$SiCl_4dp + 2Li_2{\cdot}dp \rightarrow 4LiCl + Si(dp)_3 \qquad (73)$$

$Si(dp)_3$ is converted to $SiCl_2(dp)_2$ on treatment either with Cl_2 or with $SiCl_4dp$ in tetrahydrofuran solution; with iodine it yields $SiI_4(dp)_2$. Both compounds with silicon in the oxidation state +2 or 0 are sensitive to air (*60*).

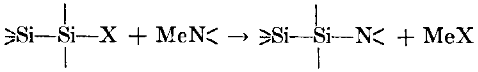
C. DISILANYL AMINES

These compounds are formed by aminolysis of disilanyl halides such as Si_2H_5Cl, Si_2H_5Br, Si_2H_5I, Si_2Cl_6, Si_2me_5Cl, $me_2ClSiSiClme_2$ with NH_3 or me_2NH:



$$\geqslant Si-\overset{|}{\underset{|}{Si}}-X + 2HN< \;\rightarrow\; \geqslant Si-\overset{|}{\underset{|}{Si}}-N< + [>N^{(+)}H_2]X^{(-)} \qquad (74)$$

Alternatively, disilanyl halides may be reacted with metallated nitrogen derivatives such as $NaN[Si(me)_3]_2$ and Ag[NCO] (or Ag[NC]):



$$\geqslant Si-\overset{|}{\underset{|}{Si}}-X + MeN< \;\rightarrow\; \geqslant Si-\overset{|}{\underset{|}{Si}}-N< + MeX \qquad (75)$$

A third method is the coupling of Si—Si bonds by photolysis (*6*):

$$2H_3SiNmeSiH_3 \rightarrow H_2 + H_3SiNme{-}SiH_2SiH_2{-}NmeSiH_3 \qquad (76)$$

Ammonia reacts with Si_2H_5I to form tris(disilanyl)amine, $N(Si_2H_5)_3$, but with me_5Si_2Cl to form only bis(pentamethyldisilanyl)amine, $HN(Si_2me_5)_2$. This is analogous to the reactions of H_3SiI and me_3SiCl, which give $N(SiH_3)_3$ and $(me_3Si)_2NH$ (*139*, *157*, *171*). With $me_2ClSiSiClme_2$ suitably diluted the tetrasilapiperazine ring system, $[-me_2Si-me_2Si-NH-]_2$, results (*157*). There is a tendency for $Si_2H_5Nme_2$ and $Si_2Cl_5N[Si(me)_3]_2$ to disproportionate into $Si_2H_4(Nme_2)_2$ and Si_2H_6 or into $[(me)_3Si]_2N{-}Si_2Cl_4{-}N[Si(me)_3]_2$

TABLE VI

DISILANYL AMINO COMPOUNDS (GROUP VIII)

No.	Compound	M.P.	B.P.	Torr	n_D	°C	D_4	°C	Prep. Eqn.	Ref.
1	$(H_3Si\text{-}H_2Si)_3N$[a]	−97°	176°	760			0.873	0	(74)	(*45*, *171*)
2	$H_3Si\text{-}H_2Si\text{-}Nme_2$[d]		66°	760					(74)	(*94*)
3	$me_2N\text{-}SiH_2SiH_2\text{-}Nme_2$[d]		129°	760					(V) (C)	(*94*)
4	$H_3SiNme\text{-}SiH_2SiH_2\text{-}NmeSiH_3$								(76)	(*6*)
5	$(me_3Si\text{-}me_2Si)_2NH$[a]	—	134°	40	1.4556	30	0.8053	30	(74)	(*139*, *157*)
6	$(me_3Si\text{-}me_2Si)_2NNa$	62°	—	—	—	—	—	—	(V) (C)	(*157*)
7	$me_3Si\text{-}me_2Si\text{-}NCO$[a]	—	160°	760	1.4337	30	0.8537	30	(75)	(*139*)
8	$me_3Si\text{-}me_2Si\text{-}CN$[b]	—	176°	760	1.4374	30	0.8136	30	(75)	(*29*)
9	$(\text{-}me_2Si\text{-}me_2Si\text{-}NH\text{-})_2$	1°	61°	2	1.4760	20	0.8458	20	(74)	(*157*)
10	$me_3Si\text{-}me_2Si\text{-}N[Si(me)_3]_2$[c]	< −70°	93°	14	1.442	20	0.822	20	(75)	(*157*)
11	$(me_2N)_3Si\text{-}Si(Nme_2)_3$	(subl. 270–280°, in high vac., 70–80°)							(74)	(*176*)

[a] Vapor pressure (log P Torr): VIII/1 $-2328{,}9/T + 8{,}0645$; VIII/5 $9{,}0138 - 3021{,}16/T$; VIII/7 $8{,}2471 - 2309/T$; VIII/8 $8{,}3347 - 2452/T$. Heat of vaporization (kcal/mole): VIII/1, 10.66; VIII/5, 13.83; VIII/7, 10.57; VIII/8, 11.22.

[b] Trouton's constant (cal/mole/deg): VIII/1, 23.7; VIII/5, 28.1; VIII/7, 24.5; VIII/8, 25.0 me_5Si_2CN and me_5Si_2NC.

[c] 90% pure.

[d] See Abedini, M., and MacDiarmid, A. G., *Inorg. Chem.* **2,** 608 (1963).

and Si_2Cl_6 (*94*, *157*). The majority of disilanyl nitrogen compounds which have been prepared are quite stable. Thus, $N(Si_2H_5)_3$ decomposes slowly at $>110°$ and $Si_2(Nme_2)_6$ sublimes without decomposition at 270–280°. Boron trifluoride cleaves $N(Si_2H_5)_3$ and $HN(Si_2me_5)_2$ forming Si_2H_5F or me_5Si_2F. Whereas $N(Si_2H_5)_3$ inflames in air and is decomposed by aqueous alkali according to the equation

$$N(Si_2H_5)_3 + 12OH^- + 12H_2O \rightarrow 18H_2 + 6H_2SiO_4^{2-} + NH_3 \qquad (77)$$

$Si_2(Nme_2)_6$ is not attacked by alkalis. The Si—Si bond is, however, cleaved in an unusual way by acids (*176*). The compound $HN(Si_2me_5)_2$ is much more difficult to metallate with $NaNH_2$ in benzene than is $HN[Si(me)_3]_2$; the resulting $NaN(Si_2me_5)_2$ is sensitive to air and moisture (*157*). The individual compounds of group VIII are listed in Table VI.

D. Iminopolysilanes($+2$ to $+3$)

Si_2Cl_6 and Si_3Cl_8 react with liquid ammonia or with gaseous ammonia in inert solvents in the same way as $SiCl_4$. Ammonium chloride is produced together with amorphous white substances of high molecular weight, which are sensitive to moisture. These contain —NH— groups in place of the halogen atoms of the starting material (iminopolysilanes; "silicon imides"):

$$Si_nCl_{2n+2} + (3n + 3)NH_3 \rightarrow 1/x[Si_n(NH)_{n+1}]_x + (2n + 2)NH_4Cl \qquad (78)$$

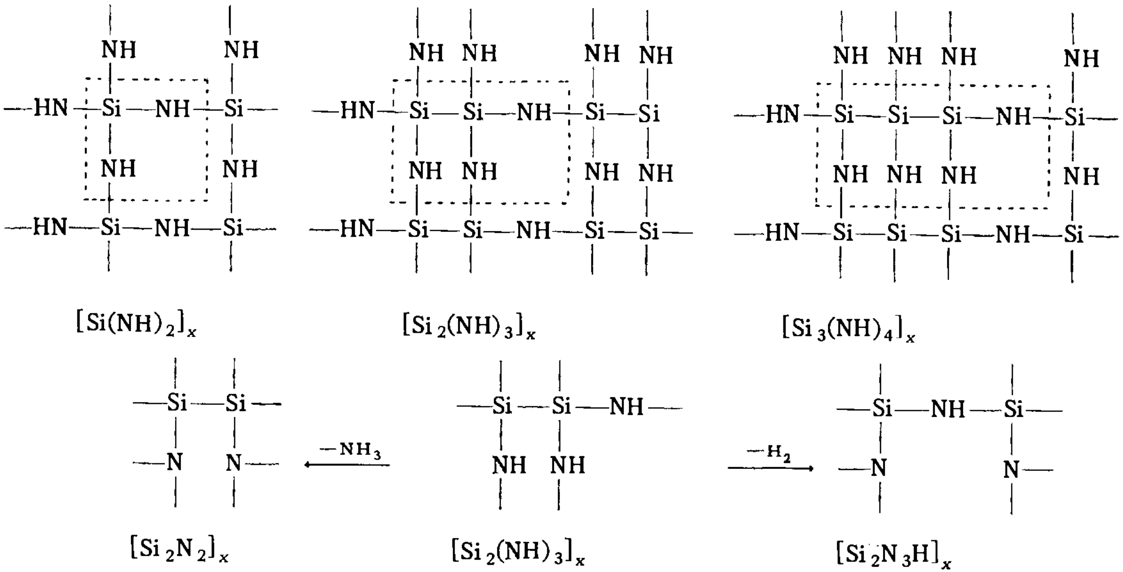
(where $n = 1, 2, 3$) (*12*, *13*).

Using liquid ammonia at low temperatures substantially more ammonia is held because of ammoniates of NH_4Cl; this is given off at higher temperatures (*14*):

$$Si_2Cl_6 + 27NH_3 \xrightarrow[(-79°)]{} Si_2(NH)_3 + 6[NH_4Cl{\cdot}3NH_3] \xrightarrow[-18NH_3]{(20°)} Si_2(NH)_3 + 6NH_4Cl \qquad (79)$$

The ammonium chloride may be washed out with liquid ammonia, though $Si_2(NH)_3$ adsorbs NH_3 strongly, just as amorphous SiO_2 adsorbs water (*10*, *125*). Pure $Si_2(NH)_3$ is obtained only on heating to 220° in vacuum (*14*). When more strongly heated, $Si_2(NH)_3$ decomposes with loss of hydrogen to form Si_2N_3H and subsequently loses ammonia to give Si_3N_4. No silicodicyanogen, $(SiN)_2$ (*125*), is obtained, even when the heating is done in vacuum, but a rearrangement occurs, giving 60% of SiNHSi— and 40% of NSiSiN— containing structures (*14*):

$$\begin{gathered}(Si_2N_2) + NH_3 \xleftarrow[\text{Secondary reaction}]{} Si_2(NH)_3 \xrightarrow[\text{Main reaction}]{225\text{–}475°} H_2 + Si_2N_3H \\ 3Si_2N_3H \xrightarrow{475°} 2Si_3N_4 + NH_3\end{gathered} \qquad (80)$$



Structural units of silicon imides and the pyrolysis product of $Si_2(NH)_3$

Catalytic quantities of tertiary amines or ammonium salts bring about disproportionation of Si_2Cl_6 at room temperature according to the equation (*180*):

$$Si_2Cl_6\ (+NR_3) \rightarrow SiCl_4 + SiCl_2\ (+NR_3) \qquad (81)$$

These products react further to form $(SiCl_2)_x$ (*180*), Si_5Cl_{12} (*67*), Si_6Cl_{14} (*66*), or with pyridine, $Cl_4Si(py)_2$ and $[Cl_2Si(py)]_x$ (*170*).

E. AMINOSILOXENES

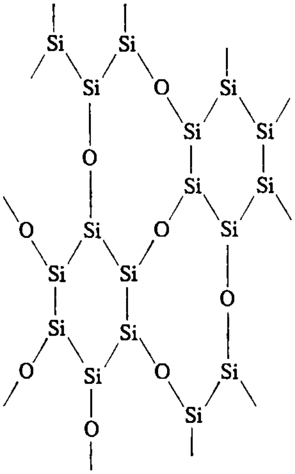
Siloxene, prepared from $CaSi_2$ by the action of hydrochloric acid in a water-alcohol mixture, may be converted into halogen-substituted siloxenes by the action of halogens or halogen hydrides, HX or H_2 being evolved. These, in turn, give aminosiloxenes and ammonium halides with ammonia or amines (*68, 69, 70*):

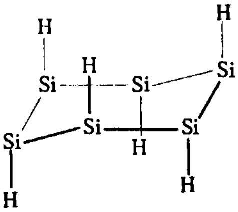
$$[(Si)_6O_{6/2}]H_6 \rightarrow [(Si)_6O_{6/2}]H_{6-n}X_n \rightarrow [(Si)_6O_{6/2}]H_{6-n}(NHR)_n \qquad (82)$$

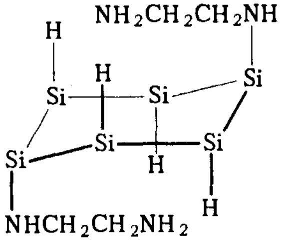
(where R = H, et, ph, $CH_2CH_2NH_2$.)

The siloxene framework consists of puckered six-membered rings of silicon atoms, with each Si linked to one H and also, by an oxygen bridge, to another Si hexagon, giving a giant two-dimensional molecule made up of $[(Si)_6O_{6/2}]H_6$ units. The H atoms, which lie alternately above and below the siloxene plane, may be substituted under carefully controlled conditions. Ammonium halides formed in Reaction 82 may be washed out with liquid ammonia.

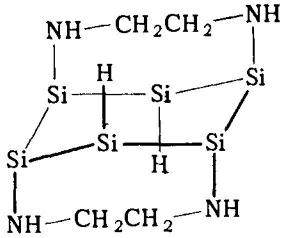
The following aminosiloxenes have so far been prepared, though not always in a pure state (the symbol [ ] denotes $[(Si)_6O_{6/2}]$): [ ] H_5NH_2,


Siloxene structure (without H atoms)


Six-membered Si ring in siloxene with positions of the H atoms (without O atoms)



Bis(ethylenediamino)siloxene
(structural unit)



Bis(ethylenediamino)siloxene
(bridged structural unit)

$[\ ]H_4(NH_2)_2$, $[\ ]H_3(NH_2)_3$, $[\ ]H_2(NH_3)_4$, $[\ ]H(NH_2)_5$, $[\ ](NH_2)_6$ (*70*), $[\ ]H_4(NHet)_2$, $[\ ]H_2(NHet)_4$, $[\ ]H_4(Net_2)_2$, $[\ ]H_5(NHph)$ (*73*), $[\ ]H_4(NHCH_2CH_2NH_2)_2$, $[\ ]H_2(NHCH_2CH_2NH)_2$ (*58*), $[\ ]H_5(NCHR)$ (*115*), $[\ ]H_4(NetCOO)(NH_2et)$, $[\ ]H_4(NetSOOH)_2$, $[\ ]H_{1.7}I_2(NHet_2)_{2.3}$ (*73*).

Aromatic nitriles add on to siloxenes, forming silicon imine structures, which are rapidly decomposed by water to aldehyde and ammonia (*115*):

$$[\ ]H_6 + NCR \rightarrow [\ ]H_5(\text{—}N{=}CH\text{—}R) \rightarrow [\ ]H_5(OH) + HNH_2 + OCHR \qquad (83)$$

Traces of water hydrolyze aminosiloxenes. Ammonia is split off, hydrogen is evolved, and Si—Si bonds are converted to Si—O—Si. Excess of water breaks down the siloxene structure to silicic acid. Liquid ammonia also destroys the aminosiloxene structure, especially in the light. Hydrogen is evolved and Si—Si bonds go to SiNHSi groups.

Bis(ethylamino)siloxene is cleaved by acids and will also add on CO_2 and SO_2 (*73*):

$$[\ ]H_4(NHet)_2 + 4RCOOH \rightarrow [\ ]H_4(OCOR)_2 + 2[etNH_3][RCOO] \qquad (R = me, et, pr) \qquad (84)$$

$$[\ ]H_4(NHet)_2 + 4HI \rightarrow [\ ]H_4I_2 + 2[etNH_3]I \qquad (85)$$

$$[\ ]H_4(NHet)_2 + CO_2 \rightarrow [\ ]H_4(NetCOO^-)(^+NH_2et) \qquad (86)$$

$$[\ ]H_4(NHet)_2 + 2SO_2 \rightarrow [\ ]H_4(NetSOOH)_2 \qquad (87)$$

Diiodosiloxenes, which are not accessible by other routes, may be prepared by Reaction 85, while monoiodosiloxenes may be made from $[\ ]H_5(NHph)$ and HI. More highly substituted aminosiloxenes are also able to substitute only two iodine atoms on treatment with excess of hydriodic acid. This is because there is room for only one of the relatively large iodine atoms above and below the six-membered silicon ring:

$$[\ ]H_{1.7}(NHet)_{4.3} + nHI \rightarrow [\ ]H_{1.7}I_2(NHet)_{2.3} + 2[etNH_3]I + (n - 4)HI \qquad (88)$$

In dibromosiloxene there is also one Br atom above and one below the plane, since it reacts with ethylene diamine according to the equation:

$$[\quad]H_4Br_2 + 3NH_2CH_2CH_2NH_2 \rightarrow [\quad]H_4(NHCH_2CH_2NH_2)_2 + [H_3NCH_2CH_2NH_3]Br_2 \qquad (89)$$

With tetrabromosiloxene all four Br atoms may be exchanged for ethylenediamine molecules, ring bridges being formed (*58*) (see diagram of structure).

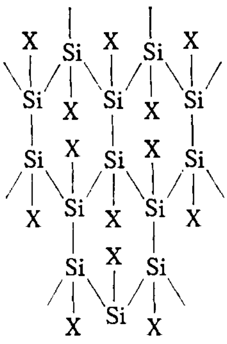
The carbamates formed by addition of CO_2 to aminosiloxene decompose in light or on access of small amounts of oxygen. Evolution of HCN and NH_3 occurs and the oxygen of the carbamate simultaneously transforms SiSi bonds into SiOSi (*71*, *72*).

F. AMINOPOLYSILANES(+1)

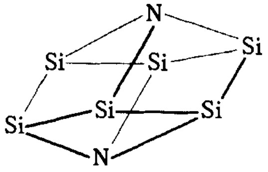
Calcium disilicide reacts with ammonium halides in a finely divided state when heated to the sublimation temperature (350–550°) according to the equation:

$$3CaSi_2 + 6NH_4Br \rightarrow 3CaBr_2 + 4NH_3 + 6H_2 + 1/x(Si_6N_2)_x \qquad (90)$$

The solid swells to a loose brown powder which is insoluble and infusible. Calcium bromide may be washed out partially with acetone. The reaction occurs most readily with NH_4Br. It also occurs with alkyl or aryl ammonium halides, but not with $[NR_4]X$; with NH_4I, iodine is formed in secondary reactions and NH_4F gives silicon tetrafluoride. The silicon(+1) nitride, $(Si_6N_2)_x$, may be regarded as derived from a polysilane(+1), $[(Si)_6H_6]_x$, by replacing three H atoms above and three below the puckered six-membered ring. The N atoms may then be arranged above and below the same but also a neighboring six-membered silicon ring (see diagram of structure).



Polysilane(+1) structure
(X = H, Cl, NH_2, etc.)



Structural unit of silicon(+1) nitride $(Si_6N_2)_x$

$(Si_6N_2)_x$ is, apart from Si_3N_4, the only definite binary silicon-nitrogen compound. It is amorphous to X-rays, stable in air and to heat, and reacts slowly with water or alcohol, but rapidly at pH > 7 according to the equation:

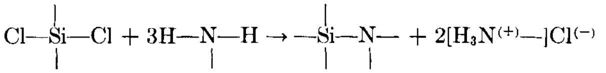
$$Si_6N_2 + 12OH^- + 12H_2O \rightarrow 6H_2SiO_4^{2-} + 2NH_3 + 9H_2 \tag{91}$$

Boron trifluoride is not added (*57*).

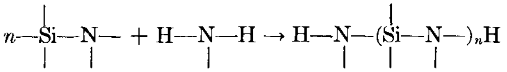
When the chloropolysilane(+1), $(SiCl)_x$, which may be obtained by pyrolyzing the higher silicon halides Si_nCl_{2n+2} ($n = 10$), is treated with NH_3, the primary product at <0° is $[Si(NH_2)]_x$. This loses hydrogen at higher temperatures and each 6–8th Si—Si bond is converted to SiNHSi (*126*). Definite aminopolysilanes(+1), $[Si(NHR)]_x$, may be prepared from $(SiCl)_x$ (*59*).

VI. Cyclic Silicon-Nitrogen Compounds

Ammonolysis or aminolysis of halogeno difunctional silanes gives polysilazanes only to a limited extent: the main products are cyclosilazanes in which 3 (preferably) or 4 SiN units are joined in a ring:

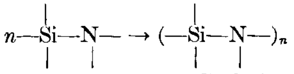


$$\mathrm{Cl{-}\overset{|}{\underset{|}{Si}}{-}Cl + 3H{-}\underset{|}{N}{-}H \rightarrow {-}\overset{|}{\underset{|}{Si}}{-}\underset{|}{N}{-} + 2[H_3N^{(+)}{-}]Cl^{(-)}} \tag{92}$$



$$n\mathrm{{-}\overset{|}{\underset{|}{Si}}{-}\underset{|}{N}{-} + H{-}\underset{|}{N}{-}H \rightarrow H{-}\underset{|}{N}{-}(\overset{|}{\underset{|}{Si}}{-}\underset{|}{N}{-})_nH} \qquad (n = 2\text{-}\infty) \tag{93}$$

Polysilazanes

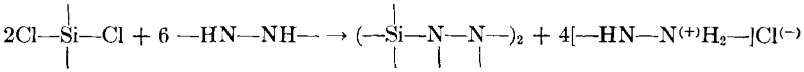


$$n\mathrm{{-}\overset{|}{\underset{|}{Si}}{-}\underset{|}{N}{-} \rightarrow ({-}\overset{|}{\underset{|}{Si}}{-}\underset{|}{N}{-})_n} \qquad (n = 3\text{–}4) \tag{94}$$

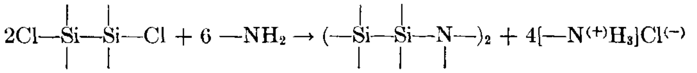
Cyclosilazanes X, XI

Monomeric units such as >Si=N— are excluded by the rules of silicon chemistry (the impossibility of having p_π—p_π bonds on silicon atoms) and have not been observed hitherto (cf. *45*, *110*).

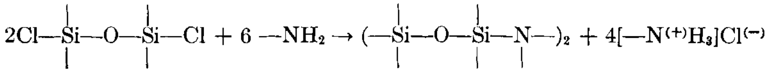
Analogously, hydrazines react to give disilatetrazacyclohexanes XII, 1,2-dihalogensilanes to give tetrasilapiperazines XIII, and α,ω-dihalogenosiloxanes to give cyclosiloxazanes XIV (*79*, *101*, *157*):



$$\mathrm{2Cl{-}\overset{|}{\underset{|}{Si}}{-}Cl + 6\ {-}HN{-}NH{-} \rightarrow ({-}\overset{|}{\underset{|}{Si}}{-}\underset{|}{N}{-}\underset{|}{N}{-})_2 + 4[{-}HN{-}N^{(+)}H_2{-}]Cl^{(-)}} \tag{95}$$

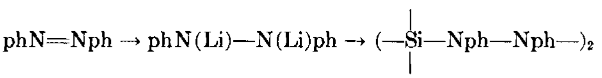


$$\mathrm{2Cl{-}\overset{|}{\underset{|}{Si}}{-}\overset{|}{\underset{|}{Si}}{-}Cl + 6\ {-}NH_2 \rightarrow ({-}\overset{|}{\underset{|}{Si}}{-}\overset{|}{\underset{|}{Si}}{-}\underset{|}{N}{-})_2 + 4[{-}N^{(+)}H_3]Cl^{(-)}} \tag{96}$$



$$\mathrm{2Cl{-}\overset{|}{\underset{|}{Si}}{-}O{-}\overset{|}{\underset{|}{Si}}{-}Cl + 6\ {-}NH_2 \rightarrow ({-}\overset{|}{\underset{|}{Si}}{-}O{-}\overset{|}{\underset{|}{Si}}{-}\underset{|}{N}{-})_2 + 4[{-}N^{(+)}H_3]Cl^{(-)}} \tag{97}$$

In those cases where the NH groups will no longer react, metallated amines are effective (*41*, *44*, *47*):



$$\mathrm{phN{=}Nph} \rightarrow \mathrm{phN(Li){-}N(Li)ph} \rightarrow (\overset{|}{\underset{|}{\mathrm{-Si}}}\mathrm{{-}Nph{-}Nph{-}})_2 \qquad (98)$$

$$\mathrm{me_3SiNHSi(me)_2NHSi(me)_3} \rightarrow \mathrm{me_3SiN(Li)Si(me)_2N(Li)Si(me)_3} \rightarrow [\mathrm{-(me_3Si)N{-}Si(me)_2{-}}]_2 \qquad (99)$$

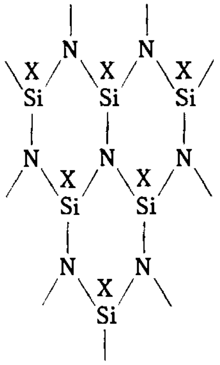
In addition to —Cl/—N< exchange reactions, condensation reactions at elevated temperatures (>200°) have been employed in the preparation of cyclic SiN compounds (*6*, *98*):

$$3\mathrm{(RO)_2Si(NH_2)_2} \rightarrow [\mathrm{-(RO)_2Si{-}NH{-}}]_3 + 3\mathrm{NH_3} \qquad (100)$$

$$4\mathrm{meN(SiH_3)_2} \rightarrow [\mathrm{-SiH_2{-}Nme{-}}]_4 + 4\mathrm{SiH_4} \qquad (101)$$

Cyclodisilazanes IX may be obtained otherwise only from the breakdown products of the reaction of $SiCl_4$ with N_2 in glow discharges or by decomposition of the apparently unstable tetrasilylcyclotetrasilazanes (*99*).

A large number of cyclotri- and cyclotetrasilazanes have been made by varying the substituents on the Si atom and to a less extent on the N atom, by use of NH_3—RNH_2 mixtures in aminolysis (→Xd/1), by amine exchange reactions, or by *N*-metallation followed by silylation of cyclosilazanes (cf. Table VII). A condensed six- and eight-ring product (XV) has also been described. High molecular cyclotrisilazanes, $(XSiN)_x$, derived from polysilanes(+1) by replacing each second Si atom by N (see structure on p. 264), have been obtained in the ammonolysis of $HSiCl_3$ (*111*, *112*) and $SiCl_4$ (*124*), and in discharge tube reactions with $SiCl_4/N_2$ mixtures (*38*, *105*).



Structural formula for $(XSiN)_x$ (*idealized*)

The cyclic silazanes are, broadly speaking, insensitive to water and particularly stable in the alkaline region. They are, however, rapidly broken down by acids (*1, 133, 161, 184*). Derivatives of disilatetrazacyclohexane (XII) are more insensitive to moisture the more the H atoms or alkyl groups are replaced by phenyl groups (*101*). Alcohols also cleave the cyclosilazanes with evolution of ammonia. This is retarded by the presence of OH^- (*1*) and accelerated by acid OH groups such as occur in phenols (*1, 97*). Alkoxyorganodisilazanes, which are otherwise difficult to produce, are formed in good yield by the appropriate addition of alcohols (*161*):

$$(-R_2Si—NH—)_n + 2nR'OH \rightarrow nNH_3 + nR_2Si(OR')_2 \qquad (102)$$

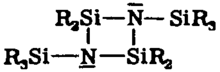
$$2(—me_2Si—NH—)_3 + 6CF_3CH_2OH \rightarrow 3[(CF_3CH_2O)me_2Si]_2NH + 3NH_3 \qquad (103)$$

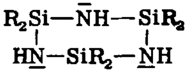
Equilibriation of $(—me_2Si—NH—)_3$ with $(me_3Si)_2NH$ leads to trisilazanes in not particularly good yield. In the treatment of cyclosilazanes with amines, ring rearrangements or amino exchange reactions have been observed (*1, 21*). Warming of $(—me_2Si—NH—)_3$ with catalytic quantities of NH_4Br at 190–300° results in loss of ammonia and formation of oligomers and high molecular silazanes containing NSi_3 groups. They begin to decompose above 500° and are very stable to alkalis (*80*). Boron halides such as R_2BCl bring about cleavage of $(—me_2Si—NH—)_3$ to me_2SiCl_2 and $(R_2B)_2NH$ (*103*).

High molecular cyclotrisilazanes, $(XSiN)_x$, are insoluble in organic solvents; $(HSiN)_x$ is transformed by HCl into $HSiCl_3$ and NH_4Cl, by HI into $HSiI_3$ and NH_4I, and by NH_3 into $Si(NH)_2$ and H_2 (*111, 112*).

Cyclosilazanes undergo stepwise metallation of the NH groups by reaction with KNH_2/liquid ammonia (*120*), $NaNH_2$/benzene (*149, 169*), $NaN[Si(me)_3]_2$ (*163*), or LiC_4H_9 (*41, 43*). The alkali derivatives, which cannot be distilled and show no definite melting points, are thermally very stable, though some are sensitive to oxygen.

From electron diffraction measurements, cyclohexamethyltrisilazane, like cyclo-octamethyltetrasilazane, is found to be puckered, with NSiN, 111 ± 5°; SiNSi, 117 ± 4°; SiC, 1.87 ± 0.05 Å; SiN 1.78 ± 0.03 Å. Infrared spectroscopic data, however, have been interpreted in terms of a planar structure (*77*), with bond angles of 109° for NSiN and 131° for SiNSi (*109*). Other infrared measurements (*81*) tend to lead to confirmation of the electron diffraction results (SiNSi, 118.5°) and to determination of bond angles for XIVa of SiOSi, 124°; SiNSi, 133.3°; for XIVb/1, SiOSi, 132°; SiNSi, 121.3°; for XIVc, SiOSi, 137°, 125°; SiNSi, 118.8°; and for $(—me_2Si—NH—)_4$, SiNSi, 121.3° [123.4° according to reference (*183*)]. The ν_{as} SiN(Si) band in the infrared and Raman spectra of cyclotrisilazanes lies in the region 925–935 cm^{-1}, *N*-silyl-substituted cyclotrisilazanes show a characteristic band at 1005–1040 cm^{-1}. [For the PMR spectra of some cyclosilazanes see reference (*81*) and for electrical properties and dipole


(IX)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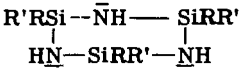
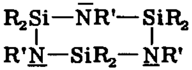
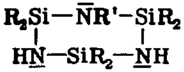

(Xb)


(Xc)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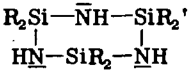
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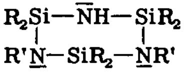
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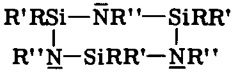
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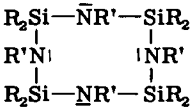
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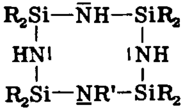
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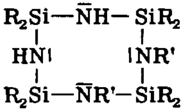
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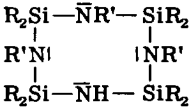
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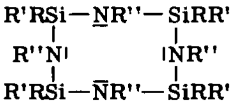
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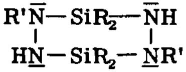
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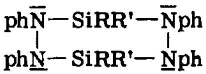
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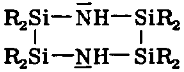
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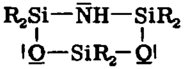
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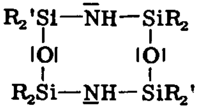
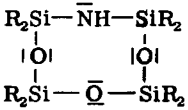

(XIVb)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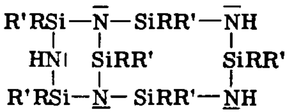
(XV)

TABLE VII
CYCLIC SILAZANES

No.	R	R′	M.P.	B.P.	Torr	n_D	°C	D_4	°C	Prep. Eqn.	Ref.
Group IX: Cyclodisilazanes											
(IX) 1	Cl		84°	—	—	—	—	—	—	(VI)	*(38, 105)*
2	me		39°	85°	7	1.4237	45	0.998	—	(99)	*(42, 174)*
Group X: Cyclotrisilazanes											
(Xa) 1	me		−10°	188° 112°	756 85	1.4448	20	0.9196	20	(92, 94)	*(21, 22)* *(53, 104)*
2	et		−41°	150°	10	1.4670	20	0.9287	20	(92, 94)	*(21, 32)*
3	^{n}bu			193°	2	1.4654	20	0.8912	20	(92, 94)	*(135)*
4	ph[a]		214°							(92, 94)	*(91)*
5	meO		186°	(185°	10)[b]	—		(1.021	15)[b]	(92, 94)	*(110,[b] 163)*
6	etO		89°	(220°	10)[b]	—		—	—	(92, 94)	*(110,[b] 163)*
7	^{i}prO		—	147°	4	—		—	—	(92, 94)	*(127, 172)*
8	^{n}buO		—	250°	12					(100)	*(92)*
9	^{t}buO		190°	—	—					(92, 94, 100)	*(46, 89, 98)*
10	chO		65–70°	—	—					(92, 94)	*(163)*
(Xb) 1	H	et	—	62°	0.5	1.4700	20	0.9596	20	(92, 94)	*(131)*
2	me	et	—	115°	13	1.4564	20	—	—	(92, 94)	*(61)*
3	me	ph	116°	220°	760	—	—	—	—	(92, 94)	*(61)*
4	me	meO	217°	115°	1.5					(92, 94)	*(163)*
5	me	etO	101°							(92, 94)	*(163)*
6	me	^{i}prO	45°							(92, 94)	*(163)*
7	me	^{t}buO	44°							(92, 94)	*(163)*
8	me	phO	95°							(92, 94)	*(163)*
9	me	chO	77°							(92, 94)	*(163)*
10	vi	meO	159°							(92, 94)	*(163)*
11	ph	meO	157° (decomp)							(92, 94)	*(163)*

Continued

TABLE VII (*Continued*)

No.	R	R′	M.P.	B.P.	Torr	n_D	°C	D_4	°C	Prep. Eqn.	Ref.
(Xc)	1 me	ph	250°	190–193°	11	—				(100)	*(2, 88)*
	2 me	me$_3$Si	−43°	333°	723	1.4823	20	0.940	20	(VI)	*(41, 43)*
	3 et	me$_3$Si	−35°	362°	720	1.4868	20			(VI)	*(41)*
	4 ph	me$_3$Si	110–120°	422°	718	—				(VI)	*(41)*
	5 ph	me$_2$SiCl	90–100°	470–480°	720	—				(VI)	*(41)*
(Xd)	1 me	ph	37°	—	—	—				—	*(2)*
	2 me	^{n}am	—	87°	1	—				—	*(2)*
	3 ph	me$_3$Si	80°	293–300°	1	—				(VI)	*(43)*
(Xe)	1 me	et	−85°	58–59°	1	1.4540	20	0.9291	20	—	*(185)*
	2 et	me	−85°	78–80°	1	1.4630	20	0.9381	20	—	*(185)*
(Xf)	1 me	me$_3$Si	−74°	261°	730	1.4422	20	0.973	20	(VI)	*(41, 43)*
	2 et	me$_3$Si	−65°	333°	720	1.4751	20	—	—	(VI)	*(41)*
	R R′	R″									
(Xg)	1 H me	me	—	56°	5	1.4580	20	0.9297	20	—	*(132)*
	2 H et	me	—	74°	1.5	1.4680	20	0.9324	20	—	*(132)*
	3 H NHet	et	—	93–97°	11	1.4472	20	0.9229	20	—	*(130)*
Group XI: Cyclotetrasilazanes											
(XIa)	1 H	me	—	liquid	—					(101)	*(6)*
	2 me	H	97°	225°	756					(92, 94)	*(21, 22)*
			—	135°	35						*(53, 104)*
	3 et	H	16°	192°	10	1.4769	20	0.9521	20	(92, 94)	*(21)*
	4 ^{i}prO	H	—	191°	2					(92, 94)	*(127, 172)*
	5 phO	H	130°	—	—					(100)	*(127)*
	6 Cl	Cl$_3$Si	50°	103°	2					(VI)	*(124)*
(XIb)	1 me	me$_3$Si	−17°	107–108°	1.5	1.4613	20	—	—	—	*(43)*
(XIc)	1 me	me$_3$Si	−32°	122–124°	3	1.4497	20	0.901	20	—	*(43)*

(XId)	1	me		me_3Si	−55°	328°	718	1.4582	20	—	—	—	*(42)*
		R	R′	R″									
(XIe)	1	H	me	H	—	54°	1	1.4780	20	1.0069	20		*(131)*
	2	H	et	H	—	102°	0.5	1.4810	20	0.9767	20		*(131)*
	3	me	H	me	—	88°	2	1.4810	20	0.9776	20		*(132)*
	4	H	NHet	et	—	122°	11	1.4527	20	0.9231	20		*(130)*

Group XII: 1,4-Disila-2,3,5,6-tetrazacyclohexanes

(XIIa)	1	ph		H	168–172°							(95)	*(101, 143)*
	2	ph		ph	254–257°							(98)	*(101, 143)*
	3	me		ph	oil							(95)	*(101, 143)*
(XIIb)	1	ph		ph	329–330°							(98)	*(47)*
	2	me		ph	240–243°							(98)	*(47)*

Group XIII: 1,2,4,5-Tetrasila-3,6-diazacyclohexanes

(XIII)	1	me			1°	61°	2	1.4760	20	0.8458	20	(96)	*(157)*

Group XIV: Cyclotri- and -tetrasiloxazanes

(XIVa)	1	me			10°	151°	760	1.4068	20	0.9895	25	(97)	*(79, 81)*
(XIVb)	1	me		me	40°	206–208°	760	—				(97)	*(79, 133)*
	2	me		et	<20°	70°	0.5	1.4308	20			(97)	*(133)*
	3	meO			—	173–175°	0.05	—				(97)	*(120)*
(XIVc)	1	me			20°	190–191°	760	1.4151	20	0.9921	26	(97)	*(79)*

Group XV: Condensed cyclotri- and -tetrasilazanes

(XV)	1	H		me	—	116°	1.5	1.4860	20	1.0371	20	—	*(131)*

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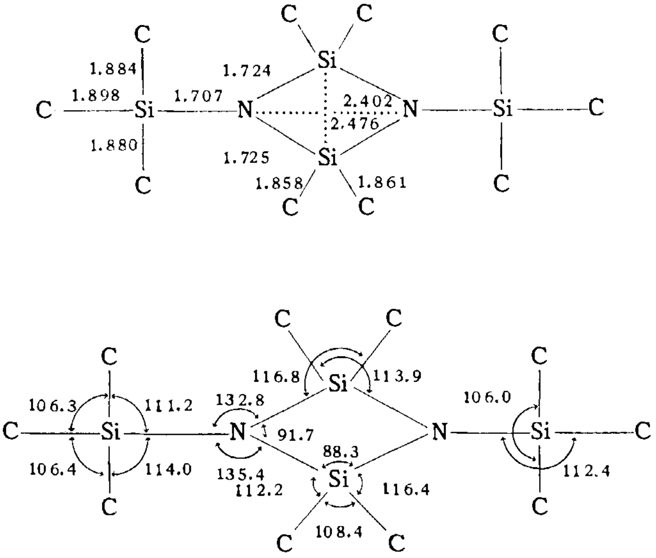
[a] Compound adds one molecule CCl_4 when crystallizing from CCl_4.

[b] Data for "$(RO)_2Si{=}NH$."

moments see reference (*104*).] A careful X-ray structural determination has been made on *N*,*N*′-bis(trimethylsilyl)cyclodisilazane (IX/2) (*174*). It is monoclinic with the space group $P2_1/n$ (a = 6.75$_9$ ± 0.02 Å, b = 13.18$_1$ ± 0.04 Å, c = 11.22$_5$ ± 0.03 Å, β = 104°23′ ± 0.5°, U = 968.7 Å^3, D_c 1.003, D_m 0.998 (flotation in methanol/diethylene glycol). It has a planar $SiNSi_2NSi$ framework.



Bond distances (in Å) and bond angles (in °) for *N*,*N*′-bis(trimethylsilyl)cyclodisilazane.

VII. Prospect

This article represents only an arbitrary section of current activity in the field of silicon-nitrogen compounds; a more complete treatment would have exceeded the available space. Some mention must, however, be made of other important sectors of Si—N chemistry and of the chief workers in each. These are: ammonolysis of $SiCl_4$ (Billy, Goubeau, Glemser); modifications of Si_3N_4 (Glemser, Popper, Ruddlesden); polyamino-substituted silanes (Tansjö); pseudohalogen derivatives with ($NSiH_3$) groups (Ebsworth); condensation reactions of silylamines with silanols (Pike); silyl-substituted amino acids (Rühlmann, Birkofer); silyl-substituted ureas, carbonic acid amides, and carbodiimides (Birkofer, Goubeau, Pump, Wannagat); polysilazanes (Rochow, Andrianov); bis(silyl)amines and their reactions (Becke-Goehring, Grosse-Ruyken, Wannagat); reactions of silyl-substituted alkali amides with organic compounds (Krüger); tris(silyl)amines (Wannagat); silylamino derivatives of the transition metals

(Bürger); phthalocyaninatosilanes (Kenney). It will be seen that the chemistry of silicon-nitrogen compounds, which occupied only a few pages of Gmelin's *Handbuch der anorganischen Chemie* ten years ago, has undergone an almost explosive development. Only the practical applications seem to be delayed. In brief, SiN compounds, thanks to the variety of types and reactions they show, may well challenge the leading place of SiC and SiO compounds in silicon chemistry, at least insofar as the scientific and preparative aspects of the subject are concerned.

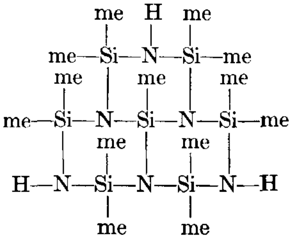
Addendum

During the past year nearly one hundred articles about SiN-chemistry have been published. Only a few of them could be woven into the text of the present review. Some of these additions to the chemistry of cyclosilazane compounds are noted here.

1. A three-membered Si_2N-ring system [—$(me_3Si)N$—$Si(me)_2$—$Si(me)_2$—$]_{ring}$, m.p. −37°, b.p. 172.7°, n_D^{20} 1.4375, D_4^{18} 0.827, was synthesized by Fink (*44a*); a five-membered Si_3N_2-ring system [—$Si(me)_2$—$Si(me)_2$—Nme—$Si(me)_2$—Nme—$]_{ring}$, m.p. −12°, b.p. 70°/13 Torr, by Wannagat (*170a*); a cyclotrisildiazoxane [—$Si(me)_2$—NH—$Si(me)_2$—NH—$Si(me)_2$—O—$]_{ring}$, m.p. 46–47°, by Andrianov and co-workers (*2b*); and a cyclohexasildiaztetroxane, [—$Si(me)_2$—NH—$Si(me)_2$—O—$Si(me)_2$—O—$]_2$, m.p. −12°, b.p. 148–150°/2 Torr, n_D^{20} 1.4269, D_4^{20} 0.9756 by Sokolov (*132b*).

2. Four-membered rings with Si,N, and B or P were prepared by Fink (*44*): [—$(me_3Si)N$—$Si(me)_2$—$N(me_3Si)$—P(ph)—$]_{ring}$, b.p. 107°/4 Torr, n_D^{20} 1.5029, and [—$(me_3Si)N$—$Si(me)_2$—$N(me_3Si)$—B(ph)—$]_{ring}$, b.p. 90–91°/1.2 Torr, n_D^{20} 1.4783. The cyclodisilazane [—$(me_3SiO)_2Si$—NH—$]_2$, m.p. 103°, b.p. 180°, was synthesized as early as 1961 by Andrianov and Delazari (*1a*). For other cyclodisilazanes of group IX see Fink (*44*) and for those of type [—(R′R)Si—Nme—$]_2$ see Lienhard and Rochow (*92a*).

3. A triple condensated cyclotrisilazane with m.p. 165–167° is derived from Xa/1 or XIa/2 by heating with KOH at 160–260° (*2a*).



4. For some unreported derivatives of groups Xb and XIe see Andrianov and co-workers (*2c*), as well as Zhinkin (*185a*) and Tansjö (*138b*).

5. (—me_2Si—NH—$)_4$, XIa/2, crystallizes in space group P2/c in a 1:1-chair and cradle structure with distance for Si-N of 1.708 to 1.750 Å and bond angles for SiNSi of 130.1 to 133.1° (*132a*).

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