NOVEL WAYS IN THE PREPARATION OF CYCLIC SILICON-NITROGEN COMPOUNDS

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INTRODUCTION

Of the elements which tend to form ring compounds with another element, nitrogen needs a prominent mention. A variety of organic N-heterocycles, borazenes, phosphazenes, and sulphur nitrogen compounds are well known. A large number of silicon–nitrogen ring compounds should be capable of existence as well, however, only the six-membered ring-systems of cyclotrisilazane and the eight-membered ring-system of cyclotetrasilazane have been discovered so far[1a]. Brewer and Haber[1b] obtained these systems for the first time in 1948 by reacting primary amines with dihalogenosilanes.

Since we know many more Si–N ring-systems today the names chosen by Brewer and Haber which are still used everywhere are somewhat misleading and insufficient. In the present communication Si–N ring-systems are termed cyclosilazanes with the number and the position of the corresponding atoms placed before the syllables "sil" and "az" respectively. For cyclotrisilazane the proposed nomenclature is cyclo-1,3,5-trisil-2,4,6-triazane, and cyclotetrasilazane will likewise be called cyclo-1,3,5,7-tetrasil-2,4,6,8-tetrazane.

In all cyclosilazane structures known to date only Si N single bonds have been noticed. Double bonds caused by $(p\text{-}p)_\pi$-overlap have not been observed. To what extent do the N–Si $(p{\rightarrow}d)_\pi$-bonds occur is not known so far but they are most likely to exist. The most common bond angles are 110° for N–Si–N and 130–135° for Si–N–Si, yet both angles can decrease to 90° in the four-membered ring-systems of the cyclodisildiazanes. The ring structure of the "cyclotrisilazane" is said to be planar, the structure of "cyclotetrasilazane" is puckered in the mode of an irregular crown[2].
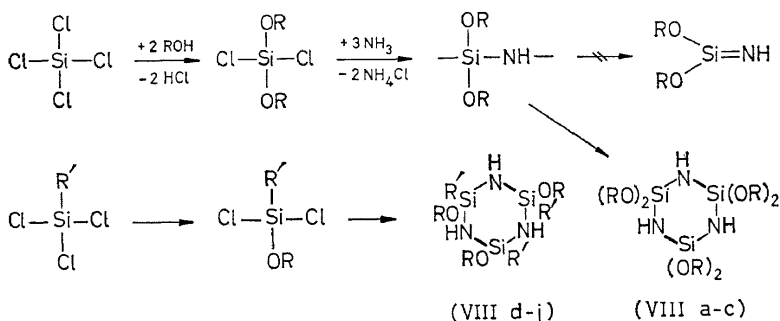
CYCLOSILAZANES AND POLYSILAZANES

Using Brewer and Haber's method many derivatives of both these ring-systems have been prepared, which tend to form simultaneously. In this process it was mainly the substituents on the silicon that could be varied. The case, however, is somewhat more complex with bulky amino substituents. In order to facilitate a ring synthesis, heating in the presence of catalytic amounts of ammonium salts does help[3a]. Theoretically silicon and nitrogen units are linked in Brewer and Haber's method but in actual practice it is left to chance whether and to what extent six-membered or eight-membered rings, or polysilazanes are formed. The corresponding yields for the most common reaction of dimethyldichlorosilane with ammonia amount, as a rule, to 45, 35, and 15 per cent respectively. In the rings thus obtained the substituents on the silicon atom are all the same. The same
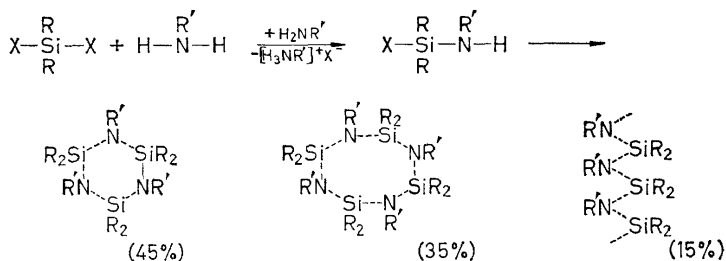
applies to the substituents on the nitrogen atoms. Andrianov and coworkers[3b] succeeded in preparing rings with different substituents on the silicon atoms by simultaneous ammonolysis of various dichlorosilanes[4]. Of course, it was not easy to isolate the pure ring compounds out of a mixture of 3, 4 or more cyclosilazanes formed in this way.

In the field of cyclosilazanes we were interested at first in the ammonolysis of dichlorodialkoxysilanes which should lead to dialkoxysilylimines as described by Rosnati[5] in 1948. As could have been expected these compounds did not form but hexaalkoxycyclotrisiltriazanes were obtained instead:

(VIII d–j)   (VIII a–c)

The yield of cyclosilazanes was not very satisfactory. It is somewhat better if one proceeds from alkylalkoxydichlorosilanes. In the case where $R' = CH_3$ and $OR = C_6H_5O$ (VIII i) cyclosilazanes with isomeric structures could be ascertained by n.m.r.-spectroscopy[6].

In the attempt to synthesize a mixed substituted disilazane with H_3Si-groups we were only able to prepare the desired triethylsilylsilylamine (b.p. $51°/14$ torr, $n_D^{20} 1\cdot 443$, $d_4^{20} 0\cdot 818$) in very poor yield (3–5 per cent). Obviously it condenses with the evolution of hydrogen, and the 2,4,6-triethylsilyl substituted cyclotrisiltriazane (VIII k) is formed[7] in a yield of 35 per cent:

$R = C_2H_5$ (VIII k)
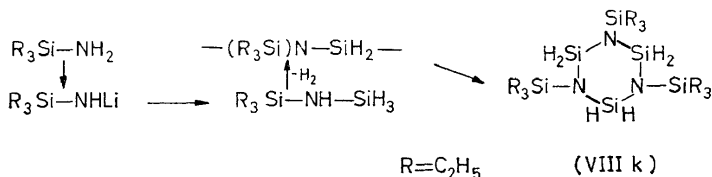
The reaction mechanism of Brewer and Haber's synthesis is still unknown. The first step, however, has to be in any case the formation of halogeno-amino-silanes (I). These could continue to react by splitting off hydrogen halogenides intramolecularly and by consecutive polymerization of the Si–N fragment to yield cyclo- and polysilazanes. The hydrogen halogenides will in any case be bound at once by the used primary amine in the form of an ammonium salt. More likely, however, is the gradual formation of larger Si–N building units where the basic units $>$SiX$_2$ and –NH$_2$ respectively are continuously coupled by condensation, and where larger building units can be condensed amongst themselves:
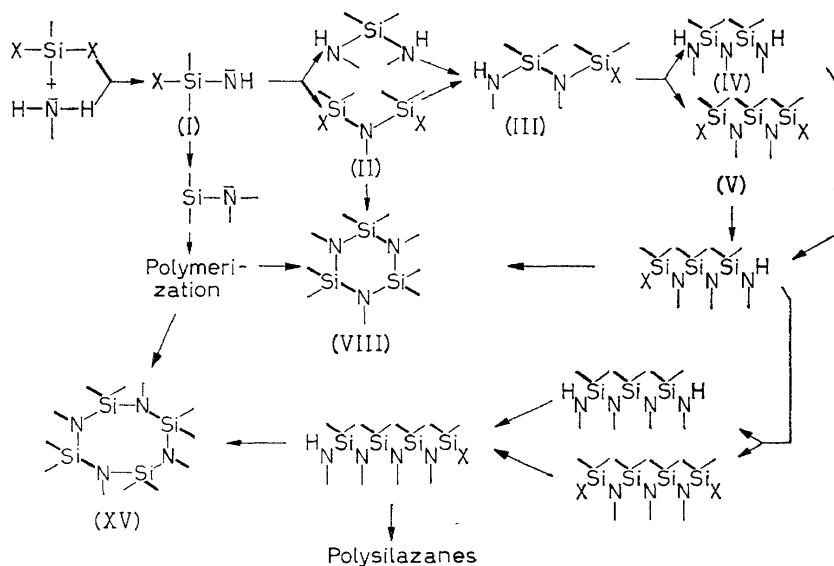
Polysilazanes

Not only will ammonium halogenides occur as condensation products but certain silazanes, e.g. α,ω-diamino-oligo-silazanes may react also by splitting off amines. Out of the numerous difunctional building units on the way towards cyclo- and polysilazanes the units N–Si–N and N–Si–N–Si–N (only a few representatives[3, 8, 9]) have been synthesized previously. We have succeeded in preparing the units X–Si–N (I), X–Si–N–Si–X (II), N–Si–N–Si–X (III), X–Si–N–Si–N–Si–X (V), and in many cases N–Si–N–Si–N (IV). The single compounds of these groups (I) to (V) are listed in *Table 1*. They can be combined both to cyclosilazanes of any desired structure and to inorganic ring-systems where apart from silicon and nitrogen other atoms may occur as links such as boron, carbon, germanium, phosphorus, oxygen, and sulphur.

HALOGENOSILAZANES

Since in the beginning we did not seem very likely to isolate all the intermediates in the Brewer and Haber's reaction, we chose the reverse procedure; using cleavage of the cyclo- and the polysilazanes with less than the stoichiometric amount of hydrogen halogenides it was possible to obtain

*Table 1.* Physical constants of the Si–N compounds (I–V) as starting materials for Si–N ring compounds

Name of the compound	Mol. formula	R^1	R^2	R^3	R^4	R^5	X	m.p. (°C.)	b.p. (°C.)	torr	n_D^{20}	d_4^{20}	Ref.
ALKYLAMINODIMETHYLCHLOROSILANES (I) $R^1NHSi(CH_3)_2Cl$													
(a) Propyl-	$C_5H_{14}ClNSi$	Pr^n	—	—	—	—	—		39–41°	13	1·4250	0·9024	15
(b) Isopropyl-	$C_5H_{14}ClNSi$	Pr^i	—	—	—	—	—		25–26°	11	1·4198	0·9026	15
(c) Butyl-	$C_6H_{16}ClNSi$	Bu^n	—	—	—	—	—		54–55°	11	1·4290	0·9182	15
(d) Isobutyl-	$C_6H_{16}ClNSi$	Bu^i	—	—	—	—	—		57°	11	1·4282	0·9092	15
(e) Cyclohexyl-	$C_8H_{18}ClNSi$	C_6H_{11}	—	—	—	—	—	—3°	87°	12	1·4624	0·9815	15
(f) Phenyl-	$C_8H_{12}ClNSi$	Ph	—	—	—	—	—		75–76°	1	1·5402	1·0912	15
1,3-DIHALOGENODISILAZANES (II) $X\text{-}SiR_2^1\text{-}NR^2\text{-}SiR^3\text{-}X$													
(a) 1,3-Difluoro-1,1,3,3-tetramethyl-	$C_4H_{13}F_2NSi_2$	Me	H	Me	—	—	F		118°	735	1·3769	0·9312	13, 14, 16
(b) 1,3-Dichloro-1,1,3,3-tetramethyl-	$C_4H_{13}Cl_2NSi_2$	Me	H	Me	—	—	Cl		63–64°	10	1·4403	1·0624	10, 16, 18
(c) 1,3-Dibromo-1,1,3,3-tetramethyl-	$C_4H_{13}Br_2NSi_2$	Me	H	Me	—	—	Br	7°	49°	0·1	1·4866	1·4887	16, 18
(d) 1,3-Dichloro-1,1-dimethyl-3,3-diphenyl-	$C_{14}H_{17}Cl_2NSi_2$	Me	H	Ph	—	—	Cl		141°	0·15	1·5596	1·1704	18
(e) 1,3-Dichloro-1,1,3,3-tetraphenyl-	$C_{24}H_{21}Cl_2NSi_2$	Ph	H	Ph	—	—	Cl	115–16°	—	—	—	—	10
(f) 1,3-Dichloro-1,1,2,3,3-pentamethyl-	$C_5H_{15}Cl_2NSi_2$	Me	Me	Me	—	—	Cl		69–71°	10	1·4511	1·0526	16, 18, 15
(g) 1,3-Dichloro-1,1,3,3-tetramethyl-2-ethyl-	$C_6H_{17}Cl_2NSi_2$	Me	Et	Me	—	—	Cl		76°	10	—	—	19
(h) 1,3-Dichloro-1,1,3,3-tetramethyl-2-butyl-	$C_8H_{21}Cl_2NSi_2$	Me	Bu	Me	—	—	Cl		40–42°	0·01	1·4540	1·0177	15, 16, 29
(i) 1,3-Dichloro-1,1-dimethyl-2-ethyl-3,3-diphenyl-	$C_{16}H_{21}Cl_2NSi_2$	Me	Et	Ph	—	—	Cl		134°	0·1	1·5562	1·1382	18
1-ALKYLAMINO-3-CHLOROTETRAALKYL-DISILAZANES (III) $R^1NH\text{-}SiR_2^2\text{-}NR^3\text{-}SiR_2^4Cl$													
(a) 1-Propylamino-2-propyl-1,1,3,3-tetramethyl-	$C_{10}H_{27}ClN_2Si_2$	Pr^n	Me	Pr^n	Me	—	—		53–55°	0·1	1·4509	0·9443	15
(b) 1-Butylamino-2-butyl-1,1,3,3-tetramethyl-	$C_{12}H_{31}ClN_2Si_2$	Bu^n	Me	Bu^n	Me	—	—		69–72°	0·2	1·4515	0·9274	15
(c) 1-Butylamino-2-ethyl-1,1-dimethyl-3,3-diphenyl-	$C_{20}H_{31}ClN_2Si_2$	Bu^n	Me	Et	Ph	—	—		142°	0·05	1·5397	1·0352	18
1,3-BIS(ALKYLAMINO)-TETRAALKYL-DISILAZANES (IV) $R^1NH\text{-}SiR_2^2\text{-}NR^3\text{-}SiR_2^4\text{-}NHR^5$													
(a) 1,3-Bis(methylamino)-1,1,3,3-tetramethyl-	$C_6H_{21}N_3Si_2$	Me	Me	H	Me	Me	—		70°	12	1·4352	0·8833	15
(b) 1,3-Bis(methylamino)-2-butyl-1,1,3,3-tetramethyl-	$C_{10}H_{29}N_3Si_2$	Me	Me	Bu	Me	Me	—		67°	1	1·4483	0·8800	15
(c) 1,3-Bis(ethylamino)-1,1,3,3-tetramethyl-	$C_8H_{25}N_3Si_2$	Et	Me	H	Me	Et	—		47°	1	1·4330	0·8534	15
(d) 1-Butylamino-3-propylamino-1,1-dimethyl-2-ethyl-3,3-diphenyl-	$C_{23}H_{39}N_3Si_2$	Bu^n	Me	Et	Ph	Pr^n	—		—	—	—	—	18
1,5-DIHALOGENOTRISILAZANES (V) $X\text{-}SiR_2^1\text{-}NR^2\text{-}SiR_2^3\text{-}NR^2\text{-}SiR_2\text{-}X$													
(a) 1,5-Difluoro-1,3,3,5,5-hexamethyl-	$C_6H_{20}F_2N_2Si_3$	Me	H	Me	F	—			73°	13	1·4147	0·9555	14
(b) 1,5-Dichloro-1,1,2,3,3,4,5,5-octamethyl-	$C_8H_{24}Cl_2N_2Si_3$	Me	Me	Me	Cl	—			124°	10	1·4643	1·0418	18

a, ω-dihalogeno-oligo-silazanes in a yield of 40 to 70 per cent, cutting out from the sequence Si–N–Si–N the Si–N–Si-fragment and fixing the N-fragment as ammonium salt[10, 11].

$$-\overset{|}{\underset{|}{Si}}-\overset{|}{N}-\overset{|}{\underset{|}{Si}}-\overset{|}{N}- \; + \; 3\,HX \; \longrightarrow \; X\overset{|}{\underset{|}{Si}}-\overset{|}{N}-\overset{|}{\underset{|}{Si}}X\,(II) \; + \left[\overset{+}{N}H_3\right]^{+}X^{-}$$
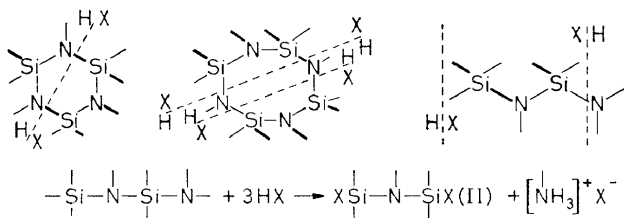
The fluoro-derivatives turned out to be the most stable while the iodo-derivatives decomposed during condensation to cyclodisildiazanes. Kriegsmann and Engelhardt[12] obtained the chloro- and bromo-derivatives already in 1961 for the first time using the following routes:

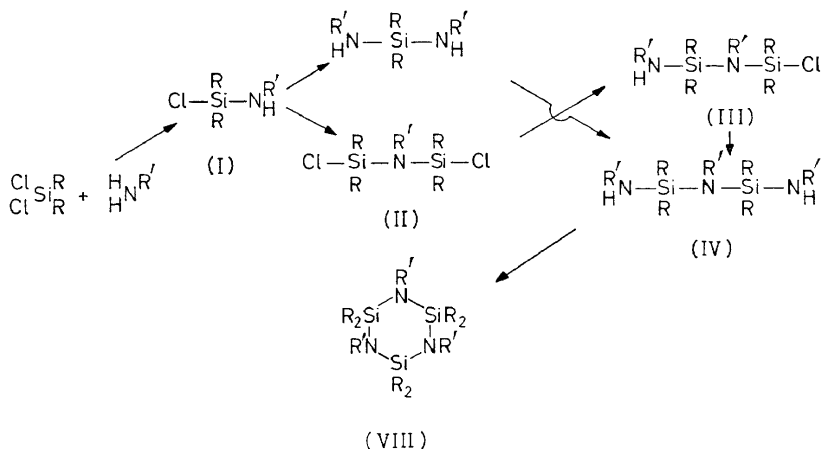$$(IIc) \qquad\qquad\qquad (IIb)$$
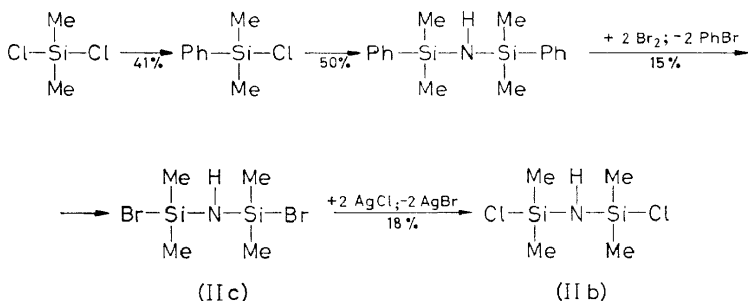
However, the yields in all cases were poor and the products were somewhat impure.

1,3-Difluorodisilazanes are also obtained by heating cyclosilazanes with the addition compound of SiF$_4$ and 2 NH$_3$. In this reaction, two fluorine atoms are exchanged for one NH-group; the principle being very similar to the hydrogen halogenide cleavage of the cyclosilazanes[13, 14]:
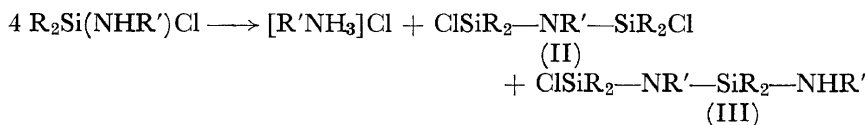

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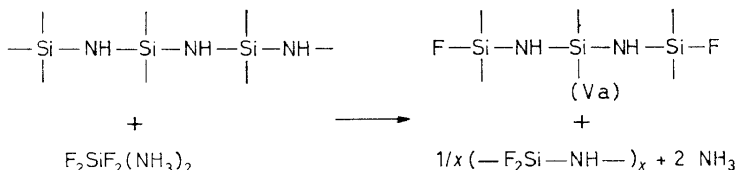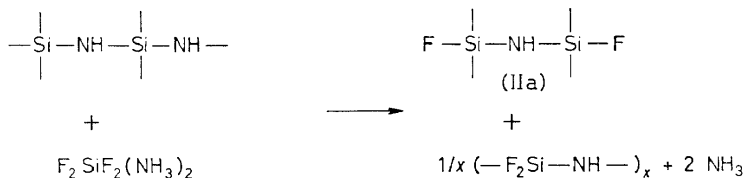
A series of 1,3-dichlorodisilazanes (II) and 1-chloro-3-aminodisilazanes (III) are formed further through the self decomposition of dialkyl-chloro-aminosilanes[15]. Whereas dialkyldichlorosilanes continue to react with the excess of primary amines to yield dialkyldiaminosilanes and partially to 1,3-diaminodisilazanes (IV), dialkyl-chloro-aminosilanes (I) are obtained by reducing the amount of the primary amines. These, however, decompose even in sealed tubes at room temperature, and faster still on refluxing.


(VIII)

The decomposition may be represented by the equation:

$$4\ R_2Si(NHR')Cl \longrightarrow [R'NH_3]Cl + ClSiR_2\text{---}NR'\text{---}SiR_2Cl$$
$$(II)$$
$$+\ ClSiR_2\text{---}NR'\text{---}SiR_2\text{---}NHR'$$
$$(III)$$

The simplest and most elegant preparation of 1,3-dichlorodisilazanes is the equilibration of cyclosilazanes with dichlorosilanes by heating the reactants in equivalent amounts[16, 17]. By this method not only yields of 80 per cent and more are obtained, but it is also possible to synthesize mixed substituted disilazanes, e.g. hexamethylcyclotrisiltriazane and diphenyldichlorosilane result in 1,3-dichloro-1,1-dimethyl-3,3-diphenyl-disilazane[18].
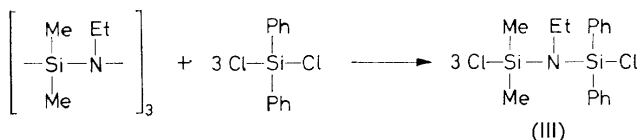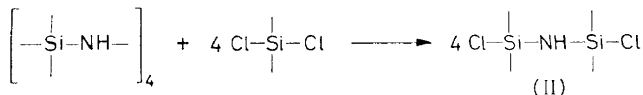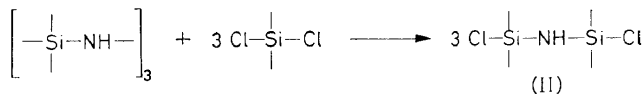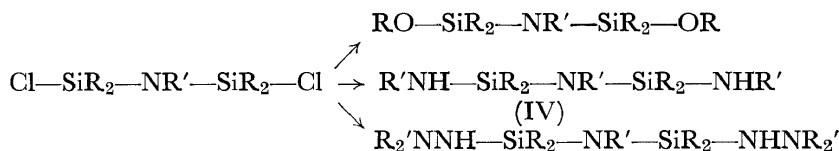
On heating N-alkylcyclosilazanes with dichlorosilanes, both 1,3-dichloro-disilazanes (II) and 1,5-dichlorotrisilazanes (V) can be isolated. The 1,5-dichlorotrisilazanes are valuable five-membered units for ring synthesis[18].
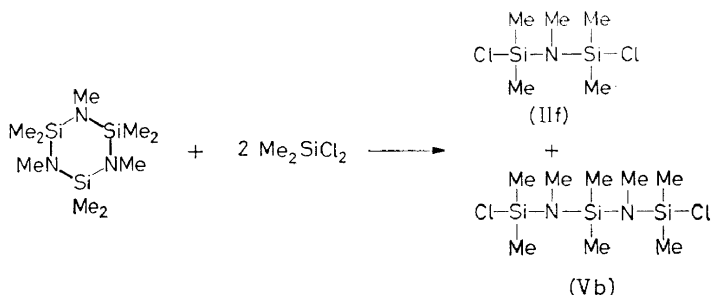
The reaction of an excess of cyclosilazanes containing free NH-groups with dichlorosilanes leads surprisingly to the formation of cyclodisildiazanes[16, 18].
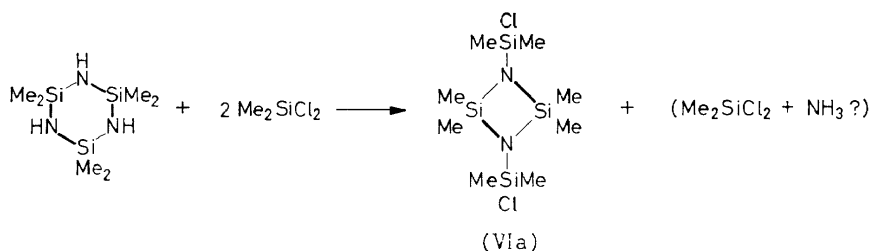

In the presence of proton acceptors the chloride atoms of 1,3-dichloro-disilazanes are easily substituted by alcohols[19], by amines[15] and by hydra-zines[18].

$$RO—SiR_2—NR'—SiR_2—OR$$
$$\nearrow$$
$$Cl—SiR_2—NR'—SiR_2—Cl \;\rightarrow\; R'NH—SiR_2—NR'—SiR_2—NHR'$$
$$\searrow \qquad\qquad (IV)$$
$$R_2'NNH—SiR_2—NR'—SiR_2—NHNR_2'$$

The 1,3-diaminodisilazanes (IV) thus obtained constitute another type of building units with five atoms, N–Si–N–Si–N, for further cyclosilazane syntheses. In case the substitution by amines cannot be achieved by proton acceptors, the reaction with metallated amines usually proves successful.

SILICON–NITROGEN RINGS FROM DICHLORODISILAZANES
The reaction of 1,3-dihalogeno-disilazanes with water, hydrogen sulphide or primary amines, in the presence of triethylamine as proton acceptor, leads to eight-membered rings in yields of 40 to 60 per cent, by linking building units in the construction way[15, 19, 20] 3 + 1 + 1 + 3.

(XII d)   (XV a)
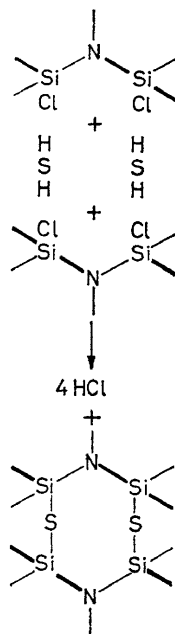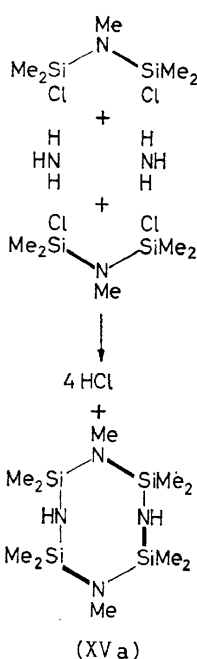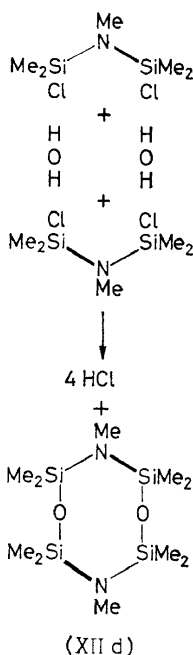
Cyclo-1,3,5,7-tetrasil-2,6-diox-4,8-diazanes (XII) have been previously prepared by ammonolysis of 1,3-dichlorodisiloxanes. The new method offers the advantage that the substituents on the nitrogen atoms are easier to be varied. So far it had not been possible to isolate the analogous cyclo-tetrasil-dithidiazanes in pure form, for on purification decomposition to cyclo-sil-thianes and cyclo-silazanes took place. In the cyclo-tetrasil-tetrazanes (XV) prepared in this way it is possible to vary the nitrogen substituents in 2,6- or 4,8-positions, respectively. *Table 2* lists the compounds prepared and their physical characteristics.

The reactions of 1,3-dichlorodisilazanes with ethylenediols or with ethylene-diamines yield seven-membered ring-systems, viz. 1,5–dioxa–2,4–disila–3–aza-cycloheptanes (XIV a, b) and 1,3,5–triaza–2,4–disila–cycloheptanes (XIV c). These rings are formed by linking a three– and a four membered building unit[18, 19].

(XIV a,b)   (XIV c)
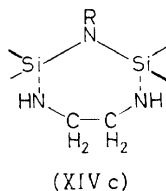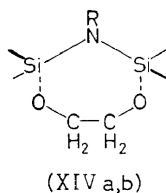
The coupling of two three-membered building units leads to six-membered rings. 1,3-Dihalogenodisilazanes and diaminosilanes may give rise to cyclo-trisil–triazanes where the substituents on one silicon atom or on one nitrogen

Table 2. Physical constants of the Si–N ring compounds (VI–XV) prepared using the novel methods

Name of the compound	Mol. formula	R¹	R²	X	m.p. (°C)	b.p. (°C)	torr.	n_D^{20}	d_4^{20}	Reference
1,1,3,3-TETRAMETHYL-CYCLO-1,3-DISIL-2,4-DIAZANES (VI) $RSiMe_2N(SiMe_2)_2NSiMe_2R$										
(a) 2,4-Bis(dimethylchlorosilyl)-	$C_8H_{24}Cl_2N_2Si_4$	Cl	—	—	69–70°	116–18°	10	—	—	16–18
(b) 2,4-Bis(dimethylbromosilyl)-	$C_8H_{24}Br_2N_2Si_4$	Br	—	—	96–97°	—	—	—	—	18, 21
(c) 2,4-Bis(dimethyliodosilyl)-	$C_8H_{24}I_2N_2Si_4$	I	—	—	108–109°	—	—	—	—	18, 21
(d) 2,4-Bis(dimethylsilyl)-	$C_8H_{26}N_2Si_4$	H	—	—	—	73°	10	1·4308	—	21
(e) 1,4-Bis(dimethylmethoxysilyl)-	$C_{10}H_{30}N_2O_2Si_4$	OMe	—	—	−10°	62°	0·2	1·4340	0·9356	18, 21
(f) 2,4-Bis(aminodimethylsilyl)-	$C_8H_{28}N_4Si_4$	NH₂	—	—	35–36°	decomp.	—	—	—	21
(g) 2,4-Bis(methylaminodimethylsilyl)-	$C_{10}H_{32}N_4Si_4$	NHMe	—	—	2–3°	122°	10	1·4508	—	21
(h) 2,4-Bis(dimethylaminodimethylsilyl)-	$C_{12}H_{36}N_4Si_4$	NMe₂	—	—	1–2°	135°	10	1·4510	—	21
FIVE MEMBERED SI–N RINGS (VII)										
(a) 1,1,2,3,3,4,4,5-Octamethyl-cyclo-1,3,4-trisil-2,5,-diazane	$C_6H_{24}N_2Si_3$				−12°	72°	12	1·4564	0·8706	27
(b) 1,1,2,3,3,4,5-Heptamethyl-cyclo-1,3-disil-2,4,5-triazane	$C_7H_{21}N_3Si_2$					58°	10	1·4412	0·8802	18
(c) Bicyclo-2,2,3,4,4,6,6,7,8,8-decamethyl-2,4,6,8-tetrasil-1,3,5,7-tetrazane	$C_{10}H_{30}N_4Si_4$				8°	97°	10	1·4510	0·9281	16, 22
CYCLO-1,3,5-TRISIL-2,4,6-TRIAZANES (VIII)										
(a) 1,1,3,3,5,5-Hexamethoxy-	$C_6H_{21}N_3O_6Si_3$				186°	—	—	—	—	6
(b) 1,1,3,3,5,5-Hexaethoxy-	$C_{12}H_{33}N_3O_6Si_3$				90°	—	—	—	—	6
(c) 1,1,3,3,5,5-Hexacyclohexyloxy-	$C_{36}H_{69}N_3O_6Si_3$				65–70°	—	—	—	—	6
(d) 1,3,5-Trimethyl-1,3,5-trimethoxy	$C_6H_{21}N_3O_3Si_3$				216–18°	—	—	—	—	6
(e) 1,3,5-Trimethyl-1,3,5-triethoxy-	$C_9H_{27}N_3O_3Si_3$				101°	—	—	—	—	6
(f) 1,3,5-Trimethyl-1,3,5-triisopropoxy-	$C_{12}H_{33}N_3O_3Si_3$				45°	—	—	—	—	6
(g) 1,3,5-Trimethyl-1,3,5-tri-*tert*-butoxy-	$C_{15}H_{39}N_3O_3Si_3$				44°	—	—	—	—	6
(h) 1,3,5-Trimethyl-1,3,5-tris(cyclohexyloxy)-	$C_{21}H_{45}N_3O_3Si_3$				77°	—	—	—	—	6
(i) 1,3,5-Trimethyl-1,3,5-triphenoxy-	$C_{21}H_{27}N_3O_3Si_3$				95°	—	—	—	—	6
(j) 1,3,5-Trivinyl-1,3,5-trimethoxy-	$C_9H_{21}N_3O_3Si_3$				159°	—	—	—	—	6
(k) 2,4,6-Tris-[triethylsilyl]-	$C_{18}H_{51}N_3Si_6$				—	234°	12	1·4912	0·9540	7
(l) 1,1,2,3,3,4,5,5,6-Nonamethyl-	$C_9H_{27}N_3Si_3$				34–35°	—	—	—	—	18, 29
(m) 1,1,2,3,3,4,5,5-Octamethyl-6-butyl-	$C_{12}H_{33}N_3Si_3$				−28°	53°	0·01	1·4573	0·9105	29
(n) 1,1,2,3,3,4,5,5-Octamethyl-	$C_8H_{25}N_3Si_3$				−43°	86–87°	10	1·4499	0·9165	18
CYCLO-1,2,4,5-TETRASIL-3,6-DIAZANES (IX)										
(a) 1,1,2,2,4,4,5,5-Octamethyl-	$C_8H_{26}N_2Si_4$				1°	61°	2	1·4760	0·8758	33
(b) 1,1,2,2,3,4,4,5,5,6-Decamethyl-	$C_{10}H_{30}N_2Si_4$				23°	62°	3	1·4873	0·9013	33
CYCLO-1,4-DISIL-2,3,5,6-TETRAZANES (X)										30–32

see *Z. anorg. allg. Chem.* **311**, 274 (1961)   *J. organomet. Chem.* **5**, 397 (1966)

Table 2. continued

Name of the compound	Mol. formula	R¹	R²	X	m.p. (°C)	b.p. (°C)	torr.	n_2^0	d^{20}	Reference
CYCLO-1,3-DISIL-5-BOR(OR GERM)-2,4,6-TRIAZANES (XI)										
(a) 1,1,2,3,3,4,6-Heptamethyl-5-phenyl-*	$C_{12}H_{26}BN_3Si_2$				59°	89–90°	0·2	—	—	18
(b) 1,1,2,3,3,4,6-Heptamethyl-5,5-dibutyl-†	$C_{15}H_{39}GeN_3Si_2$				—	98–100°	0·05	1·4735	1·0260	18
CYCLOSILOXAZANES (XII)										
(a) 1,1-diphenyl-3,3,5,5-tetramethyl-cyclo-1,3,5-trisil-2,6-diox-4-azane	$C_{16}H_{23}NO_2Si_3$				99°	—	—	—	—	21
(b) 1,1-Diphenyl-3,3,5,5-tetramethyl-4-ethyl-1,3,5-trisil-2,6-diox-4-azane	$C_{18}H_{27}NO_2Si_3$				—	117–119°	0·07	—	—	21
(c) 1,1,3,3,4,5,5,6-Octamethyl-cyclo-1,3,5-trisil-2-ox-4,6-diazane	$C_8H_{24}N_2OSi_3$				—	75°	11	1·4326	0·9244	18
(d) 1,1,3,3,5,5,7,7-Octamethyl-cyclo-	$C_8H_{26}N_2O_2Si_4$				37°	87–89°	10	—	—	19
(e) 1,1,3,3,4,5,5,7,7,8-Decamethyl-cyclo-1,3,5,7-tetrasil-2,6-diox-4,8-diazane	$C_{10}H_{30}N_2O_2Si_4$				27–28°	102°	10	—	—	19
1,3,5-TRIAZA-2,4-DISILA-CYCLOHEXANES (XIII)										
(a) 1,5-Bis(trimethylsilyl)-2,2,4,4-tetramethyl-6-oxo-	$C_{11}H_{31}N_3OSi_4$				decomp	—	—	—	—	16, 18
(b) 1,5-Bis(trimethylsilyl)-2,2,3,4,4-pentamethyl-6-oxo-	$C_{12}H_{33}N_3OSi_4$				130–40° (decomp.)	—	—	—	—	16, 18
CYCLOHEPTANES (XIV)										
(a) 2,2,4,4-Tetramethyl-1,5-dioxa-3-aza-2,4-disila-	$C_6H_{17}NO_2Si_2$				—	64°	10	1·4377	0·9986	19
(b) 2,2,3,4,4-Pentamethyl-1,5-dioxa-3-aza-2,4-disila-	$C_7H_{19}NO_2Si_2$				—	70°	10	1·4376	0·9797	19
(c) 2,2,3,4,4-Pentamethyl-1,3,5-triaza-2,4-disila-	$C_7H_{21}N_3Si_2$				—	88°	10	1·4632	0·9452	18
CYCLO-1,3,5-7-TETRASIL-2,4,6,8-TETRAZANES (XV)										
(a) 1,1,2,3,3,5,5,6,7,7-Decamethyl-	$C_{10}H_{32}N_4Si_4$				95–96°	—	—	—	—	15
(b) 1,1,2,3,3,4,5,5,6,7,7-Undecamethyl-	$C_{11}H_{34}N_4Si_4$				—	84°	0·1	1·4718	0·9608	18

* Containing boron.   † Containing germanium.

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atom respectively are different from the other two in the system. 1,3-Dichloro-disilazanes react with bis(silyl)-urea to give 1,3,5-triaza-2,4-disila-6-oxo-cyclohexanes (XIII a, b). With diphenyldihydroxysilanes cyclo-1,3,5-trisil-2,4-diox-6-azanes (XII a, b) are formed[16, 21].

(VIIIb)   (XIII)   (XII a,b)
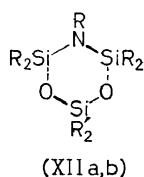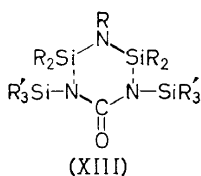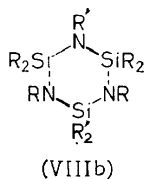
There are two routes to the five-membered ring cyclo-1,3-disil-2,4,5-triazane (VIIb). One method is the reaction of 1,3-dichloro-pentamethyl-disilazane with 1,2-dilithium-1,2-dimethylhydrazine. The *trans*-amination reaction of 1,2-dimethyl-hydrazonium dichloride with 1,3-bis(methylamino)-pentamethyldisilazane can be used as well[18] for obtaining (VIIIb).

(VIIb)
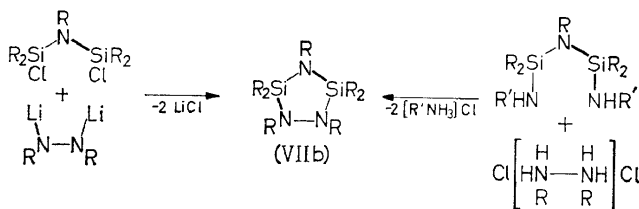
1,3-Dichloro-pentamethyl-disilazane reacts with free hydrazine in a some-what unexpected way, according to the equation[22]

$$2 \, ClSiR_2\text{—}NR\text{—}SiR_2Cl + 5 \, N_2H_4 \rightarrow 4 \, [N_2H_5] \, Cl + R_{10}Si_4N_4$$
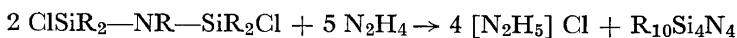
The newly isolated compound may have the structure of a condensed double five-membered ring-system (VIIc).

(VIIc)
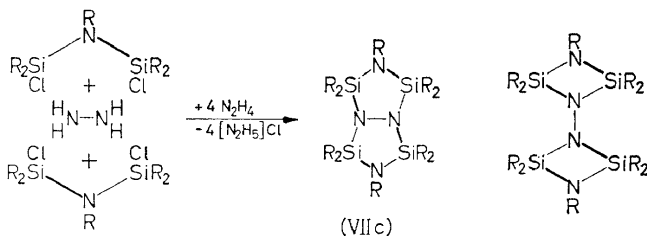
There are some spectroscopic data however, which indicate the structure to be a dicyclo-disil-diazane. Up to now we have been unable to prepare a cyclo-disil-diazane directly from 1,3-dichlorodisilazane and amino groups as in primary amines or asymmetric hydrazines, we always got the open linear structures. On the other hand we know that the five-membered ring of 1,3-disil-2,4,5-triazane (VIIb) is rather unstable. It can therefore be

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assumed that the formation of dicyclo-disil-diazane occurs via valency re-arrangement of the double five-membered ring-system by cleavage and by new formation of the central silicon–nitrogen bonds
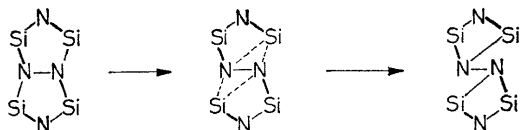
1,3-Dihalogenodisilazanes with an unsubstitituted NH-group can be used in the presence of an HCl-acceptor as starting material for the preparation of four-membered ring-systems, especially 2,4-bis(dimethylhalogenosilyl) tetramethyl-cyclo-1,3-disil-2,4-diazanes (VI). The course of reaction could not yet be ascertained but it seems most likely to be a condensation of two dihalogenodisilazanes. This ring-system is astonishingly stable. It was

(VI)

$X = Cl, Br, I$; $= H, OCH_3, NH_2, NHCH_3, N(CH_3)_2, CH_3$; $R = CH_3$
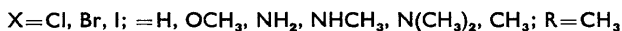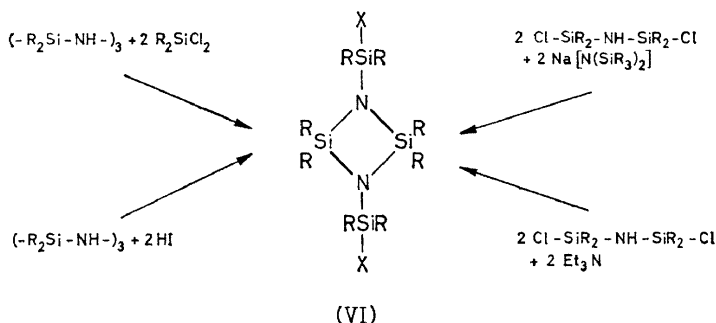
discovered for the first time by Pflugmacher and Dahmen[23], reacting N_2 and $SiCl_4$ in a glow discharge (all substituents $= Cl$). Pyrolysis of N–silylated cyclo-tri- and -tetrasilazanes at elevated tempera-tures and pressures led Fink[24] to the same four-membered system (all sub-stituents $= CH_3$). We succeeded in preparing this class of compounds[18] by splitting cyclotri- and -tetrasilazanes with hydrogen halogenides (especially hydrogen iodide) or by the reaction of dihalogenosilanes with an excess of those ring compounds or by the reaction of 1,3-dihalogenodisilazanes with triethylamine. Geymayer and Rochow[17] prepared it from the dihalogeno-disilazanes by reaction with sodium-bis(trimethylsilyl)amide. The halogen atoms can be exchanged in presence of triethylamine for alkoxy and amino groups; in the case of lithium aluminium hydride the chlorine atoms are sub-stituted by negative polarized hydrogen. Hydrogen chloride cleaves the ring to give in good yields the tris(dimethylchlorosilyl)amine.
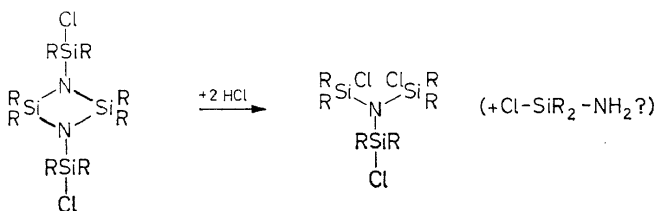
RING COMPOUNDS FROM OTHER SILICON–NITROGEN BUILDING UNITS

1,3-Dihalogenodisilazanes with their three-membered building unit Si–N–Si have surpassed the other higher building units for the synthesis of inorganic ring-systems, due to their extraordinary versatility. The inverse three-membered building unit N–Si–N has been used for ring syntheses by Lienhard and Rochow[25] as well as by Fink[26]. Thus the dilithium derivative of dimethyl-bis(methylamino)silane may be condensed with dichlorosilanes, -boranes and -phosphines to four-membered rings. By reacting with 1,2-dichlorodisilane we succeeded in synthesizing the new Si–N five-membered ring system of 1,3,4-trisil-2,5-diazane (VIIa)[27].

(VIIa)
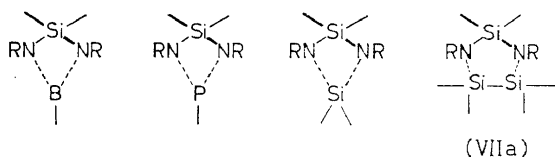
Among the five-membered building units, in general, those of 1,3-diaminodisilazanes, N–Si–N–Si–N, can be varied to a large extent. Rochow[28] described the structure of heptamethylcyclotrisiltriazanes where the two remaining substituents on the third silicon atom could be varied. Independently we found a cyclotrisiltriazane (VIIIm) where two different N-substituents R and R' were introduced by a 1,3-diaminodisilazane derived from 1,3-dihalogenodisilazanes[29]. By combination of dilithium derivatives of 1,3-diaminodisilazanes with element dichlorides it is possible to obtain hetero ring-systems such as 1,3-disil-5-bor-2,4,6-triazane (XIa) or the analogous 5-germanium-derivative (XIb)[18]. With 1,3-dichloro-tetramethyl-disilazane we got the cyclo-tetrasiltetrazane (XVb) with eleven methyl groups.

(VIIIm)   (XIa)   (XIb)   (XVb)

R=CH₃
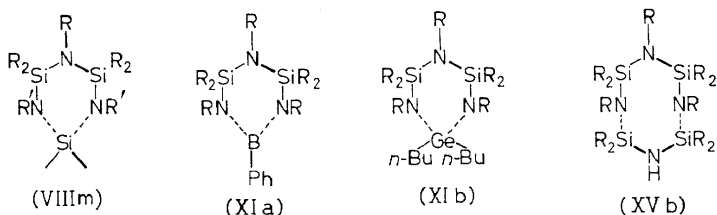
Presently we are engaged in establishing in the same way the Si–N seven-membered ring-system of 1,3,5,6-tetrasil-2,4,7-triazane, proceeding from dichlorodisilane. The synthesis of the Si–N seven-membered ring-system 1,3,5-trisil-2,4,6,7-tetrazane may follow two paths: from the three-membered building unit of N,N'-dilithium-diamino-silane and the four-membered building unit of 1,2-bis(chlorodimethylsilyl)hydrazine as well as from 1,5-dichlorotrisilazanes with hydrazines. All syntheses are now well on their way.
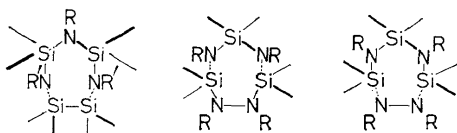
We also succeeded in synthesizing cyclotrisiltriazanes via the five-membered building unit of 1,5-dichlorotrisilazane (Vb) by simple reaction with ammonia in the presence of triethylamine. In these substances two nitrogen atoms are alkyl-substituted, the third however constitutes a free NH-group. In the same way, by reaction with water, we obtained the cyclo-1, 3,5-trisil-2-ox-4,6-diazane (XIIc)[18].

(VIII n)   (XII c)
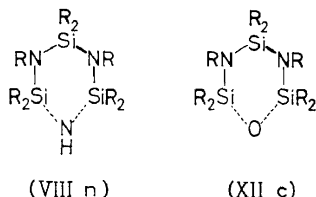
As a culminating point in our Si–N ring-synthesis we have already started to construct stepwise a cyclotrisilazane, where every silicon and every nitrogen atom carries different substituents. Dimethyldichlorosilane reacts with ethylamine to dimethyl-bis(ethylamino)silane. This condenses at elevated temperatures to triethyl-hexamethyl-cyclotrisiltriazane in the presence of ammonium sulphate. The equilibration of this compound with diphenyl-dichlorosilane leads to 1,3-dichloro-1,1-dimethyl-2-ethyl-3,3-diphenyl-disilazane, which, reacted with butylamine, yields 1–butylamino-1,1-dimethyl-2-ethyl-3,3-diphenyl-3-chlorodisilazane. Further reaction with propylamine under more vigorous conditions (eventually in the form of its lithium derivative) gives 1-butylamino-1,1-dimethyl-2-ethyl-3,3-diphenyl-3-propylaminodisilazane. This is the point where we stand now[18]. The rest is some routine work: metallation with butyl lithium and ring-closure with vinyltrichlorosilane will result in 1,1-dimethyl-2-ethyl-3,3-diphenyl-4-propyl-5-vinyl-5-chloro-6-butyl-cyclo-1,3,5-trisil-2,4,6-triazane

$$Me_2SiCl_2 \longrightarrow Me_2Si(NHEt)_2 \longrightarrow$$
$$\longrightarrow (-Me_2Si-NEt-)_3 \longrightarrow ClSiMe_2-NEt-SiPh_2Cl$$
$$\longrightarrow BuNH-SiMe_2-NEt-SiPh_2-Cl \longrightarrow$$
$$\longrightarrow BuNH-SiMe_2-NEt-SiPh_2-NHPr$$
$$BuNLi-SiMe_2-NEt-SiPh_2-NLiPr$$

Et
|
N
Me₂Si͞   ͞SiPh₂
BuN͞   ͞NPr
    Si
   Vi Cl

$$Vi = C_2H_3$$
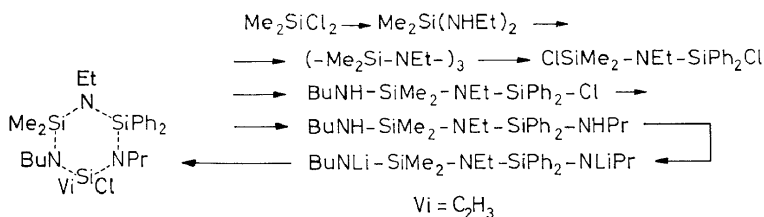
Finally I should like to report about two more syntheses of six-membered Si–N ring-systems. Cyclo-1,4-disil-2,3,5,6-tetrazanes are formed in the reactions of hydrazine and its derivatives, if necessary after metallation, with dihalogenosilanes[30-32]. Cyclo-1,2,4,5-tetrasil-3,6-diazanes can be prepared by ammonolysis of dichlorodisilanes with primary amines[27, 33].

R—N͞   ͞N—R
   Si
R—N͟   ͟N—R
   Si

(X)

R
|
N
Si   Si
Si   Si
N
|
R

(IXa, b)
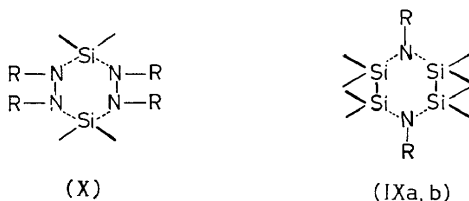
CONCLUSION

I regret not to have been in a position to mention all the known Si–N ring-systems and their methods of preparation. Some more ring-systems (listed below) are presently known or will be known in the near future.

XVI   VI   VIIa   VIIb   XVII

VIII   IX   X

XV

XVIII   VIIc   XIX

XX

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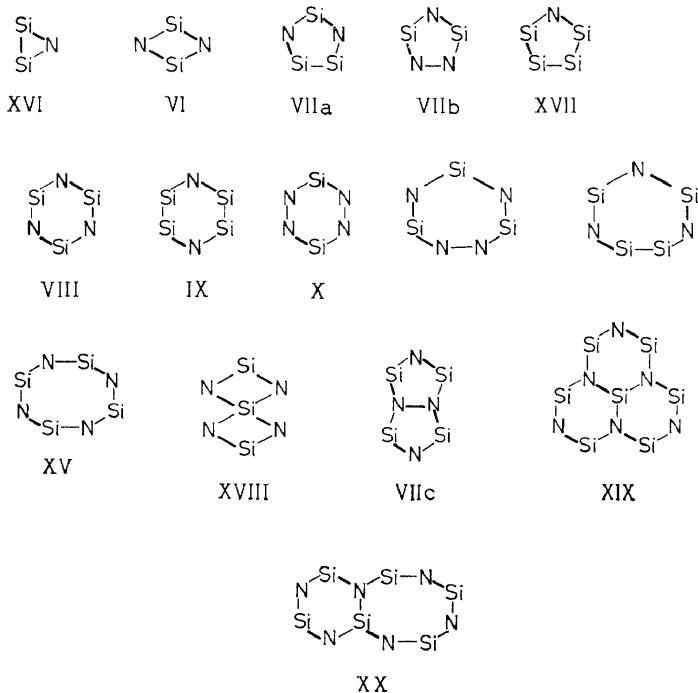
The Cyclo-1,2,-disil-3-azane (XVI) was discovered by Fink[34] in 1963, the cyclo-1,2,3,4-tetrasil-5-azane by Hengge *et al*[35], the spiro compound (XVIII) by Lienhard and Rochow[36] in 1963–64 and the condensed six-membered[37] (XIX) as well as the eight- and six-membered system (XX) by Andrianov and coworkers[38]. There are still a wide variety of unknown Si–N rings waiting for investigation, although we may predict that their preparation will become more and more difficult. Brewer and Haber's has been the only way of preparing cyclosilazanes for almost 15 years. Today the intermediate building units for ring syntheses enable us to prepare any cyclosilazane whatsoever with any substituent in every possible position. Furthermore, the possibility of synthesizing inorganic ring-systems which contain besides nitrogen and silicon other elements as ring units opens a vast, fertile field in preparative chemistry. And I am sure that for many years to come neither the intricacies of structure nor all isomeric configurations and conformations of these cyclic compounds with silicon and nitrogen atoms will have been fully exploited.

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