THE CHEMISTRY OF SILICON-NITROGEN COMPOUNDS

RALPH FESSENDEN AND JOAN SEARING FESSENDEN
Department of Chemistry, San Jose State College, San Jose, California

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CONTENTS

I. INTRODUCTION

A. SCOPE OF REVIEW

The chemistry of the silicon–nitrogen compounds embraces both inorganic and organic chemistry. This review, although attempting to bridge both fields of chemistry, emphasizes the organic nature of this class of compounds.

This paper reviews publications through December, 1959, with a few important references from papers published in 1960. The silicon pseudohalides (cyanides, isocyanates, and isothiocyanates) and silicon nitrides, the chemical behavior of which differs from that of other silicon–nitrogen compounds, have been excluded. The pseudohalides have been reviewed elsewhere (4, 132). Reactions are given in tabular form where appropriate and the physical constants of the silicon–nitrogen compounds are summarized.

B. NOMENCLATURE

The Committee on Nomenclature of the American Chemical Society and the Commission on the Nomenclature of Organic Chemistry of the International Union of Pure and Applied Chemistry have adopted a system for naming organosilicon compounds. For a detailed presentation of this system, the reader is referred to the articles by Crane (48, 49). For convenience, a short résumé of the rules for naming silicon–nitrogen compounds is included here. Specific examples are summarized in table 1.

Compounds derived from the structure H_3SiNH_2 are

TABLE 1

Nomenclature of silicon–nitrogen compounds

Formula	Preferred Name	Other Names in the Literature
$(H_3Si)_3N$	Trisilylamine	
$(H_3Si)_2NCH_3$	*N*-Methyldisilazane	Disilylmethylamine
$H_3SiN(CH_3)_2$	*N*,*N*-Dimethylsilylamine	Silyldimethylamine
$[(CH_3)_3Si]_3N$	Tris(trimethylsilyl)amine	
$(C_2H_5)_3SiNH_2$	Triethylsilylamine	Triethylaminosilane, triethylsilazane, triethylsilicylamine
$(C_2H_5)_3SiNHC_2H_5$	*N*-Ethyltriethylsilylamine	Triethyl-*N*-ethylaminosilane, *N*-ethyl-(triethylsilyl)amine
$(tert\text{-}C_4H_9)_2Si(NH_2)_2$	Di-*tert*-butylsilanediamine	Di-*tert*-butyldiaminosilane
$(C_2H_5)_2Si(NHCH_3)_2$	Bis(methylamino)diethylsilane	
$C_2H_5Si[N(CH_3)_2]_3$	Tris(dimethylamino)ethylsilane	
$[(CH_3)_3Si]_2NH$	Hexamethyldisilazane	Ditrimethylsilicylamine
$[(C_6H_5)_3Si]_2NCH_3$	*N*-Methylhexaphenyldisilazane	
$[(CH_3)_2SiNH]_3$	Hexamethylcyclotrisilazane	
$[(C_6H_5)_2SiNH]_4$	Octaphenylcyclotetrasilazane	
$(CH_3)_3SiNHNHC_6H_5$	*N*-(Trimethylsilyl)-*N'*-phenylhydrazine	

called silylamines, with the use of appropriate prefixes to designate substitution.

The system of prefix designation for nitrogen substitution becomes quite cumbersome when more than one nitrogen is attached to silicon. In these cases the amine grouping is designated as a substituent of the silane.

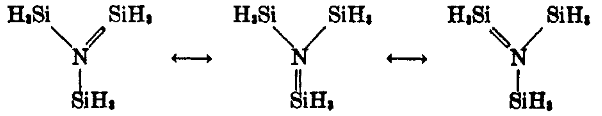
The generic name silazane is given to the series $H_3Si(NHSiH_2)_nNHSiH_3$. Compounds of this series are called disilazanes, trisilazanes, etc., depending upon the number of silicon atoms in the molecule. Two spellings of this generic name are found in the literature, silazane and silazine, with the former being preferred.

Compounds of the type $(H_2SiNH)_n$ are given the generic name cyclosilazanes, the prefix depending upon the number of silicon atoms in the ring.

In both the text and the tables, reference to normal alkyl groups will be made by the name or formula without the prefix *n*.

II. Physical Properties of Silicon–Nitrogen Compounds

The molecular structure of the simple silylamines differs markedly from that of their carbon analogs. On the basis of electron-diffraction data (89) and infrared and Raman spectra (56, 110, 160), trisilylamine is a coplanar molecule, as is tri(methylsilyl)amine (57). Tris(trimethylsilyl)amine is nonplanar (79). In conjunction with its coplanar structure, the silicon–nitrogen distance of trisilylamine is shorter than that calculated or that observed in other silicon–nitrogen systems (see table 2). These properties of the simple silylamines have been interpreted in terms of the ability of the extra pair of electrons of the nitrogen to enter into the empty *d* orbitals of the silicon (d_π–p_π overlap). (See reference 47 for a general discussion of this type of bonding.) The resonance energy of the silicon–nitrogen bond has been estimated to be 9 kcal./mole (198).



On the basis of electron-diffraction data, hexamethylcyclotrisilazane and octamethylcyclotetrasilazane have been assigned nonplanar structures (220). However, Kriegsmann (109) has studied the infrared and Raman spectra of hexamethylcyclotrisilazane and assigned a coplanar structure to this compound.

The relative basicities of trisilylamine and the other simple silylamines have been studied, using trimethylboron as the reference acid and trimethylamine as the reference base. From the standpoint of electronegativity, trisilylamine should be a strong base but it is, in fact, a very weak base. The actual pK_b has not been determined because of facile cleavage of the silicon–nitrogen bond by acidic reagents. Neither trisilylamine nor *N*-methyldisilazane enters into complex formation with trimethylboron (37, 198) or diborane (37, 67), and attempts to differentiate them with boron trifluoride or monobromodiborane failed, although there was some indication that trisilylamine was the weaker base (199). *N*,*N*-Dimethylsilylamine does form a complex with trimethylboron and, by comparison of the dissociation pressures of this complex with those of trimethylamine, the silylamine was found to be the weaker base (198). Thus the basicities of these silylamines decrease in the following order:

$$(CH_3)_3N > H_3SiN(CH_3)_2 > (H_3Si)_2NCH_3 \sim (H_3Si)_3N$$

This decrease in basicity as methyl groups are replaced

TABLE 2

Bond distances and bond angles for silicon–nitrogen compounds

Compound	Bond Distance*	N—Si—N Bond Angle	Si—N—Si Bond Angle	Reference
$[(CH_3)_2SiNH]_3$	1.78 ± 0.03	111 ± 5°	117 ± 4°	(220)
$[(CH_3)_2SiNH]_4$	—	—	123 ± 4°	(220)
$(H_3Si)_3N$	1.738 ± 0.020	—	119.6 ± 1.0°	(89)
$[(CH_3)_3Si]_2NH$	—	—	131°	(108)

* Calculated: Si—N, 1.80 A.; Si=N, 1.62 A. (89).

by silyl groups has been attributed to the addition of available *d* orbitals for participation in resonance (55).

No extensive studies of the relative basicities of higher silylamines have been undertaken, although a few other compounds have been investigated. Neither tri(methylsilyl)amine nor *N*-methyldi(methylsilyl)amine forms a complex with trimethylboron, but *N*,*N*-dimethyl(methylsilyl)amine does undergo complex formation (55). Tetrasilylhydrazine does not function as an electron acceptor or donor (9). On the other hand, hexamethyldisilazane forms complexes with boron trifluoride (145) and sulfur trioxide (13).

In the infrared spectra of trialkylsilylamines, nitrogen–hydrogen bond stretching and deformation frequencies are similar to those of normal amines (62). The silicon–nitrogen bond asymmetric stretching frequency in the simple silylamines has been observed in the 900–1000 $\mathrm{cm.}^{-1}$ region (57, 110, 160). Other tabulations and published spectra are found in the literature (39, 64, 68, 79, 108).

The mass-spectral analysis of hexamethyldisilazane has been reported (177), as have the nuclear magnetic resonance spectra of hexamethyldisilazane (93), hexamethylcyclotrisilazane (93), trisilylamine (58), *N*,*N*-dimethylsilylamine (58), and *N*-methyldisilylamine (58).

Dipole moments of some silylamines have been measured: hexamethyldisilazane, 0.67 D (145); *N*-methylhexamethyldisilazane, 0.44 D (145); trimethyl-*N*-phenylsilylamine, 1.37 D (145); tris(trimethylsilyl)amine, 0.51 D (79).

The silicon–nitrogen bond refraction is given as 2.00 ml./mole (213).

The melting points, boiling points, densities, and refractive indices of silylamines and related compounds are tabulated in table 12.

III. Synthesis of Silicon–Nitrogen Compounds

A. SYNTHESIS FROM HALOSILANES

The action of ammonia or an amine on a halosilane results in the formation of a silicon–nitrogen bond. Comparative yield data for the various halogens are not available in a sufficiently hindered system for the differences in reactivity to be detected. From the data available, the bromo- and iodosilanes appear more reactive toward a given amine than do the chlorosilanes (202). Owing to their availability, however, the chlorosilanes are most frequently employed.

The halide released during the course of the reaction is precipitated as the ammonium or amine salt. The reaction is reversible, with the halosilane being obtainable from the silylamine and the amine salt (2, 16).

$$\mathrm{R_3SiCl + 2R'NH_2 \rightleftarrows R_3SiNHR' + R'NH_3Cl}$$

Since the formation of the ammonium halide or the amine salt is common to all the reactions in this section, it will be excluded from the equations that follow.

1. From monohalosilanes

By analogy with the chemistry of the carbon compounds, the reaction of a monohalosilane with ammonia should yield four silicon–nitrogen products. However, owing to the electronic and steric nature of the compounds involved, only one or, in a few cases, two reaction products are formed (see table 3).

When the other substituents attached to the silicon are hydrogen, there is a definite tendency for complete silylation of the ammonia or the amine molecule (37, 195, 198). When silyl chloride is treated with ammonia, trisilylamine can be obtained in yields up to 80 per cent (37).

$$\mathrm{H_3SiCl + NH_3 \rightarrow (H_3Si)_3N}$$

With primary amines also, there is a great tendency for complete silylation by silyl chloride. With methylamine or ethylamine, only the completely silylated product can be isolated (59, 60, 198).

$$\mathrm{H_3SiCl + CH_3NH_2 \rightarrow CH_3N(SiH_3)_2}$$

This tendency is decreased as the size of the groups attached to the silicon is increased. The first evidence of steric transition, the preference for formation of disilazane over trisilylamine, occurs as the size of the groups attached to the silicon is increased from hydrogen to methyl. The only intermediate case studied yields a trisilylamine (55).

$$\mathrm{CH_3SiH_2Cl + NH_3 \rightarrow (CH_3H_2Si)_3N}$$

With trimethylchlorosilane, only hexamethyldisilazane can be isolated (133, 140, 145, 168, 169). An attempt to obtain the trimethylsilylamine by the use of excess liquid ammonia failed (169). This failure was probably caused by rapid condensation of the silylamine to the disilazane during attempted isolation.

$$\mathrm{(CH_3)_3SiCl + NH_3 \rightarrow (CH_3)_3SiNHSi(CH_3)_3}$$

Attempts to obtain tris(trimethylsilyl)amine directly failed (169), even at 500°C. with pyridine as solvent (79). This derivative, however, can be formed by the use of the lithium (210) or sodium (79) salt of hexamethyldisilazane.

$$\mathrm{[(CH_3)_3Si]_2NLi + (CH_3)_3SiCl \rightarrow [(CH_3)_3Si]_3N}$$

The tendency for disilazane formation is also observed in the formation of *N*-methylhexamethyldisilazane by the reaction of *N*-methyltrimethylsilylamine with trimethylchlorosilane (169)

$$\mathrm{(CH_3)_3SiNHCH_3 + (CH_3)_3SiCl \rightarrow [(CH_3)_3Si]_2NCH_3}$$

and in the reaction of diethylchlorosilane with ammonia (178).

$$\mathrm{(C_2H_5)_2SiHCl + NH_3 \rightarrow [(C_2H_5)_2HSi]_2NH}$$

Increasing the size of the substituent on the silicon atom from methyl to ethyl does not affect the degree of

TABLE 3

Synthesis of silicon–nitrogen compounds from monohalosilanes

Halosilane	Amine	Product	Yield	References
			per cent	
H_3SiCl	NH_3	$(H_3Si)_3N$	80	(37, 67, 160, 195)
	CH_3NH_2	$(H_3Si)_2NCH_3$	85	(37, 59, 60)
	$C_2H_5NH_2$	$(H_3Si)_2NC_2H_5$	—	(59, 60)
	$(CH_3)_2NH$	$H_3SiN(CH_3)_2$	—	(59, 60)
D_3SiCl	NH_3	$(D_3Si)_3N$	—	(56, 160)
H_3SiBr	NH_3	$(H_3Si)_3N$	84	(198)
	CH_3NH_2	$(H_3Si)_2NCH_3$	—	(198)
	$(CH_3)_2NH$	$H_3SiN(CH_3)_2$	—	(198)
CH_3SiH_2Cl	NH_3	$(CH_3SiH_2)_3N$	65–70	(55)
	CH_3NH_2	$(CH_3SiH_2)_2NCH_3$	65	(55)
CH_3SiH_2I	$(CH_3)_2NH$	$CH_3SiH_2N(CH_3)_2$	90	(55)
$(CH_3)_3SiCl$	NH_3	$[(CH_3)_3Si]_2NH$	45–70	(133, 140, 145, 169, 181)
	CH_3NH_2	$(CH_3)_3SiNHCH_3$	38–55	(169)
		$[(CH_3)_3Si]_2NCH_3$	40	(145)
	$(CH_3)_2NH$	$(CH_3)_3SiN(CH_3)_2$	—	(55, 140)
	$C_2H_5NH_2$	$(CH_3)_3SiNHC_2H_5$	25	(169)
	$(C_2H_5)_2NH$	$(CH_3)_3SiN(C_2H_5)_2$	32	(112, 149, 169)
	$CH_2{=}CHOC(CH_3)_2NH_2$	$(CH_3)_3SiNHC(CH_3)_2OCH{=}CH_2$	66	(50)
	tert-$C_4H_9NH_2$	$(CH_3)_3SiNH($*tert*-$C_4H_9)$	—	(149)
	$C_6H_5NH_2$	$(CH_3)_3SiNHC_6H_5$	60–80	(2, 145)
	$(CH_3)_3SiNHCH_3$	$[(CH_3)_3Si]_2NCH_3$	61	(169)
	$[(CH_3)_3Si]_2NNa$	$[(CH_3)_3Si]_3N$	60	(79)
	$[(CH_3)_3Si]_2NLi$	$[(CH_3)_3Si]_3N$	85	(210)
	$\underbrace{C_4H_4N}K$	$(CH_3)_3Si\underbrace{NC_4H_4}$	48	(64)
	$AgOSO_2NH_2$	$(CH_3)_3SiOSO_2NHSi(CH_3)_3$	94	(142)
	$NH_2CH_2COOC_2H_5$	$(CH_3)_3SiNHCH_2COOC_2H_5$	34	(20, 21)
	NH_2CH_2COONa	$(CH_3)_3SiNHCH_2COOSi(CH_3)_3$	—	(164)
	CH_3CONH_2	$(CH_3)_3SiNHCOCH_3$	—	(95)
$(CH_3)_3SiCH_2Si(CH_3)_2Br$	NH_3	$[(CH_3)_3SiCH_2Si(CH_3)_2]_2NH$	34	(141)
$(C_2H_5)_2SiHCl$	NH_3	$[(C_2H_5)_2SiH]_2NH$	63	(178)
$(CH_3)_2C_2H_5SiCl$	NH_3	$[(CH_3)_2C_2H_5Si]_2NH$	65	(179)
$(C_2H_5)_2CH_3SiCl$	NH_3	$[(C_2H_5)_2CH_3Si]_2NH$	70	(179)
$(CH_3)_2C_6H_5SiBr$	NH_3	$[(CH_3)_2C_6H_5Si]_2NH$	—	(180)
$(C_2H_5)_3SiCl$	NH_3	$(C_2H_5)_3SiNH_2$	70	(12, 169)
		$[(C_2H_5)_3Si]_2NH$	—	(169)
	CH_3NH_2	$(C_2H_5)_3SiNHCH_3$	53	(8)
	$(CH_3)_2NH$	$(C_2H_5)_3SiN(CH_3)_2$	—	(8)
	$C_2H_5NH_2$	$(C_2H_5)_3SiNHC_2H_5$	—	(8, 127, 149)
	$(C_2H_5)_2NH$	$(C_2H_5)_3SiN(C_2H_5)_2$	—	(8, 100, 149)
	$C_2H_5NHCH_2CN$	$(C_2H_5)_3SiN(C_2H_5)CH_2CH_2CN$	40	(139)
	$C_6H_5NH_2$	$(C_2H_5)_3SiNHC_6H_5$	72	(2, 127)
	$C_6H_5CH_2NH_2$	$(C_2H_5)_3SiNHCH_2C_6H_5$	—	(127)
	$C_6H_5CH(CH_3)NH_2$	$(C_2H_5)_3SiNHCH(CH_3)C_6H_5$	—	(127)
	p-$CH_3C_6H_4NH_2$	$(C_2H_5)_3SiNH(C_6H_4CH_3$-$p)$	—	(127)
	$AgOSO_2NH_2$	$(C_2H_5)_3SiOSO_2NHSi(C_2H_5)_3$	97	(142)
$(C_2H_5)_3SiBr$	$C_2H_5NH_2/Li$	$(C_2H_5)_3SiNHC_2H_5$	—	(105)
$[CH_3CH(Cl)](C_2H_5)_2SiCl$	NH_3	$[CH_3CH(Cl)](C_2H_5)_2SiNH_2$	88	(12)
$[ClCH_2CH_2](C_2H_5)_2SiCl$	NH_3	$[ClCH_2CH_2](C_2H_5)_2SiNH_2$	60	(184)
$(C_6H_5)(CH_3)(C_2H_5)SiCl$	p-$CH_3C_6H_4NH_2$	$(C_6H_5)(CH_3)(C_2H_5)SiNH(C_6H_4CH_3$-$p)$	—	(102)
$(C_6H_5CH_2)(CH_3)(C_2H_5)SiCl$	p-$CH_3C_6H_4NH_2$	$(C_6H_5CH_2)(CH_3)(C_2H_5)SiNH(C_6H_4CH_3$-$p)$	—	(103)
$(C_2H_5)_3SiCH_2Si(C_2H_5)_2Br$	NH_3	$(C_2H_5)_3SiCH_2Si(C_2H_5)_2NH_2$	61	(141)
$(C_3H_7)_3SiCl$	NH_3	$(C_3H_7)_3SiNH_2$	88	(124)
	CH_3NH_2	$(C_3H_7)_3SiNHCH_3$	30	(124)
	$(CH_3)_2NH$	$(C_3H_7)_3SiN(CH_3)_2$	70	(124)
	$C_2H_5NH_2$	$(C_3H_7)_3SiNHC_2H_5$	65	(124)
	$(C_2H_5)_2NH$	$(C_3H_7)_3SiN(C_2H_5)_2$	79	(124)
	$C_3H_7NH_2$	$(C_3H_7)_3SiNHC_3H_7$	64	(124)
	iso-$C_3H_7NH_2$	$(C_3H_7)_3SiNH($iso-$C_3H_7)$	74	(124)
$(C_3H_7)_3SiCH_2Si(C_3H_7)_2Br$	NH_3	$(C_3H_7)_3SiCH_2Si(C_3H_7)_2NH_2$	72	(141)
$(C_4H_9)_3SiCl$	NH_3	$(C_4H_9)_3SiNH_2$	—	(120)
	CH_3NH_2	$(C_4H_9)_3SiNHCH_3$	—	(120)
	$C_2H_5NH_2$	$(C_4H_9)_3SiNHC_2H_5$	—	(120)
	$(C_2H_5)_2NH$	$(C_4H_9)_3SiN(C_2H_5)_2$	—	(120)
	$C_3H_7NH_2$	$(C_4H_9)_3SiNHC_3H_7$	—	(120)
	iso-$C_3H_7NH_2$	$(C_4H_9)_3SiNH($iso-$C_3H_7)$	—	(120)
	$C_4H_9NH_2$	$(C_4H_9)_3SiNHC_4H_9$	—	(120)
$(C_4H_9)_3SiCH_2Si(C_4H_9)_2Br$	NH_3	$(C_4H_9)_3SiCH_2Si(C_4H_9)_2NH_2$	80	(141)
$(C_6H_5)_3SiCl$	NH_3	$(C_6H_5)_3SiNH_2$	—	(154)
	$C_2H_5NH_2$	$(C_6H_5)_3SiNHC_2H_5$	65–85	(16)
	$(C_4H_9)_2NLi$	$(C_6H_5)_3SiN(C_4H_9)_2$	10	(71)
	CH_3CONH_2	$(C_6H_5)_3SiNHCOCH_3$	—	(95)
$(C_6H_5)_3SiBr$	$C_2H_5NH_2$	$(C_6H_5)_3SiNHC_2H_5$	65–85	(16)
$(C_6H_5)_3SiF$	NH_3/Li	$[(C_6H_5)_3Si]_2NH$	32	(45)
	$(C_6H_5)_2NLi$	$(C_6H_5)_3SiN(C_6H_5)_2$	20	(46)
$[p$-$(CH_3)_2NC_6H_4]_3SiCl$	NH_3	$[p$-$(CH_3)_2NC_6H_4]_3SiNH_2$	95	(205)
$(p$-$CH_3C_6H_4)_3SiF$	NH_3/Li	$[(p$-$CH_3C_6H_4)_3Si]_2NH$	23	(45)

TABLE 3 (*Continued*)

Halosilane	Amine	Product	Yield	References
			per cent	
$(o\text{-}CH_3C_6H_4)_3SiCl$	$(C_4H_9)_2NLi$	$(o\text{-}CH_3C_6H_4)_3SiN(C_4H_9)_2$	55	(72)
$(1\text{-}C_{10}H_7)_3SiF$	$NaNH_2$ or NH_3/Li	$(1\text{-}C_{10}H_7)_3SiNH_2$	50	(44, 45)
$[(C_6H_5)_3Ge]_3SiBr$	NH_3	$[(C_6H_5)_3Ge]_3SiNH_2$	90	(137)
$(CH_3O)_3SiCl$	NH_3	$[(CH_3O)_3Si]_2NH$	35	(162)
$(CH_3O)_2(tert\text{-}C_4H_9O)SiCl$	NH_3	$(CH_3O)_2(tert\text{-}C_4H_9O)SiNH_2$	—	(147)
$C_6H_5(CH_3O)_2SiCl$	NH_3	$[C_6H_5(CH_3O)_2Si]_2NH$	—	(162)
$(C_2H_5O)_3SiCl$	NH_3	$[(C_2H_5O)_3Si]_2NH$	58	(162)
	$(CH_3)_2NH$	$(C_2H_5O)_3SiN(CH_3)_2$	71	(162)
$(iso\text{-}C_3H_7O)_3SiCl$	NH_3	$(iso\text{-}C_3H_7O)_3SiNH_2$	—	(175)
$(iso\text{-}C_3H_7)_2(tert\text{-}C_4H_9O)SiCl$	NH_3	$(iso\text{-}C_3H_7O)_2(tert\text{-}C_4H_9O)SiNH_2$	78	(138)
$(C_4H_9O)_3SiCl$	NH_3	$(C_4H_9O)_3SiNH_2$	82	(116, 117)
	CH_3NH_2	$(C_4H_9O)_3SiNHCH_3$	—	(117)
	$C_2H_5NH_2$	$(C_4H_9O)_3SiNHC_2H_5$	—	(116, 117)
	$(C_2H_5)_2NH$	$(C_4H_9O)_3SiN(C_2H_5)_2$	45	(99)
	$\underbrace{CH_2CH_2NH}$	$(C_4H_9O)_3Si\underbrace{NCH_2CH_2}$	—	(91)
	$C_3H_7NH_2$	$(C_4H_9O)_3SiNHC_3H_7$	—	(117)
	$C_4H_9NH_2$	$(C_4H_9O)_3SiNHC_4H_9$	—	(117)
	$C_6H_5NH_2$	$(C_4H_9O)_3SiNHC_6H_5$	57	(99, 117)
$(sec\text{-}C_4H_9O)_3SiCl$	NH_3	$(sec\text{-}C_4H_9O)_3SiNH_2$	—	(77)
$(C_4H_9O)(tert\text{-}C_4H_9O)_2SiCl$	NH_3	$(C_4H_9O)(tert\text{-}C_4H_9O)_2SiNH_2$	—	(147)
$(tert\text{-}C_4H_9O)_3SiCl$	NH_3	$(tert\text{-}C_4H_9O)_3SiNH_2$	85	(138, 147)
$(tert\text{-}C_4H_9O)_2(CH_3O)SiCl$	NH_3	$(tert\text{-}C_4H_9O)_2(CH_3O)SiNH_2$	83	(138)
$(tert\text{-}C_4H_9O)_2(C_4H_9O)SiCl$	NH_3	$(tert\text{-}C_4H_9O)_2(C_4H_9O)SiNH_2$	55	(138)
$(tert\text{-}C_4H_9O)_2(iso\text{-}C_3H_7O)SiCl$	NH_3	$(tert\text{-}C_4H_9O)_2(iso\text{-}C_3H_7O)SiNH_2$	62	(138)
$(C_6H_5O)_3SiCl$	NH_3	$(C_6H_5O)_3SiNH_2$	90	(175, 214)
		$[(C_6H_5O)_3Si]_2NH$	—	(162)
	$NH_2(CH_2)_6NH_2$	$(C_6H_5O)_3Si\underbrace{N(CH_2)_5CH_2}$	80	(175)
$[(CH_3)_2N]_3SiCl$	$(CH_3)_2NH$	$[(CH_3)_2N]_4Si$	—	(27)
$[(C_2H_5)_2N]_2SiHCl$	$(C_2H_5)_2NH$	$[(C_2H_5)_2N]_3SiH$	89	(202)
$[(C_2H_5)_2N]_2Si(CH_3)Cl$	$(C_2H_5)_2NH$	$[(C_2H_5)_2N]_3SiCH_3$	13	(202)
$[(C_2H_5)_2N]_2Si(C_2H_5)Cl$	$(C_2H_5)_2NH$	$[(C_2H_5)_2N]_3SiC_2H_5$	4	(202)
$[(C_2H_5)_2N]_2Si(C_3H_7)Cl$	NH_3	$[(C_2H_5)_2N]_2Si(C_3H_7)NH_2$	69	(200)
	$(C_2H_5)_2NH$	$[(C_2H_5)_2N]_3SiC_3H_7$	2	(202)
	$(C_2H_5)_2NMgBr$	$[(C_2H_5)_2N]_3SiC_3H_7$	32	(202)
	$iso\text{-}C_3H_7NH_2$	$[(C_2H_5)_2N]_2Si(C_3H_7)(NH\text{-}iso\text{-}C_3H_7)$	64	(200)
$[(C_2H_5)_2N]_3SiCl$	$(C_2H_5)_2NMgBr$	$[(C_2H_5)_2N]_4Si$	53	(29)
$(tert\text{-}C_4H_9NH)_2SiHCl$	$tert\text{-}C_4H_9NH_2$	$(tert\text{-}C_4H_9NH)_3SiH$	95	(202)
$(tert\text{-}C_4H_9NH)_2Si(CH_3)Cl$	$tert\text{-}C_4H_9NH_2$	$(tert\text{-}C_4H_9NH)_3SiCH_3$	48	(202)
$(tert\text{-}C_4H_9NH)_2Si(C_2H_5)Cl$	$tert\text{-}C_4H_9NH_2$	$(tert\text{-}C_4H_9NH)_3SiC_2H_5$	13	(202)
$(tert\text{-}C_4H_9NH)_2Si(C_3H_7)Cl$	NH_3	$(tert\text{-}C_4H_9NH)_2Si(C_3H_7)NH_2$	70	(200)
	$C_2H_5NH_2$	$(tert\text{-}C_4H_9NH)_2Si(C_3H_7)(NHC_2H_5)$	89	(200)
	$iso\text{-}C_3H_7NH_2$	$(tert\text{-}C_4H_9NH)_2Si(C_3H_7)(NH\text{-}iso\text{-}C_3H_7)$	73	(200)
	$tert\text{-}C_4H_9NH_2$	$(tert\text{-}C_4H_9NH)_3SiC_3H_7$	2	(202)
	$tert\text{-}C_4H_9NHMgBr$	$(tert\text{-}C_4H_9NH)_3SiC_3H_7$	42	(202)
$[\underbrace{CH_2(CH_2)_4N}]_3SiCl$	$\underbrace{CH_2(CH_2)_4N}H$	$[\underbrace{CH_2(CH_2)_4N}]_4Si$	—	(27)

silylation of the nitrogen. Both ethyldimethyl- and diethylmethylchlorosilane yield the corresponding disilazanes when treated with ammonia (179). Dimethylphenylbromosilane also gives the disilazane upon treatment with ammonia (180).

The second steric transition, the preference for formation of the silylamine, is observed in the reaction of triethylchlorosilane with ammonia. In this reaction triethylsilylamine is the major product of the reaction (12, 169), the disilazane being the minor product (169).

$$(C_2H_5)_3SiCl + NH_3 \rightarrow (C_2H_5)_3SiNH_2$$

The disilazane may be obtained by treating the silylamine with triethylchlorosilane at a higher temperature (8). Both the α- and the β-chloroethyldiethylchlorosilanes yield the corresponding silylamines when treated with ammonia (12, 184). The α-chloro isomer is stable, but the β-chloro isomer undergoes β-elimination, yielding ammonium chloride, ethylene, and other products (184).

With higher trialkylchlorosilanes, only silylamines have been reported as products (120, 124).

$$(C_4H_9)_3SiCl + NH_3 \rightarrow (C_4H_9)_3SiNH_2$$

Trimethylchlorosilane (169), triethylchlorosilane (8, 127), tripropylchlorosilane (124), and tributylchlorosilane (120) react with primary and secondary amines to yield the *N*-substituted silylamines.

$$R_3SiCl + R'NH_2 \rightarrow R_3SiNHR'$$

$$R_3SiCl + R''_2NH \rightarrow R_3SiNR''_2$$

Triphenylchlorosilane reacts with ammonia to yield the silylamine (106), while triphenylfluorosilane with lithium in liquid ammonia results in the formation of the disilazane (45).

$$(C_6H_5)_3SiCl + NH_3 \rightarrow (C_6H_5)_3SiNH_2$$

$$(C_6H_5)_3SiF + Li/NH_3 \rightarrow [(C_6H_5)_3Si]_2NH$$

The reaction of tri-1-naphthylfluorosilane with ammonia and lithium yields only the silylamine (44, 45), while the reaction of tri-*p*-tolylfluorosilane with ammonia and lithium gives the disilazane (45).

Triphenylbromosilane reacts with ethylamine either directly or with the help of lithium to yield *N*-ethyltriphenylsilylamine (16) and not the solvated free radical as originally reported (104). The reaction of triphenylchlorosilane with amines proceeds with good yield if the size of the amine is small, but when the size is increased, an alkali metal salt of the amine must be used before reaction occurs (72).

The use of alkali metal salts to "force" reaction may also be applied to syntheses of other highly hindered silylamines (28, 29, 44, 46, 72, 79, 202, 210) or in systems where the nitrogen is not basic, such as pyrrole (64).

Trialkoxychlorosilanes react with ammonia and amines in the same general fashion as do trialkyl- and triarylhalosilanes. Both trimethoxy- and triethoxychlorosilanes yield the corresponding disilazanes when treated with ammonia (162), while triisopropoxy- (175) and tributoxychlorosilanes (116, 117) yield only the silylamines. Further increase in the size of the alkoxy group has no effect upon the products obtained (see table 3). The alkoxy groups are inert to ammonia (98).

$$(CH_3O)_3SiCl + NH_3 \rightarrow [(CH_3O)_3Si]_2NH$$

$$(C_4H_9O)_3SiCl + NH_3 \rightarrow (C_4H_9O)_3SiNH_2$$

The reactions of monohalosilylamines with amines present a situation in which the greater reactivity of the bromosilanes as compared to that of the chlorosilanes is apparent (27, 28, 29, 30, 202). Tris(dimethylamino)chlorosilane reacts with dimethylamine in a sealed tube at 100°C. to yield tetrakis(dimethylamino)silane (27).

$$[(CH_3)_2N]_3SiCl + (CH_3)_2NH \rightarrow [(CH_3)_2N]_4Si$$

Tris(diethylamino)chlorosilane fails to react with diethylamine or its lithium salt (27). However, when the corresponding bromosilane is treated with the magnesium salt of diethylamine, tetrakis(diethylamino)silane is obtained (29).

$$[(C_2H_5)_2N]_3SiBr + (C_2H_5)_2NMgBr \rightarrow [(C_2H_5)_2N]_4Si$$

The reaction of a chlorosilane with an amino acid ester results in the formation of the *N*-silyl acid ester (20, 21).

$$(CH_3)_3SiCl + NH_2CH_2COOC_2H_5 \rightarrow (CH_3)_3SiNHCH_2COOC_2H_5$$

The reaction of the sodium salt of the amino acid results in the formation of the *N*- and *O*-silyl derivatives (164). With the free amino acid no reaction occurs, because of the dipolar form of the amino acid (90).

$$(CH_3)_3SiCl + NH_2CH_2COONa \rightarrow (CH_3)_3SiNHCH_2COOSi(CH_3)_3$$

The *N*-carbophenoxyamino acids undergo decomposition with trimethylchlorosilane (19), while the *N*-benzoyl derivatives give only the *O*-silyl products (90).

Amides, substituted amides, and lactams are reported to give *N*-silyl products with trimethylchlorosilane (95), but formation of silyl isocyanate occurs when triphenylchlorosilane is treated with urea or sodium urethan (70).

The silver salt of sulfamic acid reacts with trimethyl- or triethylchlorosilane to yield the *O*- and the *N*-silylsulfamides (142). The intermediate *O*-silyl derivative could not be isolated.

$$(CH_3)_3SiCl + AgOSO_2NH_2 \rightarrow (CH_3)_3SiOSO_2NHSi(CH_3)_3$$

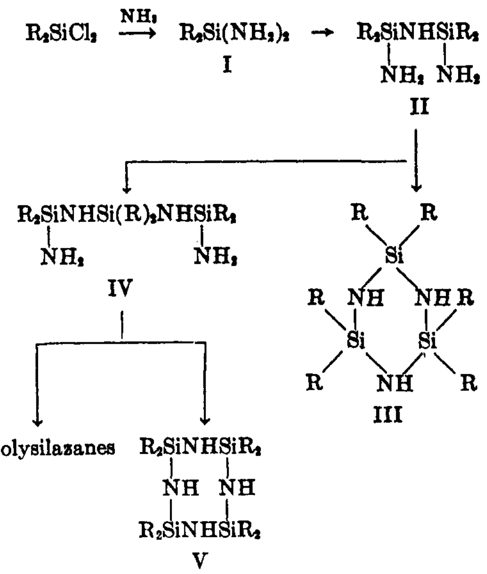
Trimethylchlorosilane reacts with acetonitrile in the presence of sodium to give rise to a number of products (153).

$$\begin{aligned}(CH_3)_3SiCl + CH_3CN \xrightarrow{Na} {} & (CH_3)_3SiCH{=}C{=}NSi(CH_3)_3 + \\ & (CH_3)_3SiCH(CN)Si(CH_3)_3 + \\ & (CH_3)_4Si + (CH_3)_3SiCN + (CH_3)_3SiCH_2CN\end{aligned}$$

2. From dihalosilanes

The reaction of a dihalosilane with ammonia or an amine results in the formation of a silylamine, a cyclosilazane, or a polysilazane depending upon the reactants and the reaction conditions (see table 4). With dihalosilanes in which there is little hindrance, the cyclosilazanes and the polysilazanes predominate as the reaction products while, with the sterically hindered dihalosilanes, compounds with the diamine structure can be isolated. Dilution favors the formation of cyclosilazane over that of polysilazane.

The reaction of a dihalosilane with ammonia may be visualized as proceeding according to the following scheme:



The condensation reactions might occur either by silylamine condensation or by reaction of the silylamine with a dihalosilane. Both reactions are known, and it

TABLE 4

Synthesis of silicon-nitrogen compounds from dihalosilanes

Halosilane	Amine	Product	Yield	References
			per cent	
H_2SiCl_2	NH_3	Polysilazane	—	(195)
CH_3SiHCl_2	NH_3	Polysilazane	—	(33)
$(CH_3)_2SiCl_2$	NH_3	Polysilazane	—	(83, 163)
		$[(CH_3)_2SiNH]_3$	36–50	(33, 128, 145)
		$[(CH_3)_2SiNH]_4$	26–42	(33, 34, 82, 145)
	CH_3NH_2	$(CH_3)_2Si(NHCH_3)_2$	58	(128)
	$(CH_3)_2NH$	$(CH_3)_2Si[N(CH_3)_2]_2$	82	(3)
	$C_2H_5NH_2$	$(CH_3)_2Si(NHC_2H_5)_2$	68	(128)
	$\underbrace{CH_2CH_2NH}$	$(CH_3)_2Si[\underbrace{NCH_2CH_2}]_2$	—	(91)
	$(C_2H_5)_2NH$	$(CH_3)_2Si[N(C_2H_5)_2]_2$	—	(150)
	$C_6H_5NH_2$	$(CH_3)_2Si(NHC_6H_5)_2$	68	(128)
		$[(CH_3)_2Si(NC_6H_5)]_3$	65	(128)
	$NH_2CH_2COOC_2H_5$	$(CH_3)_2Si(OC_2H_5)_2$	—	(21)
$(CH_3)(C_2H_5)SiCl_2$	NH_3	$[(CH_3)(C_2H_5)SiNH]_3$	53	(92)
$(CH_3)(C_6H_5)SiCl_2$	NH_3	$[(CH_3)(C_6H_5)SiNH]_3$	43	(92)
$(C_2H_5)_2SiCl_2$	NH_3	Polysilazane	—	(40)
		$[(C_2H_5)_2SiNH]_3$	85	(33)
		$[(C_2H_5)_2SiNH]_4$	—	(33)
	$(C_2H_5)_2NH$	$(C_2H_5)_2Si[N(C_2H_5)_2]_2$	—	(100)
		$(C_2H_5)_2Si[N(C_2H_5)_2]Cl$	—	(100)
$(C_4H_9)_2SiCl_2$	NH_3	$[(C_4H_9)_2SiNH]_3$	—	(186)
$(\mathit{tert}\text{-}C_4H_9)(CH_3)SiCl_2$	NH_3	$(\mathit{tert}\text{-}C_4H_9)(CH_3)Si(NH_2)_2$	65	(186)
$(\mathit{tert}\text{-}C_4H_9)_2SiCl_2$	NH_3	$(\mathit{tert}\text{-}C_4H_9)_2Si(NH_2)_2$	50	(186)
$(\mathit{tert}\text{-}C_4H_9)(C_6H_5)SiCl_2$	NH_3	$(\mathit{tert}\text{-}C_4H_9)(C_6H_5)Si(NH_2)_2$	80	(186)
$(\mathit{tert}\text{-}C_4H_9)(C_{16}H_{33})SiCl_2$	NH_3	$(\mathit{tert}\text{-}C_4H_9)(C_6H_5)Si(NH_2)_2$	85	(186)
$(C_6H_5)_2SiCl_2$	NH_3	$[(C_6H_5)_2SiNH]_3$	62	(121)
	CH_3NH_2	$(C_6H_5)_2Si(NHCH_3)_2$	—	(121)
	$C_3H_7NH_2$	$(C_6H_5)_2Si(NHC_3H_7)_2$	70	(121)
	$C_6H_{11}NH_2$	$(C_6H_5)_2Si(NHC_6H_{11})_2$	—	(121)
	$C_6H_5NH_2$	$(C_6H_5)_2Si(NHC_6H_5)_2$	35	(2)
	$C_6H_5CH_2NH_2$	$(C_6H_5)_2Si(NHCH_2C_6H_5)_2$	—	(121)
$(C_6H_5CH_2)_2SiCl_2$	$\underbrace{CH_2CH_2NH}$	$(C_6H_5CH_2)_2Si[\underbrace{NCH_2CH_2}]_2$	—	(91)
	$CH_3\underbrace{CHCH_2NH}$	$(C_6H_5CH_2)_2Si[\underbrace{NCH_2CH}CH_3]_2$	—	(91)
$(1\text{-}C_{10}H_7)_2SiF_2$	NH_3	$(1\text{-}C_{10}H_7)_2Si(NH_2)_2$	100	(44)
	$C_6H_5NH_2$	$(1\text{-}C_{10}H_7)_2Si(NHC_6H_5)_2$	72	(44)
$(CH_3O)_2SiCl_2$	NH_3	$[(CH_3O)_2SiNH]_x$	—	(162)
	$\underbrace{CH_2CH_2NH}$	$(CH_3O)_2Si[\underbrace{NCH_2CH_2}]_2$	—	(91)
$(\text{iso-}C_3H_7O)_2SiCl_2$	NH_3	$[(\text{iso-}C_3H_7O)_2SiNH]_3$	20	(214)
		$[(\text{iso-}C_3H_7O)_2Si(NH_2)]_2NH$	80	(175)
$(C_4H_9O)_2SiCl_2$	NH_3	$[(C_4H_9O)_2SiNH]_3$	—	(116)
	CH_3NH_2	$(C_4H_9O)_2Si(NHCH_3)_2$	79	(118)
	$C_2H_5NH_2$	$(C_4H_9O)_2Si(NHC_2H_5)_2$	—	(116, 118)
	$\underbrace{CH_2CH_2NH}$	$(C_4H_9O)_2Si[\underbrace{NCH_2CH_2}]_2$	—	(91)
	$C_3H_7NH_2$	$(C_4H_9O)_2Si(NHC_3H_7)_2$	—	(118)
	$C_4H_9NH_2$	$(C_4H_9O)_2Si(NHC_4H_9)_2$	—	(118)
	$C_6H_5NH_2$	$(C_4H_9O)_2Si(NHC_6H_5)_2$	39	(99, 118)
$(\mathit{tert}\text{-}C_4H_9O)(CH_3O)SiCl_2$	NH_3	$(\mathit{tert}\text{-}C_4H_9O)(CH_3O)Si(NH_2)_2$	20	(138)
$(\mathit{tert}\text{-}C_4H_9O)(C_2H_5O)SiCl_2$	NH_3	$(\mathit{tert}\text{-}C_4H_9O)(C_2H_5O)Si(NH_2)_2$	65	(138)
$(\mathit{tert}\text{-}C_4H_9O)(\text{iso-}C_3H_7O)SiCl_2$	NH_3	$(\mathit{tert}\text{-}C_4H_9O)(\text{iso-}C_3H_7O)Si(NH_2)_2$	62	(138)
$(\mathit{tert}\text{-}C_4H_9O)(C_4H_9O)SiCl_2$	NH_3	$(\mathit{tert}\text{-}C_4H_9O)(C_4H_9O)Si(NH_2)_2$	48	(138)
$(\mathit{tert}\text{-}C_4H_9O)(\mathit{sec}\text{-}C_4H_9O)SiCl_2$	NH_3	$(\mathit{tert}\text{-}C_4H_9O)(\mathit{sec}\text{-}C_4H_9O)Si(NH_2)_2$	70	(138)
$(\mathit{tert}\text{-}C_4H_9O)_2SiCl_2$	NH_3	$[(\mathit{tert}\text{-}C_4H_9O)_2SiNH]_3$	—	(129)
		$[(\mathit{tert}\text{-}C_4H_9O)_2Si(NH_2)]_2NH$	—	(129)
		$(\mathit{tert}\text{-}C_4H_9O)_2Si(NH_2)_2$	81–84	(129, 138, 147)
	$C_2H_5NH_2$	$(\mathit{tert}\text{-}C_4H_9O)_2Si(NHC_2H_5)_2$	—	(129)
	$C_7H_{15}NH_2$	$(\mathit{tert}\text{-}C_4H_9O)_2Si(NHC_7H_{15})_2$	—	(129)
	$C_6H_5NH_2$	$(\mathit{tert}\text{-}C_4H_9O)_2Si(NHC_6H_5)_2$	—	(129)
	$C_6H_5CH_2NH_2$	$(\mathit{tert}\text{-}C_4H_9O)_2Si(NHCH_2C_6H_5)_2$	—	(129)
$(\mathit{tert}\text{-}C_5H_{11}O)_2SiCl_2$	NH_3	$(\mathit{tert}\text{-}C_5H_{11}O)_2Si(NH_2)_2$	71	(138)
$(C_6H_5O)_2SiCl_2$	NH_3	$[(C_6H_5O)_2SiNH]_3$	50	(175)
		$[(C_6H_5O)_2SiNH]_4$	50	(175)
$[(C_2H_5)_2N]_2SiCl_2$	$(C_2H_5)_2NH$	$[(C_2H_5)_2N]_3SiCl$	91	(27, 202)
$[(C_2H_5)_2N](C_3H_7)SiCl_2$	$\text{iso-}C_3H_7NH_2$	$[(C_2H_5)_2N](C_3H_7)Si[NH(\text{iso-}C_3H_7)]_2$	82	(200)
$(\text{iso-}C_3H_7NH)(C_3H_7)SiCl_2$	$\text{iso-}C_3H_7NH_2$	$(\text{iso-}C_3H_7NH)_3SiC_3H_7$	57	(200)
$(\mathit{tert}\text{-}C_4H_9NH)(C_3H_7)SiCl_2$	$\text{iso-}C_3H_7NH_2$	$(\mathit{tert}\text{-}C_4H_9NH)(\text{iso-}C_3H_7NH)_2SiC_3H_7$	76	(200)
$[(\underbrace{CH_2(CH_2)_4CH})_2N](C_3H_7)SiCl_2$	$\text{iso-}C_3H_7NH_2$	$[(\underbrace{CH_2(CH_2)_4CH})_2N](\text{iso-}C_3H_7NH)Si(C_3H_7)$	77	(200)
$[C_6H_5(CH_3)N](C_3H_7)SiCl_2$	$\text{iso-}C_3H_7NH_2$	$[C_6H_5(CH_3)N](\text{iso-}C_3H_7NH)_2SiC_3H_7$	10	(200)
$(\mathit{tert}\text{-}C_4H_9NH)_2SiCl_2$	$\mathit{tert}\text{-}C_4H_9NH_2$	$(\mathit{tert}\text{-}C_4H_9NH)_3SiCl$	92	(30, 32, 202)
$[\underbrace{CH_2(CH_2)_4N}]_2SiCl_2$	$\underbrace{CH_2(CH_2)_4NH}$	$[\underbrace{CH_2(CH_2)_4N}]_3SiCl$	—	(27)

is probable that they occur simultaneously.

With dichlorosilane (195) and with methylchlorosilane (33) only polysilazanes have been obtained. Higher monoalkyl- or monoaryldichlorosilanes have not been reported.

With dimethyldichlorosilane, cyclization to hexamethylcyclotrisilazane (III: $R = CH_3$) and octamethylcyclotetrasilazane (V: $R = CH_3$) is the predominant reaction if a solvent is used (33, 34, 128, 145). The cyclotrisilazane is the main product (145). Condensation to polysilazanes is observed when no solvent is employed (163). No compounds corresponding to II or IV have been reported.

Cyclotrisilazanes are the only products reported for the treatment of ethylmethyldichlorosilane and methylphenyldichlorosilane with ammonia (92). However, with diethyldichlorosilane both the cyclotetrasilazane (V: $R = C_2H_5$) and the cyclotrisilazane (IV: $R = C_2H_5$) have been obtained, with the latter compound being produced in higher yield (33). Dibutyldichlorosilane yielded only the cyclotrisilazane (186).

As observed in the reactions of the monohalosilanes, there is a tendency in the dihalosilane series for the formation of multiple silicon–nitrogen bonds. This tendency decreases with increasing hindrance of the system. If the size of at least one of the groups attached to the silicon is increased to *tert*-butyl, the condensation reactions are blocked and the silanediamine may be isolated in good yield (186).

$$(tert\text{-}C_4H_9)_2SiCl_2 + NH_3 \rightarrow (tert\text{-}C_4H_9)_2Si(NH_2)_2$$

Methyl-, phenyl-, and hexadecyl-*tert*-butyldichlorosilanes give stable silanediamines on treatment with ammonia (186). Also, di-1-naphthyldifluorosilane can be converted to a stable silanediamine (44).

Diphenyldichlorosilane yields the cyclotrisilazane when treated with ammonia (121) and there is some evidence for the formation of tetraphenyldiaminodisilazane (II: $R = C_6H_5$) (121).

$$(C_6H_5)_2SiCl_2 + NH_3 \rightarrow [(C_6H_5)_2SiNH]_3$$

The dialkoxydichlorosilanes react with ammonia in the same general manner as do the dialkyl- and the diaryldichlorosilanes. Dimethoxy- (162), diisopropoxy- (175, 214), dibutoxy- (116), and di-*tert*-butoxydichlorosilanes (129) yield the corresponding cyclotrisilazanes upon treatment with ammonia. Dimethoxydichlorosilane was first reported to yield the imide, $(CH_3O)_2Si{=}NH$ (162); however, this has been discounted by Larsson, who has suggested that the compound is a cyclosilazane (129).

The diisopropoxydichlorosilane with ammonia yields, besides the cyclotrisilazane, the diaminodisilazane (II: $R = \text{iso-}C_3H_7O$) (129). The latter compound may be converted to the cyclotrisilazane (175, 214) and to the cyclotetrasilazane (175) by heating.

The product obtained from the reaction of di-*tert*-butoxydichlorosilane and ammonia depends upon reaction conditions. Cyclotrisilazane is synthesized by bubbling ammonia through a refluxing solution of the dichlorosilane in carbon tetrachloride (129). However, if the dichlorosilane is added to liquid ammonia, both di-*tert*-butoxydiaminodisilazane (129, 138) and tetra-*tert*-butoxydiaminodisilazane (II: $R = tert\text{-}C_4H_9O$) are obtained.

As in the case of the *tert*-butyl group, the presence of at least one *tert*-alkoxy group on the silicon allows the isolation of stable silanediamines (138). Specific examples are found in table 4. It is interesting to compare the yields of *tert*-butoxymethoxysilanediamine (20 per cent), *tert*-butoxyethoxysilanediamine (65 per cent), and *tert*-butylmethylsilanediamine (65 per cent). When compared to the higher yield of *tert*-butylmethylsilanediamine, the increase in yield proceeding from *tert*-butoxymethoxysilanediamine to *tert*-butoxyethoxysilanediamine suggests that the *tert*-butoxy group requires "steric assistance" from some other group attached to the silicon. Further evidence for this observation is provided by the fact that di-*tert*-butoxysilanediamine condenses to yield the cyclotrisilazane (68), while di-*tert*-butylsilanediamine does not (186).

The action of an amine upon a dihalosilane usually results in the formation of a bis(*N*-substituted amino) silane. However, there is one reported case in which cyclization occurred. Dimethyldichlorosilane when heated with aniline in carbon tetrachloride yields hexamethyltri(*N*-phenyl)cyclotrisilazane in 65 per cent yield (128). The dimethylbis(phenylamino)silane was also obtained when less strenuous conditions were employed (128).

$$(CH_3)_2SiCl_2 + C_6H_5NH_2 \rightarrow [(CH_3)_2SiNC_6H_5]_3$$

When the size of the groups around the silicon is fairly large, reaction may still occur (44). If both the amino group and the silicon atom have intermediate hindrance, proper adjustment of the molar ratios of reactants may allow isolation of the chlorosilylamines (30, 32, 200, 202).

$$(1\text{-}C_{10}H_7)_2SiF_2 + C_6H_5NH_2 \rightarrow (1\text{-}C_{10}H_7)_2Si(NHC_6H_5)_2$$

$$(C_2H_5)_2SiCl_2 + (C_2H_5)_2NH \rightarrow (C_2H_5)_2[(C_2H_5)_2N]SiCl$$

When both reactants are very hindered, such as in the case of tri(*tert*-butylamine)chlorosilane and *tert*-butylamine, the reaction fails (30).

Evaluation or study of the steric hindrance trends in these silylamines must include the consideration of the reactivity of the halosilane. Although information is available to demonstrate the greater reactivity of the bromosilanes over the chlorosilanes (202), evaluation of the relative importance of (*a*) hindrance around the silicon atom, (*b*) increasing size of the amine molecule, and (*c*) variation of the halogen is not possible on the basis of present knowledge.

3. *From trihalosilanes*

The reaction of a trihalosilane with ammonia results in the formation of polysilazanes. There is one reported case of a silanetriamine being formed (101), but the assignments of structure are doubtful. In one case where a triamine might be expected, the reaction of 1-naphthyltrifluorosilane with ammonia, only polymeric material was obtained (44). The evidence, of course, does not prove that silanetriamines cannot be synthesized, since no investigation has been directed toward preparation of such compounds. As in the case of the silanetriols, one would expect that these compounds would be very reactive and would require special techniques for isolation.

The polysilazanes obtained from the reaction of ammonia with trihalosilanes (as well as those obtained from the reaction with dihalosilanes) have found commercial use as water repellents, anti-foaming agents, and silicone resin modifiers (15, 34, 40, 41, 42, 43, 77, 83, 94, 100, 146, 163, 190). No cyclic products have been reported from the reaction of a trihalosilane with ammonia or an amine.

With both primary and secondary amines, reaction proceeds with the stepwise replacement of the halogens

$$RSiCl_3 + R'_2NH \rightarrow RSiCl_2NR'_2$$

$$RSiCl_2NR'_2 + R'_2NH \rightarrow RSiCl(NR'_2)_2$$

$$RSiCl(NR'_2)_2 + R'_2NH \rightarrow RSi(NR'_2)_3$$

and may result in the formation of the tri(*N*-substituted)silanetriamine. The intermediate halosilylamines may be obtained by varying the molar ratios of the reactants. As with the dihalosilanes, the yield of the silylamine is influenced both by the halogen used and by the hindrance of the amine. In this series, however, the influence of the one remaining alkyl group attached to the silicon is minimized (for specific examples, see table 5).

4. *From tetrahalosilanes and higher halosilanes*

The reaction of ammonia and silicon tetrachloride yields a heterogeneous polymeric material of the general formula $(SiNH)_x$ (17, 25, 76, 111, 173, 221). There is no general agreement as to its composition, probably because of the variety of reaction conditions employed. Pyrolysis of this polysilazane results in the formation of pure α-silicon nitride (α-Si_2N_3) (75). Silicon nitride may also be obtained by reaction of nitrogen or ammonia with silicon metal at 1350–1450°C. (18, 75). Here, however, both the α- and the β-silicon nitrides are formed, with the α-form being favored at the lower reaction temperatures (75). From a gaseous, high-temperature (825°C.) reaction of ammonia and silicon tetrachloride, hexachlorodisilazane was isolated along with other silicon–nitrogen products of a polymeric nature (173). When a glow discharge is used, silicon tetrachloride and nitrogen yield tris(trichlorosilyl)-amine (148).

Amines react with tetrahalosilanes to give stepwise substitution, each halogen being replaced with greater difficulty (30, 32). The reported reactions of the higher halosilanes with ammonia and amines are summarized in table 6.

B. SYNTHESIS FROM COMPOUNDS CONTAINING A SILICON–HYDROGEN BOND

The synthesis of a silylamine from a compound containing a silicon–hydrogen bond generally requires the use of a highly nucleophilic reagent, such as the alkali metal salt of either ammonia or an amine. Triethylsilane reacts with lithium, sodium, or potassium metal in liquid ammonia to yield both the silylamine and the disilazane (53, 105).

$$(C_2H_5)_3SiH + Li + NH_3 \rightarrow (C_2H_5)_3SiNH_2 + [(C_2H_5)_3Si]_2NH$$

The percentages of the two products formed in this reaction are markedly influenced by the metal used. Using sodium, 46 per cent of the silylamine is produced; with potassium, 66 per cent of the disilazane is formed; while the use of lithium gives 34 per cent of the silylamine and 51 per cent of the disilazane (53).

Triethylsilane gives no reaction with ammonia at 80°C. in a sealed tube (53), while, with potassium amide and ammonia, the potassium salt of the disilazane can be isolated (105).

Triphenylsilane with sodium in liquid ammonia yields the disilazane (154).

$$(C_6H_5)_3SiH + Na + NH_3 \rightarrow [(C_6H_5)_3Si]_2NH$$

The alkali metal salts of both primary and secondary amines react with silanes to give the *N*-substituted silylamines.

$$(C_6H_5)_3SiH + LiNHR \rightarrow (C_6H_5)_3SiNHR$$

Both lithium (71) and potassium (53) salts of amines have been employed in this reaction. The lithium salts of carbazole, *N*-methylaniline, diphenylamine, and 2,5-dimethylpyrrole, however, fail to react with triphenylsilane (71).

When treated with primary and secondary amines in the presence of chloroplatinic acid, compounds containing a silicon–hydrogen bond have been reported to yield silylamines (167).

C. SYNTHESIS BY THE SILYLAMINE–AMINE EXCHANGE REACTION

The silylamine–amine exchange reaction has been widely utilized for the preparation of silylamines. It would appear that the success of this reaction is due

TABLE 5

Synthesis of silicon–nitrogen compounds from trihalosilanes

Halosilane	Amine	Product	Yield	References
			per cent	
$HSiCl_3$	NH_3	Polysilazane	—	(166)
	$(C_2H_5)_2NH$	$HSi[N(C_2H_5)_2]_2Cl$	—	(202)
	tert-$C_4H_9NH_2$	$HSi[NH(tert\text{-}C_4H_9)]_2Cl$	—	(202)
	$C_6H_5NH_2$	$HSi(NHC_6H_5)_3$	—	(165)
	$\underline{C_4H_4NK}$	$Si[\underline{NC_4H_4}]_4$	—	(157)
		$HSi[\underline{NC_4H_4}]_3$	—	(157)
CH_3SiCl_3	NH_3	Polysilazane	—	(92)
	$(CH_3)_2NH$	$CH_3Si[N(CH_3)_2]_3$	83	(3)
	$(C_2H_5)_2NH$	$CH_3Si[N(C_2H_5)_2]_2Cl$	—	(202)
	tert-$C_4H_9NH_2$	$CH_3Si[NH(tert\text{-}C_4H_9)]_2Cl$	—	(202)
	$NH_2CH_2COOC_2H_5$	$CH_3Si(OC_2H_5)_3$	—	(21)
$C_2H_5SiCl_3$	NH_3	Polysilazane	95	(41)
	$(C_2H_5)_2NH$	$C_2H_5Si[N(C_2H_5)_2]_2Cl$	—	(202)
	tert-$C_4H_9NH_2$	$C_2H_5Si[NH(tert\text{-}C_4H_9)]_2Cl$	—	(202)
	$C_6H_5NH_2$	$C_2H_5Si(NHC_6H_5)_3$	72	(2)
$C_3H_7SiCl_3$	CH_3NH_2	$C_3H_7Si(NHCH_3)_3$	88	(200)
	$(CH_3)_2NH$	$C_3H_7Si[N(CH_3)_2]_3$	74	(200)
	$C_2H_5NH_2$	$C_3H_7Si[NHC_2H_5]_3$	93	(200)
	$(C_2H_5)_2NH$	$C_3H_7Si[N(C_2H_5)_2]_2Cl$	73	(200)
		$C_3H_7Si[N(C_2H_5)_2]Cl_2$	72	(200)
	$C_3H_7NH_2$	$C_3H_7Si(NHC_3H_7)_3$	90	(200)
	iso-$C_3H_7NH_2$	$C_3H_7Si[NH(iso\text{-}C_3H_7)]_3$	86	(200)
		$C_3H_7Si[NH(iso\text{-}C_3H_7)]Cl_2$	53	(200)
	$C_4H_9NH_2$	$C_3H_7Si(NHC_4H_9)_3$	77	(200)
	iso-$C_4H_9NH_2$	$C_3H_7Si[NH(iso\text{-}C_4H_9)]_3$	81	(200)
	sec-$C_4H_9NH_2$	$C_3H_7Si[NH(sec\text{-}C_4H_9)]_3$	68	(200)
	tert-$C_4H_9NH_2$	$C_3H_7Si[NH(tert\text{-}C_4H_9)]_2Cl$	81	(200)
		$C_3H_7Si[NH(tert\text{-}C_4H_9)]Cl_2$	67	(200)
	$C_6H_{11}NH_2$	$C_3H_7Si(NHC_6H_{11})_3$	77	(200)
	$\underline{CH_2(CH_2)_4NH}$	$C_3H_7Si[\underline{N(CH_2)_4CH_2}]_3$	68	(200)
	$C_6H_5NH_2$	$C_3H_7Si(NHC_6H_5)_3$	85	(200)
	$C_6H_5(CH_3)NH$	$C_3H_7Si[N(CH_3)C_6H_5]_3$	36	(200)
		$C_3H_7Si[N(CH_3)C_6H_5]Cl_2$	11	(200)
$C_3H_7SiBr_3$	$(C_2H_5)_2NH$	$C_3H_7Si[N(C_2H_5)_2]_3$	50	(202)
	$(iso\text{-}C_3H_7)_2NH$	$C_3H_7Si[N(iso\text{-}C_3H_7)_2]Br_2$	68	(202)
	$C_6H_5(CH_3)NH$	$C_3H_7Si[N(CH_3)C_6H_5]_2Br$	30	(202)
$C_3H_7SiI_3$	*tert*-$C_4H_9NH_2$	$C_3H_7Si[NH(tert\text{-}C_4H_9)]_3$	85	(202)
$C_{18}H_{37}SiCl_3$	$(C_2H_5)_2NH$	$C_{18}H_{37}Si[N(C_2H_5)_2]_3$	—	(100)
1-$C_{10}H_7SiF_3$	NH_3	Polysilazane	—	(44)
	$C_6H_5NH_2$	1-$C_{10}H_7Si(NHC_6H_5)_3$	100	(44)
$C_4H_9OSiCl_3$	NH_3	Polysilazane	—	(116)
	CH_3NH_2	$C_4H_9OSi(NHCH_3)_3$	51	(119)
	$C_2H_5NH_2$	$C_4H_9OSi(NHC_2H_5)_3$	—	(116, 119)
	$C_3H_7NH_2$	$C_4H_9OSi(NHC_3H_7)_3$	—	(119)
	$C_4H_9NH_2$	$C_4H_9OSi(NHC_4H_9)_3$	—	(119)
	$C_6H_5NH_2$	$C_4H_9OSi(NHC_6H_5)_3$	—	(119)
$(C_2H_5)_2NSiCl_3$	$\underline{CH_2CH_2NH}$	$(C_2H_5)_2NSi[\underline{NCH_2CH_2}]_3$	—	(91)
$\underline{CH_2(CH_2)_4N}SiCl_3$	$\underline{CH_2(CH_2)_4NH}$	$[\underline{CH_2(CH_2)_4N}]_2SiCl_2$	—	(27)

to the fact that an equilibrium exists between amines and silylamines. The success of the reaction also requires that either ammonia or a volatile amine be produced.

$$R_3SiNHR' + R''NH_2 \rightleftarrows R_3SiNHR'' + R'NH_2$$

The exchange reaction is acid catalyzed, with both ammonium salts (115, 201) and trimethylchlorosilane (112) having been recommended as catalysts. The function of the catalyst has been postulated as that of furnishing a proton to the nitrogen of the silylamine, with the protonated intermediate then undergoing nucleophilic attack by the amine (112, 201).

The nitrogen of the starting silylamines studied in this reaction has been unsubstituted (22, 23, 120, 122, 124), substituted with a methyl group (120, 201) or, more commonly, with an ethyl group (117, 118, 126, 128, 201). Higher alkyl groups, such as propyl (124) or *tert*-butyl (50), have also been used but have not been extensively studied. Silanediamines and silanetriamines with *N*-methyl and *N*-ethyl substitution give good yields in the exchange reaction (118, 119, 201).

Hexaphenylcyclotrisilazane reacts with aniline to give the *N*-phenylsilylamine (121). Hexamethyldisilazane has been studied more extensively and undergoes reaction with a variety of amines (13, 14, 23, 63, 64, 112, 139, 193).

$$[(CH_3)_3Si]_2NH + 2RNH_2 \rightarrow 2(CH_3)_3SiNHR + NH_3$$

The success of the exchange reaction requires that

TABLE 6

Synthesis of silicon–nitrogen compounds from tetrahalosilanes and higher halosilanes

Halosilane	Amine	Product	Yield	References
			per cent	
$SiCl_4$	NH_3	Polysilazane	—	(17, 18, 25, 76, 111, 173, 196, 221)
	$(CH_3)_2NH$	$[(CH_3)_2N]_4Si$	87	(3)
		$[(CH_3)_2N]_3SiCl$	—	(27, 38)
		$[(CH_3)_2N]_2SiCl_2$	—	(38)
	$C_2H_5NH_2$	$C_2H_5NHSiCl_3$	—	(131)
	$(C_2H_5)_2NH$	$[(C_2H_5)_2N]_2SiCl_2$	—	(27)
		$(C_2H_5)_2NSiCl_3$	—	(27)
	$(iso\text{-}C_3H_7)_2NH$	$[(iso\text{-}C_3H_7)_2N]_2SiCl_2$	25	(31)
		$(iso\text{-}C_3H_7)_2NSiCl_3$	48	(31)
	$tert\text{-}C_4H_9NH_2$	$tert\text{-}C_4H_9NHSiCl_3$	—	(30, 32)
		$(tert\text{-}C_4H_9NH)_2SiCl_2$	—	(30, 32)
	$(iso\text{-}C_4H_9)_2NH$	$(iso\text{-}C_4H_9)_2NSiCl_3$	—	(131)
	$CH_2(CH_2)_4NH$	$CH_2(CH_2)_4NSiCl_3$	—	(27)
	C_4H_4NK	$[C_4H_4N]_4Si$	4.5	(64, 156)
	$C_6H_5(C_2H_5)NH$	$[C_6H_5(C_2H_5)N]_2SiCl_2$	62	(31)
		$C_6H_5(C_2H_5)NSiCl_3$	67	(31)
	$C_6H_5NH_2$	$(C_6H_5NH)_4Si$	—	(155)
		$(C_6H_5NH)_2SiCl_2$	—	(85, 86)
	$o\text{-}CH_3C_6H_4NH_2$	$(o\text{-}CH_3C_6H_4NH)_4Si$	—	(155)
		$(o\text{-}CH_3C_6H_4NH)_2SiCl_2$	—	(85, 86)
	$p\text{-}CH_3C_6H_4NH_2$	$(p\text{-}CH_3C_6H_4NH)_4Si$	—	(155)
	$1\text{-}C_{10}H_7NH_2$	$(1\text{-}C_{10}H_7NH)_4Si$	—	(155)
		$(1\text{-}C_{10}H_7NH)_2SiCl_2$	—	(85)
	$2\text{-}C_{10}H_7NH_2$	$(2\text{-}C_{10}H_7NH)_4Si$	—	(155)
		$(2\text{-}C_{10}H_7NH)_2SiCl_2$	—	(85)
	$NH_2CH_2COOC_2H_5$	$(C_2H_5O)_4Si$	—	(21)
$SiBr_4$	NH_3	Polysilazane	—	(18)
$(Cl_3Si)_2O$	NH_3	Polysilazane		(172)
	$(C_2H_5)_2NH$	$\{[(C_2H_5)_2N]_3Si\}_2O$	76	(3)
$(Cl_3Si)_2$	NH_3	Polysilazane	—	(174)

the attacking amine be less volatile than the one it replaces. Primary amines have been most extensively studied (see table 8); however, recent work has shown that secondary amines also undergo reaction in good yield (63).

The exchange reaction has also been used with heterocyclic compounds which contain an N—H function (22, 63, 64) and with organic (51) and inorganic amides (13, 14, 142).

D. SYNTHESIS BY MISCELLANEOUS METHODS

1. *By basic cleavage*

Sodium amide cleaves chloromethyltrimethylsilane

TABLE 7

Synthesis of silicon–nitrogen compounds from compounds containing a silicon–hydrogen bond

Silane	Amine	Product	Yield	References
			per cent	
$HSiCl_3$	C_4H_4NK	$HSi[NC_4H_4]_3$	—	(157)
		$Si[NC_4H_4]_4$	—	(157)
$(C_2H_5)_3SiH$	NH_3/Li	$(C_2H_5)_3SiNH_2$	34	(53)
		$[(C_2H_5)_3Si]_2NH$	51	(53)
	NH_3/Na	$(C_2H_5)_3SiNH_2$	46	(53)
		$[(C_2H_5)_3Si]_2NH$	—	(53)
	NH_3/K	$[(C_2H_5)_3Si]_2NH$	66	(53, 105)
	$C_2H_5NH_2$/K or Li	$(C_2H_5)_3SiNHC_2H_5$	91	(53, 105)
	$(C_2H_5)_2NH/K$	$(C_2H_5)_3SiN(C_2H_5)_2$	—	(53)
	$C_3H_7NH_2/K$	$(C_2H_5)_3SiNHC_3H_7$	—	(53)
	$iso\text{-}C_3H_7NH_2/K$	$(C_2H_5)_3SiNH(iso\text{-}C_3H_7)$	—	(53)
	$(iso\text{-}C_3H_7)_2NH/K$	$(C_2H_5)_3SiN(iso\text{-}C_3H_7)_2$	—	(53)
	$tert\text{-}C_4H_9NH_2/K$	$(C_2H_5)_3SiNH(tert\text{-}C_4H_9)$	—	(53)
	$(C_4H_9)_2NH/K$	$(C_2H_5)_3SiN(C_4H_9)_2$	—	(53)
	$C_2H_5C(CH_3)_2NH_2$	$(C_2H_5)_3SiNHC(CH_3)_2C_2H_5$	—	(53)
	$C_6H_5NH_2$	$(C_2H_5)_3SiNHC_6H_5$	—	(53)
	$(C_2H_5)_3SiNH_2$	$[(C_2H_5)_3Si]_2NH$	—	(53)
$(C_6H_5)_3SiH$	NH_3/Na	$[(C_6H_5)_3Si]_2NH$	—	(154)
	$(CH_3)_2NLi$	$(C_6H_5)_3SiN(CH_3)_2$	74	(71)
	$(C_2H_5)_2NLi$	$(C_6H_5)_3SiN(C_2H_5)_2$	74	(71)
	$(C_4H_9)_2NLi$	$(C_6H_5)_3SiN(C_4H_9)_2$	63	(71)

TABLE 8

Synthesis of silicon–nitrogen compounds by the silylamine–amine exchange reaction

Silylamine	Amine	Product	Yield	References
			per cent	
$(CH_3)_3SiNHCH_3$	$NH_2SO_2NH_2$	$[(CH_3)_3SiNH]_2SO_2$	85–90	(13)
	$C_6H_5SO_2NH_2$	$C_6H_5SO_2NHSi(CH_3)_3$	85	(13)
	$(C_6H_5O)_2P(O)NH_2$	$(C_6H_5O)_2P(O)NHSi(CH_3)_3$	85–90	(13)
	$(C_6H_5O)P(O)(NH_2)_2$	$(C_6H_5O)P(O)[NHSi(CH_3)_3]_2$	85	(14)
$(CH_3)_3SiNH(tert\text{-}C_4H_9)$	NH_2CONH_2	$(CH_3)_3SiNHCONH_2$	—	(51)
	$CH_2{=}CHO(CH_2)_2NH_2$	$(CH_3)_3SiNH(CH_2)_2OCH{=}CH_2$	—	(50)
	$CH_2{=}CHO(CH_2)_2NHCH_3$	$(CH_3)_3SiN(CH_3)(CH_2)_2OCH{=}CH_2$	—	(50)
$(C_2H_5)_3SiNH_2$	$C_4H_9NH_2$	$(C_2H_5)_3SiNHC_4H_9$	72	(122)
	$C_6H_{13}NH_2$	$(C_2H_5)_3SiNHC_6H_{13}$	83	(122)
	$C_7H_{15}NH_2$	$(C_2H_5)_3SiNHC_7H_{15}$	95	(122)
	$\underbracket{CH_2(CH_2)_4CH}NH_2$	$(C_2H_5)_3SiNH\underbracket{CH(CH_2)_4CH_2}$	72	(122)
	$C_6H_5NH_2$	$(C_2H_5)_3SiNHC_6H_5$	61	(122)
	$o\text{-}CH_3C_6H_4NH_2$	$(C_2H_5)_3SiNH(C_6H_4CH_3\text{-}o)$	—	(122)
	$p\text{-}CH_3C_6H_4NH_2$	$(C_2H_5)_3SiNH(C_6H_4CH_3\text{-}p)$	—	(122)
	$C_6H_5CH_2NH_2$	$(C_2H_5)_3SiNHCH_2C_6H_5$	52	(122)
	2-Aminothiazole	2-$(C_2H_5)_3SiNH$-thiazole	—	(122)
	Uric acid	Tetrakis(triethylsilyl)uric acid	90	(22)
	$(CH_3)_2CHCH_2CH(NH_2)COOH$	$(C_2H_5)_3SiNH[CHCH_2CH(CH_3)_2]COOSi(C_2H_5)_3$	47	(23)
$(C_2H_5)_3SiNHC_2H_5$	$C_6H_{13}NH_2$	$(C_2H_5)_3SiNHC_6H_{13}$	—	(126)
	$C_7H_{15}NH_2$	$(C_2H_5)_3SiNHC_7H_{15}$	—	(126)
	$C_6H_5CH_2NH_2$	$(C_2H_5)_3SiNHCH_2C_6H_5$	—	(126)
	$C_6H_5CH_2CH_2NH_2$	$(C_2H_5)_3SiNHCH_2CH_2C_6H_5$	—	(126)
	$C_6H_5CH(CH_3)NH_2$	$(C_2H_5)_3SiNHCH(CH_3)C_6H_5$	—	(126)
$(C_3H_7)_3SiNH_2$	$C_6H_5NH_2$	$(C_3H_7)_3SiNHC_6H_5$	75	(124)
	$C_6H_5CH_2NH_2$	$(C_3H_7)_3SiNHCH_2C_6H_5$	80	(124)
	$C_6H_5CH_2CH_2NH_2$	$(C_3H_7)_3SiNHCH_2CH_2C_6H_5$	87	(124)
$(C_3H_7)_3SiNHC_3H_7$	$C_6H_5CH_2NH_2$	$(C_3H_7)_3SiNHCH_2C_6H_5$	81	(124)
$(C_4H_9)_3SiNH_2$	$C_6H_5NH_2$	$(C_4H_9)_3SiNHC_6H_5$	—	(120)
$(C_4H_9)_3SiNHCH_3$	$C_6H_5CH_2NH_2$	$(C_4H_9)_3SiNHCH_2C_6H_5$	—	(120)
$(CH_3)_2Si(NHC_2H_5)_2$	$C_7H_{15}NH_2$	$(CH_3)_2Si(NHC_7H_{15})_2$	66	(128)
	$C_6H_5CH_2NH_2$	$(CH_3)_2Si(NHCH_2C_6H_5)_2$	84	(128)
$(CH_3)_2Si[NH(tert\text{-}C_4H_9)]_2$	$CH_2{=}CHO(CH_2)_2NH_2$	$(CH_3)_2Si[NH(CH_2)_2OCH{=}CH_2]_2$	—	(50)
$(C_4H_9O)_2Si(NHC_2H_5)_2$	$C_6H_5CH_2NH_2$	$(C_4H_9O)_2Si(NHCH_2C_6H_5)_2$	71	(118)
$C_3H_7Si(NHCH_3)_3$	$C_4H_9NH_2$	$C_3H_7Si(NHC_4H_9)_3$	70	(201)
	$C_5H_{11}NH_2$	$C_3H_7Si(NHC_5H_{11})_3$	65–71	(201)
	$C_6H_5NH_2$	$C_3H_7Si(NHC_6H_5)_3$	78	(201)
$C_3H_7Si(NHC_2H_5)_3$	$C_5H_{11}NH_2$	$C_3H_7Si(NHC_5H_{11})_3$	30	(201)
	$C_6H_{13}NH_2$	$C_3H_7Si(NHC_6H_{13})_3$	75	(201)
	$\underbracket{CH_2(CH_2)_4CH}NH_2$	$C_3H_7Si[NH\underbracket{CH(CH_2)_4CH_2}]_3$	83	(201)
	$C_6H_5CH_2NH_2$	$C_3H_7Si(NHCH_2C_6H_5)_3$	77	(201)
$C_4H_9OSi(NHC_2H_5)_3$	$C_6H_5CH_2NH_2$	$C_4H_9OSi(NHCH_2C_6H_5)_3$	67	(119)
$[(CH_3)_3Si]_2NH$	$CH_2{=}CHCH_2NH_2$	$(CH_3)_3SiNHCH_2CH{=}CH_2$	—	(193)
	$C_4H_9NH_2$	$(CH_3)_3SiNHC_4H_9$	43	(112, 149)
	$C_5H_{11}NH_2$	$(CH_3)_3SiNHC_5H_{11}$	51	(112)
	$C_6H_5NH_2$	$(CH_3)_3SiNHC_6H_5$	—	(140)
	$\underbracket{C_4H_4N}H$	$(CH_3)_3Si[\underbracket{NC}_4H_4]$	51–64	(64)
	$C_6H_5CH_2NH_2$	$(CH_3)_3SiNHCH_2C_6H_5$	—	(140)
	$C_6H_5CH_2CH_2NH_2$	$(CH_3)_3SiNHCH_2C_6H_5$	—	(140)
	NH_2CH_2COOH	$(CH_3)_3SiNHCH_2COOSi(CH_3)_3$	65	(23)
	$NH_2CH(CH_3)COOH$	$(CH_3)_3SiNHCH(CH_3)COOSi(CH_3)_3$	67	(23)
	$NH_2CH[CH(CH_3)_2]COOH$	$(CH_3)_3SiNHCH[CH(CH_3)_2]COOSi(CH_3)_3$	77	(23)
	$NH_2CH[CH_2CH(CH_3)_2]COOH$	$(CH_3)_3SiNHCH[CH_2CH(CH_3)_2]COOSi(CH_3)_3$	82	(13)
	$NH_2SO_2NH_2$	$[(CH_3)_3SiNH]_2SO_2$	85	(13)
	$C_6H_5SO_2NH_2$	$(CH_3)_3SiNHSO_2C_6H_5$	70	(13)
	$(C_6H_5O)_2P(O)NH_2$	$(CH_3)_3SiNHP(O)(OC_6H_5)_2$	93	(13)
	$(C_6H_5O)P(O)(NH_2)_2$	$[(CH_3)_3SiNH]_2P(O)(OC_6H_5)$	75–85	(14)
$[(C_6H_5)_2SiNH]_3$	$C_6H_5NH_2$	$(C_6H_5)_2Si(NHC_6H_5)_2$	70	(121)

(apparently with rearrangement) to yield N-methyltrimethylsilylamine, which in turn undergoes condensation to N-methylhexamethyldisilazane during isolation (143). If (α-chlorobenzyl)trimethylsilane is treated with sodium amide in liquid ammonia, hexamethyldisilazane and stilbene are obtained (88).

$$(CH_3)_3SiCH_2Cl + NaNH_2 \rightarrow (CH_3)_3SiNHCH_3$$

$$(CH_3)_3SiCH(Cl)C_6H_5 + NaNH_2 \rightarrow [(CH_3)_3Si]_2NH + C_6H_5CH{=}CHC_6H_5$$

Both tetraphenyl- and tetrabenzylsilane undergo complete degradation with potassium amide (84), while trimethylphenylsilane and benzyltrimethylsilane yield the disilazane (87).

$$(CH_3)_3SiCH_2C_6H_5 + KNH_2 \rightarrow [(CH_3)_3Si]_2NH + C_6H_5CH_3$$

Not only are certain silicon–carbon bonds susceptible to cleavage by strong base, but hexamethyldisiloxane also undergoes reaction with sodium amide to yield the disilazane (97).

$$(CH_3)_3SiOSi(CH_3)_3 + NaNH_2 \rightarrow [(CH_3)_3Si]_2NH + (CH_3)_3SiONa$$

2. From organosilylmetallic compounds

The reaction of organosilylmetallic compounds with amines has been reviewed elsewhere (219). In general, triphenylsilyllithium reacts with primary and secondary amines to give excellent yields of the corresponding silylamines (219).

$$(C_6H_5)_3SiLi + R_2NH \rightarrow [(C_6H_5)_3SiH + R_2NLi] \rightarrow (C_6H_5)_3SiNR_2 + LiH$$

It appears that the first step is simple metallation of the amine and that the second step is similar to that observed in the formation of the silylamines from compounds containing a silicon–hydrogen bond.

Triphenylsilylpotassium also adds to benzophenone anil to yield the corresponding silylamine (218).

$$(C_6H_5)_3SiK + (C_6H_5)_2C{=}NC_6H_5 \xrightarrow{H_2O} (C_6H_5)_3SiN(C_6H_5)CH(C_6H_5)_2$$

3. From silanols

One reaction in which a silylamine was obtained from the reaction of a silanol and an amine has been reported: the reaction of tris(*p*-dimethylaminophenyl)silanol with dibutylamine (71).

$$[p\text{-}(CH_3)_2NC_6H_4]_3SiOH + (C_4H_9)_2NH \rightarrow [p\text{-}(CH_3)_2NC_6H_4]_3SiN(C_4H_9)_2 + H_2O$$

Triphenylsilanol with amines yields only the corresponding disiloxane, but there is some evidence that the silylamine exists in transition (71).

4. From silane salts

Trimethylsilyl sulfate yields hexamethyldisilazane in 71 per cent yield when treated with ammonia (185). Other silyl salts have not been studied.

$$[(CH_3)_3Si]_2SO_4 + 3NH_3 \rightarrow [(CH_3)_3Si]_2NH + (NH_4)_2SO_4$$

5. From silicon disulfide

Silicon disulfide (SiS_2) is reported to react with both primary and secondary amines at high temperature to yield polysilazanes along with unseparatable polysulfides (130).

6. From tertiary amines

Both dimethyl- and diethylaniline have been reported to react with silicon tetrabromide at 180°C. with cleavage of the carbon–nitrogen bond (26).

$$C_6H_5N(CH_3)_2 + SiBr_4 \rightarrow C_6H_5N(CH_3)SiBr_3 + CH_3Br$$

IV. Reactions of Silicon–Nitrogen Compounds

A. REACTIONS WITH WATER

Silicon–nitrogen compounds react with water, resulting in the cleavage of the silicon–nitrogen bond. The hydrolytic reaction seems to be affected both by the solvent system used and by the pH of the solution. Some studies have used homogeneous conditions (aqueous acetone, methanol, or ethanol as solvent), while others have employed heterogeneous conditions (usually ether–water). These variations in reaction conditions make correlation difficult. Changes in reactivity are often masked by the choice of reaction conditions. No single study has been directed toward the elucidation of the major factors affecting the hydrolysis of silylamines.

The first step of the hydrolysis is the formation of a silanol. Depending upon its stability and upon the reaction conditions, the silanol may either be isolated or undergo condensation with a silanol or silylamine to yield the disiloxane.

$$R_3SiNH_2 + H_2O \rightarrow R_3SiOH + NH_3$$

$$2R_3SiOH \rightarrow R_3SiOSiR_3 + H_2O$$

$$R_3SiOH + R_3SiNH_2 \rightarrow R_3SiOSiR_3 + NH_3$$

Partial hydrolysis of a silanediamine or silanetriamine has not been reported.

The use of dilute mineral acid greatly facilitates the hydrolysis of silylamines in either heterogeneous (99, 178, 179, 180, 181) or homogeneous media (46, 218). The acid functions as a neutralizing agent for the ammonia or amine released by the hydrolysis and probably also serves as a catalyst. Compounds containing a silicon–hydrogen bond must be hydrolyzed under mild acidic conditions to prevent the cleavage of the silicon–hydrogen bond (178). Base has been reported both to retard (79, 99, 154, 169) and to accelerate (78, 99, 157) the hydrolysis of silicon–nitrogen compounds.

The degree to which the hydrolysis of silicon–nitrogen compounds proceeds is also influenced by the degree of hindrance around the silicon–nitrogen bond. With increasing hindrance there is a decreasing tendency towards hydrolysis. Exposure to air is sufficient for the hydrolysis of *N*-substituted trimethylsilylamines (145). Triethyl-*N*-methylsilylamine, triethyl-*N*,*N*-dimethylsilylamine, and *N*-ethyltriethylsilylamine undergo heterogeneous hydrolysis (8); however, *N*,*N*-diethyltriethylsilylamine requires the use of homogeneous conditions if hydrolysis is to proceed (8). The *N*-alkyltributylsilylamines also hydrolyze slowly unless homogeneous conditions are employed (120). The hydrolysis of di-*tert*-butylsilanediamine requires homogeneous acidic conditions (the product being the silanediol) (186), while di-*tert*-butoxysilanediamine reacts with ice water (138). Other alkoxysilylamines react in a manner similar to that of their alkyl analogs (77, 78, 99, 162).

The disilazanes undergo hydrolytic cleavage as do the silylamines (105, 145, 154, 169, 179, 180, 181). Tris(trimethylsilyl)amine (79) and hexaphenylcyclotrisilazane (121) are not readily cleaved even under acidic homogeneous conditions.

The *N*-silyl inorganic amides (13, 14) and the *N*-silyl amino acid esters (20, 164) are readily susceptible to hydrolysis.

B. REACTIONS WITH ALCOHOLS, PHENOLS, AND SILANOLS

Silylamines react with alcohols, phenols, and silanols to form alkoxysilanes, phenoxysilanes, and disiloxanes, respectively (see table 9). The extent and rate of reaction are dependent on (*a*) hindrance around both the silicon–nitrogen bond and the hydroxyl group of the alcohol or silanol and (*b*) the acidity of the attacking alcohol (149, 150). The alcoholysis is catalyzed by acid (64, 112, 149, 159). The addition of base may increase (149, 150), decrease (112), or have no effect on (149) the rate of reaction. If the reaction is run in aqueous alcohol the silanol is the predominant product (46, 120, 169, 186).

$$R_3SiNH_2 + R'OH \rightarrow R_3SiOR' + NH_3$$

$$R_3SiNH_2 + R'_3SiOH \rightarrow R_3SiOSiR'_3 + NH_3$$

As the substituents on the silicon are increased in size from methyl to butyl, a decrease in the rate of reaction with a given silanol is observed (149). Substituents on the nitrogen of the silylamine do not substantially affect the yield of alkoxysilane or disiloxane, although they do influence the rate of reaction. In comparing the reaction rates of *N*-substituted silylamines with a given silanol, Pike has observed that the *N*,*N*-dialkylsilylamines condense at a faster rate than do the NH-alkylsilylamines (149). Thus, the hindrance around the nitrogen appears to play a minor role in this reaction.

The comparative reactivity of different alcohols toward silylamines is demonstrated by the alcoholysis of di-*tert*-butoxysilanediamine.

$$(tert\text{-}C_4H_9O)_2Si(NH_2)_2 + ROH \rightarrow (tert\text{-}C_4H_9O)_2(RO)SiNH_2 + NH_3$$

$$(tert\text{-}C_4H_9O)_2(RO)SiNH_2 + ROH \rightarrow (tert\text{-}C_4H_9O)_2Si(OR)_2 + NH_3$$

With methanol, two moles of ammonia are liberated at room temperature, while with other primary and secondary alcohols, the first mole of ammonia is liberated at room temperature and the second only upon warming. Tertiary alcohols, on the other hand, react slowly with the first amino group and not at all with the second (138). With a less hindered silylamine, triphenylsilanol has been observed to undergo condensation at a faster rate than does triphenylcarbinol (150).

Hexamethyldisilazane reacts with a variety of alcohols and phenols to yield the alkoxytrimethylsilanes or the trimethylphenoxysilanes (6, 13, 112, 114, 189, 191). The reaction is sluggish with aliphatic alcohols unless an acid catalyst is employed (112).

$$[(CH_3)_3Si]_2NH + 2ROH \rightarrow 2ROSi(CH_3)_3 + NH_3$$

The reaction of a silylamine with hydroxysilicones offers an alternate route for the modification of silicone polymers (150).

C. REACTIONS WITH HYDROGEN SULFIDE AND THIOLS

Silylamines and disilazanes are far less reactive toward hydrogen sulfide and thiols than toward water and alcohols. Triethylsilylamine, tripropylsilylamine, and triethyl-*N*-(2-phenylethyl)silylamine react with hydrogen sulfide to yield the silyl disulfide and a small amount of silylthiol (123, 125).

$$(C_2H_5)_3SiNH_2 + H_2S \rightarrow [(C_2H_5)_3SiS]_2 + (C_2H_5)_3SiSH$$

Hexamethyldisilazane reacts with hydrogen sulfide with difficulty and trimethyl-*N*-phenylsilylamine gives only 14 per cent of the trimethylsilylthiol (123). Bis(methylamino)dimethylsilane and hydrogen sulfide (in a 1:1 molar ratio) yield the silylaminethiol (125).

$$(CH_3)_2Si(NHCH_3)_2 + H_2S \rightarrow (CH_3)_2Si(SH)(NHCH_3) + CH_3NH_2$$

With thiols, silylamines react to yield the *S*-substituted silylthiols; however, only a few cases have been reported. Tripropylsilylamine reacts with phenylthiol (125). Hexamethyldisilazane reacts with allylthiol (191), but fails to react with butylthiol (112).

$$(C_3H_7)_3SiNH_2 + C_6H_5SH \rightarrow (C_3H_7)_3SiSC_6H_5 + NH_3$$

D. REACTIONS WITH ACIDS

1. With inorganic acids and their derivatives

The action of hydrogen halides on the silicon–nitrogen bond results in the formation of halosilanes (X = F, Cl, Br, I):

$$R_3SiNH_2 + HX \rightarrow R_3SiX + NH_4X$$

Dry hydrogen chloride reacts with trisilylamine (195), tri(methylsilyl)amine (55), or *N*-methyldisilazane (55, 198) to form the chlorosilane or methylchlorosilane. Hydrogen bromide gives similar results (198).

$$(CH_3SiH_2)_3N + 4HCl \rightarrow 3CH_3SiH_2Cl + NH_4Cl$$

The reactions of triethylsilylamine and (α-chloroethyl)diethylsilylamine with 48 per cent hydrofluoric acid, hydrobromic acid, or hydrochloric acid (either anhydrous or concentrated aqueous) give the halosilanes in yields up to 89 per cent. The α-chloro substituent has little effect upon the reaction (12).

Acid-sensitive substituents on silicon, such as alkoxy or phenyl, limit the scope of the reaction. In one case, with careful control of the conditions, the silicon–nitrogen bond has been broken in preference to the silicon–oxygen bond. Di-*tert*-butoxysilanediamine with a limited amount of hydrogen chloride gas gave a 67 per cent yield of the dichlorosilane; however, with concentrated hydrochloric acid only *tert*-butyl chloride was obtained (68).

TABLE 9

Reactions of silicon–nitrogen compounds with alcohols, phenols, and silanols

Silylamine	Alcohol, Phenol, or Silanol	Product	Yield	References
Reaction with alcohols				
			per cent	
$(CH_3)_3SiNHCH_3$	C_2H_5OH	$(CH_3)_3SiOC_2H_5$	90–95	(13)
$(CH_3)_3SiN(C_2H_5)_2$	C_3H_7OH	$(CH_3)_3SiOC_3H_7$	81	(149)
$(CH_3)_3SiNHC_6H_5$	CH_3OH	$(CH_3)_3SiOCH_3$	91	(107)
	C_2H_5OH	$(CH_3)_3SiOC_2H_5$	93	(107)
$(C_2H_5)_3SiNH_2$	C_2H_5OH	$(C_2H_5)_3SiOC_2H_5$	80	(8)
	C_3H_7OH	$(C_2H_5)_3SiOC_3H_7$	—	(8)
	$\text{iso-}C_3H_7OH$	$(C_2H_5)_3SiO(\text{iso-}C_3H_7)$	—	(8)
	C_4H_9OH	$(C_2H_5)_3SiOC_4H_9$	—	(8)
	$(CH_3)_2CHCH_2OH$	$(C_2H_5)_3SiOCH_2CH(CH_3)_2$	—	(8)
	$(CH_3)_2CHCH_2CH_2OH$	$(C_2H_5)_3SiOCH_2CH_2CH(CH_3)_2$	—	(8)
	$C_8H_{17}OH$	$(C_2H_5)_3SiOC_8H_{17}$	—	(8)
$(C_2H_5)_3SiNHC_2H_5$	CH_3OH	$(C_2H_5)_3SiOCH_3$	—	(127)
$(C_3H_7)_3SiNHC_3H_7$	CH_3OH	$(C_3H_7)_3SiOCH_3$	60	(124)
$(CH_3)_2Si(NHC_6H_5)_2$	CH_3OH	$(CH_3)_2Si(OCH_3)_2$	87	(107)
	C_2H_5OH	$(CH_3)_2Si(OC_2H_5)_2$	80	(107)
$(\textit{tert}\text{-}C_4H_9O)_2Si(NH_2)_2$	$ClCH_2CH_2OH$	$(\textit{tert}\text{-}C_4H_9O)_2Si(OCH_2CH_2Cl)_2$	53	(68)
	$NCCH_2CH_2OH$	$(\textit{tert}\text{-}C_4H_9O)_2Si(OCH_2CH_2CN)_2$	60	(68)
	$H_2NCH_2CH_2OH$	$(\textit{tert}\text{-}C_4H_9O)_2Si(OCH_2CH_2NH_2)_2$	63	(51)
	$(C_2H_5)_2NCH_2CH_2OH$	$(\textit{tert}\text{-}C_4H_9O)_2Si[OCH_2CH_2N(C_2H_5)_2]_2$	43	(51)
	$H_2NCH_2CH(CH_3)CH_2OH$	$(\textit{tert}\text{-}C_4H_9O)_2Si[OCH_2CH(CH_3)CH_2NH_2]_2$	72	(51)
	$CH_3CH_2CH(NH_2)CH_2OH$	$(\textit{tert}\text{-}C_4H_9O)_2Si[OCH_2CH(NH_2)CH_2CH_3]_2$	47	(51)
	$CH_3C(NH_2)(CH_3)CH_2OH$	$(\textit{tert}\text{-}C_4H_9O)_2Si[OCH_2C(CH_3)(NH_2)CH_3]_2$	47	(51)
	$H_2N(CH_2)_2NH(CH_2)_2OH$	$(\textit{tert}\text{-}C_4H_9O)_2Si[O(CH_2)_2NH(CH_2)_2NH_2]_2$	41	(51)
$[(CH_3)_3Si]_2NH$	CH_3OH	$(CH_3)_3SiOCH_3$	—	(112)
	C_2H_5OH	$(CH_3)_3SiOC_2H_5$	90–95	(112)
	CH_2OHCH_2OH	$(CH_3)_3SiOCH_2CH_2OSi(CH_3)_3$	75	(112)
	$HOCH_2CH_2NH_2$	$(CH_3)_3SiOCH_2CH_2NH_2$	80	(6)
	C_3H_7OH	$(CH_3)_3SiOC_3H_7$	60	(112)
	$CH_3CHOHCH_2OH$	$(CH_3)_3SiOCH_2CH[OSi(CH_3)_3]CH_3$	—	(112)
	$\text{iso-}C_4H_9OH$	$(CH_3)_3SiO(\text{iso-}C_4H_9)$	—	(112)
	$C_5H_{11}OH$	$(CH_3)_3SiOC_5H_{11}$	—	(112)
	$\text{iso-}C_5H_{11}OH$	$(CH_3)_3SiO(\text{iso-}C_5H_{11})$	—	(112)
	$CH_3CH_2CH(CH_3)CH_2OH$	$(CH_3)_3SiOCH_2CH(CH_3)CH_2CH_3$	75	(112)
	$Cl(CH_2)_5OH$	$(CH_3)_3SiO(CH_2)_5Cl$	96	(189)
	$CH_3CH_2CH(CH_3)CH_2CH_2OH$	$(CH_3)_3SiOCH_2CH_2CH(CH_3)CH_2CH_3$	—	(112)
	$C_7H_{15}OH$	$(CH_3)_3SiOC_7H_{15}$	82	(112)
	$C_8H_{17}OH$	$(CH_3)_3SiOC_8H_{17}$	—	(112)
	$CH_3(CH_2)_3CH(C_2H_5)CH_2OH$	$(CH_3)_3SiOCH_2CH(C_2H_5)(CH_2)_3CH_3$	—	(112)
	$C_9H_{19}OH$	$(CH_3)_3SiOC_9H_{19}$	94	(112)
	$C_{11}H_{23}OH$	$(CH_3)_3SiOC_{11}H_{23}$	—	(112)
	$C_{12}H_{25}OH$	$(CH_3)_3SiOC_{12}H_{25}$	—	(112)
	$2,5\text{-}(HO)(Cl)C_6H_3CH(CH_3)C_6H_4Cl\text{-}4$	$2\text{-}[(CH_3)_3SiO]\text{-}5\text{-}ClC_6H_3CH(CH_3)(C_6H_4Cl\text{-}4)$	—	(191)
$[(\textit{tert}\text{-}C_4H_9O)_2Si(NH_2)]_2NH$	$C_6H_{13}OH$	$(\textit{tert}\text{-}C_4H_9O)_2Si(NH_2)(OC_6H_{13})$	—	(129)
$[(CH_3)_2SiNH]_3$	$CH_2OHCHOHCH_2OH$	 $(CH_3)_2SiOCH_2CH(OH)CH_2O$	—	(134)
Reaction with phenols				
$(CH_3)_3SiNHCH_3$	C_6H_5OH	$(CH_3)_3SiOC_6H_5$	90–95	(13)
$[(CH_3)_3Si]_2NH$	C_6H_5OH	$(CH_3)_3SiOC_6H_5$	90–95	(13, 114)
	$o\text{-}CH_3C_6H_4OH$ (also *m*- and *p*-)	$(CH_3)_3SiO(C_6H_4CH_3\text{-}o)$	—	(114)
	$o\text{-}CH_3CH_2C_6H_4OH$ (also *m*- and *p*-)	$(CH_3)_3SiO(C_6H_4C_2H_5\text{-}o)$	—	(114)
	$2,3\text{-}(CH_3)_2C_6H_3OH$ (also 2,4-, 2,5-, 2,6-, 3,4-, and 3,5-)	$(CH_3)_3SiOC_6H_3(CH_3)_2\text{-}2,3$	—	(114)
	$2,4,6\text{-}(CH_3)_3C_6H_2OH$	$(CH_3)_3SiOC_6H_2(CH_3)_3\text{-}2,4,6$	—	(114)
	$o\text{-}CH_3OC_6H_4OH$	$(CH_3)_3SiO(C_6H_4OCH_3\text{-}o)$	—	(114)
Reaction with silanols				
$(CH_3)_3SiNHC_4H_9$	$(C_2H_5)_3SiOH$	$(CH_3)_3SiOSi(C_2H_5)_3$	43	(149)
	$(C_6H_5)_3SiOH$	$(CH_3)_3SiOSi(C_6H_5)_3$	53	(149)
	$(C_2H_5)_2Si(OH)_2$	$[(CH_3)_3SiO]_2Si(C_2H_5)_2$	54	(150)
	$(C_6H_5)_2Si(OH)_2$	$[(CH_3)_3SiO]_2Si(C_6H_5)_2$	87	(150)
$(CH_3)_3SiN(C_2H_5)_2$	$(C_2H_5)_3SiOH$	$(CH_3)_3SiOSi(C_2H_5)_3$	65	(149)
	$(C_6H_5)_3SiOH$	$(CH_3)_3SiOSi(C_6H_5)_3$	83	(149)
	$(C_2H_5)_2Si(OH)_2$	$[(CH_3)_3SiO]_2Si(C_2H_5)_2$	54	(150)
	$(C_6H_5)_2Si(OH)_2$	$[(CH_3)_3SiO]_2Si(C_6H_5)_2$	87	(150)
	$HO[Si(CH_3)_2O]_3H$	$(CH_3)_3SiO[Si(CH_3)_2O]_3Si(CH_3)_3$	84	(150)
	$HO[Si(C_6H_5)_2O]_2H$	$(CH_3)_3SiO[Si(CH_3)_2O]_2Si(CH_3)_3$	70	(150)
$(CH_3)_3SiNH(\textit{tert}\text{-}C_4H_9)$	$(C_6H_5)_3SiOH$	$(CH_3)_3SiOSi(C_6H_5)_3$	56	(149)
$(C_2H_5)_3SiNHC_2H_5$	$(C_6H_5)_3SiOH$	$(C_2H_5)_3SiOSi(C_6H_5)_3$	61–68	(149)
$(C_2H_5)_3SiN(C_2H_5)_2$	$(C_6H_5)_3SiOH$	$(C_2H_5)_3SiOSi(C_6H_5)_3$	53	(149)
$(C_4H_9)_3SiN(C_2H_5)_2$	$(C_6H_5)_3SiOH$	$(C_4H_9)_3SiOSi(C_6H_5)_3$	30	(149)
$(\textit{sec}\text{-}C_4H_9O)_3SiNH_2$	$(\textit{sec}\text{-}C_4H_9O)_3SiOH$	$[(\textit{sec}\text{-}C_4H_9O)_3Si]_2O$	—	(77)
$(CH_3)_2Si[N(C_2H_5)_2]_2$	$(C_6H_5)_2Si(OH)_2$	Polymer	62	(150)
	$HO[Si(CH_3)_2O]_3H$	Polymer	88	(150)
$(\textit{tert}\text{-}C_4H_9O)_2Si(NH_2)_2$	$(C_2H_5)_3SiOH$	$(\textit{tert}\text{-}C_4H_9O)_2Si(NH_2)[OSi(C_2H_5)_3]$	68	(182)

Evidence is insufficient to show any clearly defined trends due to steric effects in these reactions. A decrease in yield is observed when the substituents on the silicon in the *N*-phenylsilylamine series are increased from methyl to isopropyl (see table 10) (1). On the other hand, tris(triphenylgermanyl)chlorosilane is readily obtained from the corresponding amine (137). Compounds in which there is phenyl substitution on the nitrogen have been studied, and these silylamines undergo reaction with hydrogen iodide (1, 5, 165) and hydrogen chloride (165) to yield halosilanes. If this reaction is used for the conversion of a chlorosilane to the iodosilane, the intermediate silylamine need not be isolated (1, 5).

$$R_3SiCl + C_6H_5NH_2 \rightarrow [R_3SiNHC_6H_5] \xrightarrow{HI} R_3SiI + C_6H_5NH_3I + HCl$$

Disilazanes, such as hexamethyldisilazane, also react with the halogen acids to yield the corresponding halosilanes (169). In the one instance in which the reaction of halogen acids with a cyclosilazane has been reported, hexa-*tert*-butoxycyclotrisilazane was found to undergo almost complete degradation (68).

Derivatives of the mineral acids may react with *N*-substituted silylamines with cleavage of the nitrogen–hydrogen bond rather than the silicon–nitrogen bond (13, 14). *N*-Methyltrimethylsilylamine, for example, reacts with ethyl chlorosulfonate to give the silylsulfamide (13).

$$(CH_3)_3SiNHCH_3 + ClSO_2OC_2H_5 \rightarrow (CH_3)_3SiN(CH_3)SO_2OC_2H_5 + HCl$$

The reaction of hexamethyldisilazane with sulfuryl chloride, however, results in cleavage of the silicon–nitrogen bond (13).

$$2[(CH_3)_3Si]_2NH + SO_2Cl_2 \rightarrow [(CH_3)_3SiN]_2SO_2 + 2(CH_3)_3SiCl$$

Phosphoric acid and its derivatives with hexamethyldisilazane or *N*-methyltrimethylsilylamine yield *O*-silylphosphates (14).

2. With organic acids and their derivatives

Reaction of silicon–nitrogen compounds with carboxylic acids results in cleavage of the silicon–nitrogen bond (23, 138).

$$(tert\text{-}RO)_2Si(NH_2)_2 + 2R'COOH \rightarrow (tert\text{-}RO)_2Si(OOR')_2 + 2NH_3$$

Acid chlorides react with silylamines to yield chlorosilanes (3).

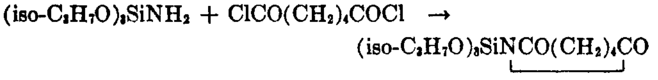
$$CH_3Si[N(CH_3)_2]_3 + C_6H_5COCl \rightarrow CH_3SiCl_3$$

Schotten–Baumann reactions with hexamethyldisilazane (169) and *N*-methylhexamethyldisilazane (143) gave only benzamide and *N*-methylbenzamide, respectively. Adipoyl chloride with triisopropoxysilylamine is reported to undergo ring closure without affecting the silicon–nitrogen bond (175).

TABLE 10

Reactions of silicon–nitrogen compounds with hydrogen halides

Silylamine	Hydrogen Halide	Product	Yield	References
			per cent	
$(H_3Si)_2NCH_3$	HCl (gas)	H_3SiCl	100	(59, 60)
	HBr (gas)	H_3SiBr	96	(198)
$(CH_3SiH_2)_3N$	HCl (gas)	CH_3SiH_2Cl	—	(55)
$(CH_3SiH_2)_2NCH_3$	HCl (gas)	CH_3SiH_2Cl	—	(55)
$CH_3SiH_2N(CH_3)_2$	HCl (gas)	CH_3SiH_2Cl	—	(55)
$(CH_3)_3SiN(CH_3)_2$	HCl (gas)	$(CH_3)_3SiCl$	—	(55)
$(C_2H_5)_3SiNH_2$	HF (48%)	$(C_2H_5)_3SiF$	89	(12)
	HCl (gas)	$(C_2H_5)_3SiCl$	80	(12)
	HCl (concd.)	$(C_2H_5)_3SiCl$	80	(12)
	HBr (gas)	$(C_2H_5)_3SiBr$	70	(12)
	$HBr–H_2SO_4$	$(C_2H_5)_3SiBr$	55	(12)
$[CH_3CH(Cl)](C_2H_5)_2SiNH_2$	HF (48%)	$CH_3CHCl(C_2H_5)_2SiF$	82	(12)
	HCl (gas)	$CH_3CHCl(C_2H_5)_2SiCl$	76	(12)
	HCl (concd.)	$CH_3CHCl(C_2H_5)_2SiCl$	79	(12)
	HBr (gas)	$CH_3CHCl(C_2H_5)_2SiBr$	26	(12)
	$HBr–H_2SO_4$	$CH_3CHCl(C_2H_5)_2SiBr$	81	(12)
$(C_2H_5O)_3SiN(CH_3)_2$	HCl (gas)	$(C_2H_5O)_3SiCl$	—	(162)
$[(C_6H_5)_3Ge]_3SiNH_2$	HCl (gas)	$[(C_6H_5)_3Ge]_3SiCl$	—	(137)
$(CH_3)_2Si(NHC_6H_5)_2$	HI (gas)	$(CH_3)_2SiI_2$	55	(1)
$(tert\text{-}C_4H_9O)_2Si(NH_2)_2$	HCl (gas)	$(tert\text{-}C_4H_9O)_2SiCl_2$	10–67	(68)
	HCl (concd.)	$(tert\text{-}C_4H_9O)_2SiCl_2$	58	(68)
$HSi(NHC_6H_5)_3$	HCl (gas)	$HSiCl_3$	—	(165)
	HBr (gas)	$HSiBr_3$	—	(165)
	HI (gas)	$HSiI_3$	—	(165)
$C_3H_7Si(NHC_6H_5)_3$	HI (gas)	$C_3H_7SiI_3$	46	(1)
iso-$C_3H_7Si(NHC_6H_5)_3$	HI (gas)	iso-$C_3H_7SiI_3$	37	(1)
$Si(NHC_6H_5)_4$	HCl	$SiCl_4$	—	(155)
$[(CH_3)_3Si]_2NH$	HCl (gas)	$(CH_3)_3SiCl$	63	(169)
$[(C_2H_5O)_3Si]_2NH$	HCl (gas)	$(C_2H_5O)_3SiCl$	—	(162)



$$(\text{iso-}C_3H_7O)_3SiNH_2 + ClCO(CH_2)_4COCl \rightarrow (\text{iso-}C_3H_7O)_3SiNCO(CH_2)_4CO$$

Acetic anhydride results in cleavage of the silicon–nitrogen bond (115a).

E. REACTIONS WITH BORON COMPOUNDS

The simple silylamines undergo cleavage of the silicon–nitrogen bond with boron trifluoride or boron trichloride. The reaction of trisilylamine and boron trichloride (37) or boron trifluoride (37, 199) at −78° C. yields the silyl halide and silylborazole.

$$(H_3Si)_3N + BCl_3 \rightarrow H_3SiCl + (H_3Si)_2NBCl_2$$

N-Methyldisilazane also reacts with boron trichloride at −78°C., but at higher temperature the borazole decomposes (37).

$$CH_3N(SiH_3)_2 + BCl_3 \rightarrow H_3SiCl + CH_3N(SiH_3)(BCl_2)$$

$$CH_3N(SiH_3)(BCl_2) \rightarrow H_3SiCl + (CH_3NBCl)_3$$

Trisilylamine is cleaved by dimethylboron bromide giving silyl bromide along with silane, trimethylboron, and *N*,*N*-bis(silylenebromide)dimethylborazole, $(CH_3)_2BN(SiH_2Br)_2$ (37).

Diborane does not react with trisilylamine (67); however, the reaction with bromodiborane yields silyl bromide and bis(silyl)aminoborine, which appears both as the monomer and as the dimer (37).

$$(H_3Si)_3N + B_2H_5Br \rightarrow H_3SiBr + (H_3Si)_2NBH_2$$

N-Methyldisilazane undergoes a similar reaction with bromodiborane, but the aminoborine formed is unstable (37).

F. REACTIONS WITH ALKALI METALS AND ORGANOMETALLIC COMPOUNDS

The nitrogen–hydrogen bond of silylamines and disilazanes is relatively inert to the action of alkali metals. *N*-Methyltrimethylsilylamine fails to react with sodium (169), and *N*-ethyltriethylsilylamine fails to react with lithium in ethylamine (105). *N*-Ethyltriphenylsilylamine, however, reacts with lithium in ethylamine with the loss of a phenyl group (16).

$$(C_6H_5)_3SiNHC_2H_5 + Li + C_2H_5NH_2 \rightarrow (C_6H_5)_2Si(NHC_2H_5)_2$$

Hexamethyldisilazane (79, 169) and hexaethoxydisilazane (162) fail to react with sodium or potassium under reflux, but the former reacts with sodium in styrene (79), phenyllithium (210), or a methyl Grignard reagent (168) to yield the salt of the disilazane.

$$[(CH_3)_3Si]_2NH + C_6H_5Li \rightarrow [(CH_3)_3Si]_2NLi + C_6H_6$$

G. CONDENSATION AND REDISTRIBUTION REACTIONS

Silylamines undergo self-condensation to yield disilazanes (62, 116, 175, 205, 214). This reaction is similar to the silylamine–amine exchange reaction and,

$$2R_3SiNH_2 \rightarrow R_3SiNHSiR_3 + NH_3$$

like the exchange reaction, is acid catalyzed. Although triethylsilylamine fails to condense upon prolonged reflux (8), the addition of ammonium sulfate catalyzes the reaction so that the disilazane may be obtained (62). Tributoxysilylamine (116), triphenoxysilylamine (175, 214), and tris(*p*-dimethylaminophenyl)silylamine (205) have been reported to form disilazanes upon prolonged reflux.

$$2(C_4H_9O)_3SiNH_2 \rightarrow [(C_4H_9O)_3Si]_2NH + NH_3$$

N-Substituted trimethylsilylamines undergo condensation to the *N*-substituted hexamethyldisilazanes (128, 143, 193).

$$2(CH_3)_3SiNHCH_3 \rightarrow [(CH_3)_3Si]_2NCH_3 + CH_3NH_2$$

A mixture of tris(methylamino)propylsilane and tris(ethylamino)propylsilane undergoes redistribution of the RNH— groups when heated with ammonium sulfate (201).

Silanediamines undergo condensation to cyclosilazanes when heated with ammonium sulfate, the cyclotrisilazane being the predominant product (68, 138, 175). Di-*tert*-butylsilanediamine, however, does not undergo condensation (186).

$$3(\textit{tert-}C_4H_9O)_2Si(NH_2)_2 \rightarrow [(\textit{tert-}C_4H_9O)_2SiNH]_3 + 3NH_3$$

Polysilazanes may be pyrolyzed to cyclosilazanes (82).

Hexamethylcyclotrisilazane when heated in a sealed tube with ammonium chloride yields hexamethyldisilazane and octamethyltetrasilazane (33).

H. REACTIONS WITH HALOSILANES

The reaction of a silylamine with a halosilane may result in the cleavage of either the silicon–nitrogen or the nitrogen–hydrogen bond. When *N*,*N*-dimethyltrimethylsilylamine is heated with silicon tetrachloride in a sealed tube, bis(dimethylamino)dichlorosilane and trimethylchlorosilane are produced (81).

$$2(CH_3)_3SiN(CH_3)_2 + SiCl_4 \xrightarrow{\text{heat}} [(CH_3)_2N]_2SiCl_2 + 2(CH_3)_3SiCl$$

Under similar conditions, hexamethyldisilazane yields trimethyltrichlorodisilazane, while *N*-methylhexamethyldisilazane is converted to *N*-methyltrimethyltrichlorodisilazane (81).

$$[(CH_3)_3Si]_2NCH_3 + SiCl_4 \xrightarrow{\text{heat}} (CH_3)_3SiN(CH_3)SiCl_3 + (CH_3)_3SiCl$$

The action of halosilanes other than silicon tetrachloride under these conditions has not been reported.

In contrast to the reactions noted when a sealed-tube system is used, the silicon–nitrogen bond of hexamethyldisilazane (79, 169) or hexaethoxydisilazane (162) is not broken when these compounds are heated under reflux with halosilanes.

Reactions of silylamines and halosilanes which involve cleavage of the nitrogen–hydrogen bond yield disilazanes (8, 141, 169). This reaction is reversible (169) (see Section IV,D,1).

$$R_3SiNH_2 + R'_3SiCl \rightleftarrows R_3SiNHSiR'_3 + HCl$$

I. MISCELLANEOUS REACTIONS

Both *N*,*N*-dimethyltrichlorosilylamine and bis(dimethylamino)dichlorosilane are reduced and undergo cleavage of the silicon–nitrogen bond with lithium aluminum hydride (38).

$$(CH_3)_2NSiCl_3 + LiAlH_4 \rightarrow SiH_4$$

Hexaphenyldisilazane reacts with bromine to yield triphenylsilyl bromide and bromobenzene (154).

The reaction of hexamethyldisilazane with hydrogen cyanide to give trimethylsilyl cyanide has been reported (24).

$$[(CH_3)_3Si]_2NH + HCN \rightarrow (CH_3)_3SiCN$$

There is one report of the addition of a disilazane to a double bond (139).

$$[(C_2H_5)_3Si]_2NH + CH_2{=}CHCN \rightarrow [(C_2H_5)_3Si]_2NCH_2CH_2CN$$

None of these reactions has been investigated extensively.

V. SILYLHYDRAZINES

Four methods for the preparation of silylhydrazines have been reported. The first (method A, table 11) is the treatment of a hydrazine or a substituted hydrazine with a halosilane. The reaction of silyl iodide with hydrazine yields the tetrasilylhydrazine (9), while trimethylchlorosilane gives the *N*,*N'*-bis(trimethylsilyl)hydrazine (206). Disubstitution on the same nitrogen of the hydrazine does not occur when trialkyl- or triaryl-substituted halosilanes are used (206, 207). The monosilylhydrazines may be prepared by increasing the ratio of hydrazine to chlorosilane (207).

$$2(CH_3)_3SiCl + 3NH_2NH_2 \rightarrow (CH_3)_3SiNHNHSi(CH_3)_3 + 2NH_2NH_2 \cdot HCl$$

In the reaction of a chlorosilane with a substituted hydrazine, the silyl group shows a preference for the unsubstituted nitrogen of the hydrazine. Both alkyl- and aryl-substituted hydrazines have been utilized (206, 208).

$$(CH_3)_3SiCl + 2NH_2NHC_6H_5 \rightarrow (CH_3)_3SiNHNHC_6H_5 + C_6H_5NHNH_2 \cdot HCl$$

N-Methyl-*N'*-(trimethylsilyl)hydrazine, prepared by

TABLE 11

Preparation and physical constants of the silylhydrazines

Silylhydrazine	Method of Preparation*	Yield	Melting Point	Boiling Point	*d*	n_D	References
		per cent	°*C.*	°*C.*			
$(H_3Si)_2NN(SiH_3)_2$	A		−24	109	0.83 (20°)		(9)
$(CH_3)_3SiNHNHCH_3$	A	99.5		96–97			(208)
$(CH_3)_3SiNCH_3NHCH_3$	A	88		61–63/260 mm.		1.3818 (20°)	(208)
$(CH_3)_3SiNHN(CH_3)_2$	A	91		100	0.9658 (20°)	1.4018 (22°)	(208)
$(CH_3)_3SiNHN(C_2H_5)_2$	A			144.5	0.7948 (20°)	1.4195 (20°)	(176)
$(CH_3)_3SiNHNHSi(CH_3)_3$	A	98		69/40 mm.	0.8165 (21°)	1.4268 (22°)	(206, 207)
$(CH_3)_3SiNHN(CH_3)Si(CH_3)_3$	A	95		73–75/40 mm.	0.7708 (19°)	1.3820 (19°)	(206, 208)
$[(CH_3)_3Si]_2NN(CH_3)_2$	B	90		67/12 mm.	0.8431 (19°)	1.4390 (20°)	(210)
$[(CH_3)_3Si]_2NNHSi(CH_3)_3$	B	90		89/13 mm.	0.8460 (24°)	1.4442 (20°)	(210)
$(CH_3)_3SiNHNHC_6H_5$	A	93		115–116/12 mm.	0.9768 (20°)	1.5409 (19°)	(206, 208)
$(CH_3)_3SiN(C_2H_5)NHC_6H_5$	B	90		113/10 mm.	0.9329 (24°)	1.5152 (20°)	(210)
$(CH_3)_3SiN(C_6H_5)NHC_6H_5$	B		55	138/1 mm.			(210)
$[(CH_3)_3Si]_2NNHC_6H_5$	B	90		124/10 mm.	0.9292 (24°)	1.5078 (20°)	(210)
$(CH_3)_3SiNHNHP(O)(OC_6H_5)_2$	D	92	53–54				(14)
$(C_2H_5)_3SiNHN(CH_3)_2$	A			55–56/8 mm.	0.8202 (20°)	1.4348 (20°)	(176)
$(C_2H_5)_3SiNHN(C_2H_5)_2$	A			85–87/10–11 mm.	0.8340 (20°)	1.4441 (20°)	(176)
$(C_2H_5)_3SiNHNHSi(CH_3)_3$	A	97		72/3 mm.	0.8417 (22°)	1.4422 (17°)	(206, 207)
$(C_2H_5)_3SiNHNHSi(C_2H_5)_3$	A	90		142/20 mm.	0.8595 (23°)	1.4562 (20°)	(206, 207)
$[(C_2H_5)_3Si][(CH_3)_3Si]NNHSi(CH_3)_3$	B	90		126/9 mm.	0.8723 (24°)	1.4612 (20°)	(210)
$[(C_2H_5)_3Si][(CH_3)_3Si]NNHSi(C_2H_5)_3$	B	90		164/3 mm.	0.8918 (21°)	1.4764 (20°)	(210)
$(C_2H_5)_3SiNHNHC_6H_5$	A	95		129–130/1 mm.		1.5210 (20°)	(206, 208)
$(C_3H_7)_3SiNHN(CH_3)_2$	A			87–89/7 mm.	0.8209 (20°)	1.4405 (20°)	(176)
$(C_3H_7)_3SiNHN(C_2H_5)_2$	A			114–115/10 mm.	0.8301 (20°)	1.4471 (20°)	(176)
$(C_3H_7)_3SiNHNHSi(C_3H_7)_3$	A	88		189–190/20 mm.	0.8481 (21°)	1.4562 (24°)	(206, 207)
$(C_3H_7)_3SiNHNHC_6H_5$	A	90		145/1 mm.		1.4918 (20°)	(208)
$(C_6H_5)_3SiNHNH_2$	A		90–92				(206, 207)
$(C_6H_5)_3SiNHNHC_6H_5$	A	75	80–82				(206, 208)
$(C_6H_5)_3SiNHNHSi(C_6H_5)_3$	A	82	138–140				(206, 207)
$(C_6H_5)_3SiN(C_6H_5)NHC_6H_5$	B, C	68–74	136–138				(218)
$(C_6H_5)_3SiN(C_6H_5)N(C_6H_5)Si(C_6H_5)_3$	B	17	265–266				(218)
$(C_6H_5)_2Si[NHN(CH_3)_2]_2$	A		42–43	191–193			(209)
$(C_6H_5)_2Si(NHNHC_6H_5)_2$	A		115 (d.)				(209)

* Method of preparation: A. chlorosilane + hydrazine; B. chlorosilane + alkali metal salt of hydrazine; C. $(C_6H_5)_3SiLi + C_6H_5N{=}NC_6H_5$; D. $(C_6H_5O)_2P(O)NHNH_2 + (CH_3)_3SiNHR$.

this method, undergoes autocondensation with the release of methylhydrazine (208).

$$2CH_3NHNHSi(CH_3)_3 \xrightarrow{\text{heat}} [(CH_3)_3Si](CH_3)NNHSi(CH_3)_3 + CH_3NHNH_2$$

When dichlorosilanes react with hydrazines, either polymers or bis(hydrazino)silanes are formed. Dimethyldichlorosilane and hydrazine form a polymer of molecular weight ca. 3500 (206), but diphenyldichlorosilane forms bis(hydrazino)diphenylsilane (209). Diphenyldichlorosilane and substituted hydrazines yield bis(*N′*-substituted hydrazino)silanes (209).

$$(C_6H_5)_2SiCl_2 + 4NH_2NHC_6H_5 \rightarrow (C_6H_5)_2Si(NHNHC_6H_5)_2 + 2C_6H_5NHNH_2\cdot HCl$$

The second method of preparation of silylhydrazines (method B, table 11) is the use of the lithium salt of a hydrazine (218).

$$C_6H_5NLiNLiC_6H_5 + (C_6H_5)_3SiCl \rightarrow (C_6H_5)_3SiN(C_6H_5)NH(C_6H_5) + (C_6H_5)_3SiN(C_6H_5)N(C_6H_5)Si(C_6H_5)_3$$

The preparation of more complex silylhydrazines has been accomplished by a variation of this reaction, in which the lithium salt of a silylhydrazine is treated with either a chlorosilane or an alkyl halide to introduce a second silyl group (or alkyl group) to the substituted nitrogen of the silylhydrazine (210).

$$(CH_3)_3SiN(Li)NHSi(CH_3)_3 + (CH_3)_3SiCl \rightarrow [(CH_3)_3Si]_2NNHSi(CH_3)_3$$

Lithium hydrazide has been treated with triphenylsilane, but hydrolysis during work-up prevented the isolation of the silylhydrazine (71).

The third method of preparation (method C, table 11) is the reaction of triphenylsilyllithium (or potassium) with azobenzene (218) or azoxybenzene (219).

$$(C_6H_5)_3SiLi + C_6H_5N{=}NC_6H_5 \xrightarrow{H_2O} [(C_6H_5)_3Si](C_6H_5)NNHC_6H_5$$

This method is limited to compounds which will form a silicon–metal bond and results in the introduction of a single silyl group into the hydrazine molecule.

The fourth method (method D, table 11) is the reaction of the diphenyl ester of hydrazinophosphoric acid with either hexamethyldisilazane or *N*-methyltrimethylsilylamine (14). This reaction is a variation of the silylamine–amine exchange reaction.

$$(C_6H_5O)_2P(O)NHNH_2 + (CH_3)_3SiNHSi(CH_3)_3\ [\text{or } CH_3NHSi(CH_3)_3] \rightarrow (C_6H_5O)_2P(O)NHNHSi(CH_3)_3$$

The investigations of the silylhydrazines which have been reported were directed toward synthetic techniques with no emphasis on study of their chemical properties; however, it has been observed by workers in this field that these compounds are sensitive to moisture.

VI. The Amine–Halosilane Complex

Under the proper conditions, halosilanes react with ammonia or amines to yield amine–halosilane complexes. These complexes are probably formed as unstable intermediates when chlorosilanes react with ammonia or amines, with the reaction normally proceeding to the formation of silylamines and related compounds. With the fluorosilanes, however, the complex may be of sufficient stability to resist further reaction and permit isolation of various adducts. These adducts are characterized by giving the ratio of halosilane to amine in the complex (e.g., $SiF_4\cdot 2NH_3$ is the 1:2 adduct).

The reaction of silicon tetrafluoride has been studied extensively. It will react with ammonia to yield a stable 1:2 adduct (69, 136).

$$SiF_4 + 2NH_3 \rightarrow SiF_4\cdot 2NH_3$$

This compound does not react further with ammonia, even at 300°C. (136), but is decomposed by reaction with water at moderate temperatures (136).

$$2SiF_4\cdot 2NH_3 + 2H_2O \rightarrow (NH_4)_2SiF_6\cdot NH_4F + SiO_2 + NH_4F$$

With trimethylamine, silicon tetrafluoride yields both the 1:1 and the 1:2 adducts (217). With excess silicon tetrafluoride, the 1:1 adduct predominates, while with excess trimethylamine the 1:2 adduct is formed. The 1:1 derivative is converted to the 1:2 on addition of trimethylamine, while the reverse is accomplished upon vacuum distillation, i.e., 1:2 becomes 1:1 (217).

$$SiF_4 + (CH_3)_3N \rightarrow SiF_4\cdot N(CH_3)_3 + SiF_4\cdot 2N(CH_3)_3$$

Silicon tetrafluoride yields a 1:1 complex with ethylenediamine. A chelate structure has been suggested, the amino groups occupying two of the six coördination positions of the silicon (171). The reaction of dichlorodifluorosilane with *N*,*N*,*N′*,*N′*-tetramethylethylenediamine also gives a stable 1:1 adduct (61). Tributylamine was reported to yield a solid product with silicon tetrafluoride, but no analytical results were given (69).

Formamide is decomposed by silicon tetrafluoride (151); acetamide gives a solid product which was not further characterized (69); and *N*,*N*-dimethylformamide gives a 1:2 adduct (151). In the last case, the infrared spectrum of the complex exhibits a carbonyl peak; consequently, the dative bond has been assigned to the nitrogen (151).

Other fluorosilanes give adduct formation, but the reports are found only in the secondary literature (35).

With the chlorofluorosilanes both 1:1 and 1:2 adducts are obtained. There is some evidence of halogen rearrangement during the course of the reaction (61).

The chlorosilanes are distinctly less capable of forming stable adducts than are the fluorosilanes. Reactions with ammonia or amines (primary and secondary) result in cleavage of the silicon–chlorine bond with no stable adduct being formed. Using the system silicon tetrachloride–trimethylamine, it was barely possible to demonstrate the presence of a small amount of 1:1 adduct (36). In the light of this work, which was based on deviation of the mixed vapor pressure of the system from ideality at low temperature, other reports (46, 152, 188) of highly hindered, stable, chlorosilane–amine complexes must be regarded with caution.

The chlorosilanes intermediate between silicon tetrachloride and silane form stable complexes with trimethylamine (36), although silane (36) and the alkylsilanes (54) do not form complexes. The decreasing order of the ability of the chlorosilanes to enter into complex formation is:

$$SiH_3Cl = SiH_2Cl_2 > SiHCl_3 > SiCl_4$$

These results have been interpreted in terms of "steric shielding" of the silicon by the chlorine atoms. However, the fact that silane does not form complexes and that the complexing power of dichloro- and monochlorosilanes are equivalent indicates that electronegativity is also an important factor (36).

Silicon tetrachloride forms a stable adduct with pyridine (85, 151, 212); however, it fails to form complexes with either tributylamine or *N,N*-dimethylaniline (151). The basicity of pyridine is between that of the other two amines, but it is the least sterically hindered, emphasizing the importance of the steric character of the amine in complex formation (151).

The silicon tetrachloride–pyridine complex has been reported to be a 1:4 adduct (203); however, on the basis of investigations by other authors, the ratio of 1:2 must be assigned to this complex (85, 151, 211, 212). Silicon tetrabromide (158, 211), silicon tetrafluoride (211), and trichlorosilane (211) all form 1:2 adducts with pyridine; silicon tetraiodide apparently does yield a 1:4 complex (211). Silicon tetrachloride and quinoline also form a 1:2 complex (85).

Trimethylchlorosilane has been reported to yield complexes with pyridine, the picolines, quinoline, and isoquinoline, but the ratios of chlorosilane to base in these complexes were not given (204).

The reaction of silicon tetrachloride with formamide yields a 1:10 adduct and with *N,N*-dimethylformamide, a 1:5 adduct (73). The unusually high molar ratios may be due to dimerization of the amide (73) or to ionization of the chlorosilane in these solvents (74, 151). Alkyltrichlorosilanes also yield complexes with dimethylformamide (96).

Iodosilane yields a 1:2 complex with trimethylamine (11) and a 1:1 adduct with tetramethylhydrazine in the gaseous state (10). In the liquid phase, the adduct was 2:1 (two silyl groups to one tetramethylhydrazine) (10).

The silicon atom in these complexes utilizes either its sp^3d orbitals (1:1 adduct) or its sp^3d^2 orbitals (1:2 adduct). The *d*-orbital bonding by the silicon atom in these compounds, as well as in other silicon compounds, has been reviewed elsewhere (197) and will not be discussed here. Alternate theories of bonding involving either ionization or halogen bridging have also been suggested (61).

All halosilane–amine complexes are unstable toward water and similar reagents; however, in general, the chemistry of these complexes has not been investigated. Reports of water-soluble complexes (66, 188) require further authentification. The basic chemical property of the complexes has been "pyrolysis" (warming from −70°C. to room temperature), which results either in dissociation to the original reactants or in rearrangement of the halide groups (60, 61).

VII. Other Compounds Containing a Silicon–Nitrogen Bond

Silicon tetrachloride reacts with sodium azide to yield silicon tetraazide (216), an explosive.

$$SiCl_4 + 4NaN_3 \rightarrow Si(N_3)_4 + 4NaCl$$

Silane and HN_3 give no reaction (216).

Attempts to obtain nitrosilicon compounds (silicon bonded to the nitrogen of the nitro group) have failed. Reactions of silicon tetrachloride with silver nitrite, nitrogen tetroxide, and amyl nitrite gave products which were not identified (80). The reaction of ethyltrichlorosilane with nitrogen dioxide gives nitroethyltrichlorosilanes (144). Trimethylchlorosilane and silver nitrate yield the *O*-silyl product (170).

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TABLE 12

Physical constants of silicon–nitrogen compounds

Compound	Melting Point	Boiling Point	d	n_D	References
	°C.	°C.			
Silylamines:					
$H_3SiN(CH_3)_2$	3.3–3.4				(198)
$H_3SiN(CH_3)BF_3$					(199)
$H_3SiN(CH_3)B_2H_5$	−39				(37)
$H_3SiN(CH_3)(B_2H_5)N(CH_3)_2$					(37)
$H_2Si(CH_3)N(CH_3)_2$	−150 to −160	45			(55)
$(CH_3)_3SiNHCH_3$		71	0.7395 (20°)	1.3905 (20°)	(169)
$(CH_3)_3SiNHC_2H_5$		90.1–90.8		1.3912 (20°)	(169)
$(CH_3)_3SiNHCH_2CH{=}CH_2$		110	0.7675 (25°)	1.4130 (25°)	(167, 193)
$(CH_3)_3SiHC_4H_9$		134–135	0.765 (20°)	1.4094 (20°)	(112)
$(CH_3)_3SiNH(tert\text{-}C_4H_9)$		118–127		1.4060 (25°)	(51)
$(CH_3)_3SiNH(C_6H_{11})$		161.4–162.4	0.772 (20°)	1.4154 (20°)	(112)
$(CH_3)_3SiNH(C_7H_{13})$		92–93/26 mm.			(140)
$(CH_3)_3SiNHCH_2CH_2OCH{=}CH_2$		49–53/12 mm.			(50)
$(CH_3)_3SiNHC(CH_3)_2CH_2OCH{=}CH_2$		77/24 mm.			(50)
$(CH_3)_3SiNHC_{11}H_{22}SiH_2(C_6H_5)$		95/0.01 mm.	0.902 (25°)	1.4952 (25°)	(192)
$(CH_3)_3SiN(CH_3)_2$		85–86			(55, 79, 140)
$(CH_3)_3SiN(C_2H_5)_2$		126.8–127.1		1.4109 (20°)	(51, 112, 169)
$(CH_3)_3SiCH{=}C{=}NSi(CH_3)_3$		117/30 mm.	0.822 (20°)	1.4573 (20°)	(153)
$(CH_3)_3SiN(CH_3)CH_2CH_2OCH{=}CH_2$		56–58/12 mm.			(50)
$(CH_3)_3SiNHC_6H_5$		96–98/24 mm.	0.940 (20°)		(2, 140)
$(CH_3)_3SiNHCH_2C_6H_5$		95–96/15 mm.		1.4918 (25°)	(83, 140)
$(CH_3)_3SiNHCH_2CH_2C_6H_5$		107/20 mm.			(140)
$(CH_3)_3SiNH[C_6H_4COOSi(CH_3)_3\text{-}p]$		125/0.6 mm.		1.5416 (20°)	(164)
$(CH_3)_3SiNHSO_2C_6H_5$	64–65				(13)
$(CH_3)_3SiNHSO_2OSi(CH_3)_3$	50–51	110–112/2.8 mm.			(13, 142)
$(CH_3)_3SiNHSO_2NHSi(CH_3)_3$	104–105				(13)
$(CH_3)_3SiN(CH_3)SO_2OSi(CH_3)_3$		72/0.05 mm.			(13)
$(CH_3)_3SiNHP(O)Cl_2$	94–95				(14)
$[(CH_3)_3SiNH]_2P(O)OC_6H_5$	119–120				(14)
$(CH_3)_3SiNCH_2COOC_2H_5$		68–71/13 mm.			(20, 21)
$(CH_3)_3SiNHCH_2COOSi(CH_3)_3$		97/22 mm.	0.8975 (20°)	1.4229 (20°)	(23, 164)
$(CH_3)_3SiNHCH_2CH_2COOC_2H_5$		96–100/14 mm.			(20, 21)
$(CH_3)_3SiNHCH(CH_3)COOSi(CH_3)_3$		73/10 mm.	0.8831 (20°)	1.4177 (20°)	(23, 164)
$(CH_3)_3SiNHCH(CH_3)CH_2COOC_2H_5$		90–95/20 mm.			(20, 21)
$(CH_3)_3SiNH(CH_2)_3COOSi(CH_3)_3$		115/1.1 mm.	0.9539 (20°)	1.4390 (20°)	(164)
$(CH_3)_3SiNHCH(iso\text{-}C_3H_7)COOSi(CH_3)_3$		93/10 mm.		1.4226 (20°)	(23)
$(CH_3)_3SiNHCH(iso\text{-}C_4H_9)COOC_2H_5$		107–112/12 mm.			(21)
$(CH_3)_3SiNHCH(iso\text{-}C_4H_9)COOSi(CH_3)_3$		105/12 mm.		1.4236 (20°)	(23)
$(CH_3)_3SiNHCH(sec\text{-}C_4H_9)COOSi(CH_3)_3$		64/0.7 mm.	0.8804 (20°)	1.4267 (20°)	(164)
$(CH_3)_3SiNH(CH_2)_5COOSi(CH_3)_3$		114/2.5 mm.	0.8925 (20°)	1.4331 (20°)	(164)
$(CH_3)_3SiNH[C_6H_4COOSi(CH_3)_3\text{-}o]$	34	104/0.7 mm.	1.0566 (20°)	1.5348 (20°)	(164)
$(CH_3)_3SiNHCH(CH_2C_6H_5)COOSi(CH_3)_3$		110/1.1 mm.	0.9930 (20°)	1.4853 (20°)	(164)
$(C_2H_5)_3SiNH_2$		137	0.7982 (20°)	1.4275 (20°)	(8, 12, 53, 169)
$(ClCH_2CH_2)(C_2H_5)_2SiNH_2$		65–65.5/7 mm.	0.9769 (20°)	1.4624 (20°)	(184)
$(CH_3CHCl)(C_2H_5)_2SiNH_2$		93/38 mm.	0.9604 (20°)	1.4570 (20°)	(12)
$(C_2H_5)_3SiNHCH_3$		151–153	0.8011 (20°)	1.4295 (20°)	(8)
$(C_2H_5)_3SiNHC_2H_5$		166–167	0.7995 (20°)	1.4300 (20°)	(8, 53, 105, 127)
$(C_2H_5)_3SiNHC_3H_7$		189.4	0.8038 (20°)	1.4332 (20°)	(53)
$(C_2H_5)_3SiNH(iso\text{-}C_3H_7)$		179.6	0.7962 (20°)	1.4282 (20°)	(53)
$(C_2H_5)_3SiNHC_4H_9$		85–86/12 mm.			(122)
$(C_2H_5)_3SiNH(tert\text{-}C_4H_9)$		193	0.8082 (20°)	1.4360 (20°)	(53)
$(C_2H_5)_3SiNHC(CH_3)_2C_2H_5$		212–214	0.8194 (20°)	1.4400 (20°)	(53)
$(C_2H_5)_3SiNHC_6H_{11}$		117/15 mm.			(122, 126)
$(C_2H_5)_3SiNH\underline{CH(CH_2)_4CH_2}$		112–113/10 mm.			(122)
$(C_2H_5)_3SiNHC_7H_{15}$		125/13 mm.			(122, 126)
$(C_2H_5)_3SiN(CH_3)_2$		166–167	0.8044 (20°)	1.4325 (20°)	(8)
$(C_2H_5)_3SiN(C_2H_5)_2$		199.5–201	0.8167 (20°)	1.4400 (20°)	(8, 53)
$(C_2H_5)_3SiN(C_2H_5)(CH_2CH_2CN)$		262	0.8914 (20°)	1.4575 (20°)	(139)
$(C_2H_5)_3SiN(C_4H_9)_2$		253–254	0.8280 (20°)	1.4475 (20°)	(53)
$(C_2H_5)_3SiNHC_6H_5$		134–135/12 mm.	0.934 (20°)		(2, 53, 122, 127)
$(C_2H_5)_3SiNH(C_6H_4CH_3\text{-}o)$		137/9 mm.			(122)
$(C_2H_5)_3SiNH(C_6H_4CH_3\text{-}p)$		143/12 mm.			(122, 127)
$(C_2H_5)_3SiNHCH_2C_6H_5$		133/9 mm.			(122, 126, 127)
$(C_2H_5)_3SiNHCH(CH_3)C_6H_5$		142/14 mm.			(126, 127)
$(C_2H_5)_3SiNHCH(CH_3)CH_2C_6H_5$		146/13 mm.			(126)
2-$(C_2H_5)_3SiNH$(thiazole)					(122)
$(C_2H_5)_3SiNHSO_2OSi(C_2H_5)_3$		141–143/1.5 mm.			(142)
$(C_2H_5)_3SiNHCH[CH_2CH(CH_3)_2]COOSi(C_2H_5)_3$		162/7 mm.			(23)
$(C_3H_7)_3SiNH_2$		70–72/9 mm.			(124)
$(C_3H_7)_3SiNHCH_3$		195–196			(124)
$(C_3H_7)_3SiNHC_2H_5$		75–76/3 mm.			(124)
$(C_3H_7)_3SiNHC_3H_7$		95/6 mm.			(124)
$(C_3H_7)_3SiNH(iso\text{-}C_3H_7)$		78–80/9 mm.			(124)
$(C_3H_7)_3SiN(CH_3)_2$		58–60/3 mm.			(124)

TABLE 12 (*Continued*)

Compound	Melting Point	Boiling Point	*d*	n_D	References
	°C.	*°C.*			
Silylamines:					
$(C_3H_7)_3SiN(C_2H_5)_2$		95–96/7 mm.			(124)
$(C_3H_7)_3SiNHC_6H_5$		142–143/5 mm.			(124)
$(C_3H_7)_3SiNHCH_2C_6H_5$		147–148/6 mm.			(124)
$(C_3H_7)_3SiNHCH_2CH_2C_6H_5$		154–155/3 mm.			(124)
$(C_4H_9)_3SiNH_2$		118–120/14 mm.			(120)
$(C_4H_9)_3SiNHCH_3$		117–118/9 mm.			(120)
$(C_4H_9)_3SiNHC_2H_5$		125/9 mm.			(120)
$(C_4H_9)_3SiNHC_3H_7$		131–133/8 mm.			(120)
$(C_4H_9)_3SiNH(\text{iso-}C_3H_7)$		126–127/9 mm.			(120)
$(C_4H_9)_3SiNHC_4H_9$		150–152/16 mm.			(120)
$(C_4H_9)_3SiNHC_6H_5$		190–192/19 mm.			(120)
$(C_4H_9)_3SiNHCH_2C_6H_5$		148/1 mm.			(120)
$(C_2H_5)_2[(C_2H_5)_3SiCH_2]SiNH_2$		105/6 mm.	0.8578 (20°)	1.4633 (20°)	(141)
$(C_3H_7)_2[(C_3H_7)_3SiCH_2]SiNH_2$		133/3 mm.	0.8480 (20°)	1.4610 (20°)	(141)
$(C_4H_9)_2[(C_4H_9)_3SiCH_2]SiNH_2$		174/3 mm.	0.8435 (20°)	1.4638 (20°)	(141)
$(C_6H_5)(C_2H_5)(C_3H_7)SiNH(C_6H_4CH_3\text{-}p)$					(102)
$(C_6H_5CH_2)(C_2H_5)(C_3H_7)SiNH(C_6H_4CH_3\text{-}p)$		260–265/70 mm.			(103)
$(C_6H_5)_3SiNH_2$	55–56				(106)
$(C_6H_5)_3SiNHC_2H_5$	47–48	163–165/0.5 mm.			(16)
$(C_6H_5)_3SiN(CH_3)_2$	80–81				(71)
$(C_6H_5)_3SiN(C_2H_5)_2$	84–85				(71)
$(C_6H_5)_3SiN(C_4H_9)_2$	62				(71)
$(C_6H_5)_3SiN(C_6H_5)_2$	224				(46)
$(o\text{-}CH_3C_6H_4)_3SiN(C_4H_9)_2$	123.5–125	190/2 mm.			(72)
$[p\text{-}(CH_3)_2NC_6H_4]_3SiNH_2$	170				(205)
$[p\text{-}(CH_3)_2NC_6H_4]_3SiN(C_4H_9)_2$	62–64				(71)
$(1\text{-}C_{10}H_7)_3SiNH_2$	204–206				(44, 45)
$(1\text{-}C_{10}H_7)_3SiNHC_6H_5$	198–200				(44)
$(CH_3O)_2(\text{tert-}C_4H_9O)SiNH_2$		80–90/50 mm.			(147)
$(C_2H_5O)_3SiN(CH_3)_2$		166–167	0.9125 (15°)		(162)
$(\text{iso-}C_3H_7O)_3SiNH_2$		181			(175)
$(\text{iso-}C_3H_7O)_2(\text{tert-}C_4H_9O)SiNH_2$		57–60/3 mm.	0.884 (20°)	1.4015 (20°)	(138)
$(CH_3O)(\text{tert-}C_4H_9O)_2SiNH_2$		72–73/15 mm.	0.924 (20°)	1.4052 (20°)	(138)
$(\text{iso-}C_3H_7O)(\text{tert-}C_4H_9O)_2SiNH_2$		83–84/17 mm.	0.899 (20°)	1.4053 (20°)	(138)
$(C_4H_9O)_3SiNH_2$		129–131/13 mm.			(116, 117)
$(C_4H_9O)_3SiNHCH_3$		136–137/13 mm.			(117)
$(C_4H_9O)_3SiNHC_2H_5$		139–140/15 mm.			(116, 117)
$(C_4H_9O)_3SiNHC_3H_7$		149/15 mm.			(117)
$(C_4H_9O)_3SiNHC_4H_9$		161–163/15 mm.			(117)
$(C_4H_9O)_3SiN(C_2H_5)_2$		145–147/13 mm.			(99)
$(C_4H_9O)_3SiNCH_2CH_2$		100/1 mm.			(91)
$(C_4H_9O)_3SiNHC_6H_5$		198–201/25 mm.	0.9598 (20°)	1.4684 (20°)	(99, 117)
$(C_4H_9O)_3SiNHCH_2C_6H_5$		202/15 mm.			(117)
$(\text{sec-}C_4H_9O)_3SiNH_2$		194–199°F./3 mm.			(77)
$(C_4H_9O)(\text{tert-}C_4H_9O)_2SiNH_2$		113–114/15 mm.	0.901 (20°)	1.4149 (20°)	(138)
$(\text{tert-}C_4H_9O)_3SiNH_2$		82–85/10 mm.	0.882 (20°)	1.4060 (20°)	(138, 147)
$(\text{tert-}C_4H_9O)_2(C_6H_{11}O)SiNH_2$		137–138/22 mm.	0.8967 (20°)	1.4168 (20°)	(129)
$[(C_2H_5)_3SiO](\text{tert-}C_4H_9O)_2SiNH_2$		110–111/7 mm.	0.9063	1.4211 (20°)	(182)
$[(\text{tert-}C_4H_9O)_2SiNH_2]_2O$		134–136/13 mm.		1.4165 (20°)	(147)
$(C_6H_5O)_3SiNH_2$	47.5				(175, 214)
$(C_6H_5O)_3SiN(CH_2)_5CH_2$	54				(175)
$(C_2H_5)_2SiClN(C_2H_5)_2$					(100)
$C_3H_7SiCl_2N(C_2H_5)_2$		86–88/17 mm.			(200)
$C_3H_7SiCl_2N(\text{iso-}C_3H_7)_2$		105/15 mm.	1.0192 (20°)	1.4557 (20°)	(200)
$C_3H_7SiBr_2N(\text{iso-}C_3H_7)_2$		114–115/10 mm.			(202)
$C_3H_7SiCl_2NH(\text{tert-}C_4H_9)$		73–74/11 mm.			(200)
$C_3H_7SiCl_2N(C_6H_{11})_2$		180–181/10 mm.		1.499 (20°)	(200)
$C_3H_7SiCl_2NCH_3(C_6H_5)$		125/11 mm.			(200)
$Cl_3SiNH(\text{tert-}C_4H_9)$	−51 to −48	48–51/12 mm.			(30, 32)
$Cl_3SiN(C_2H_5)_2$		55–60/17 mm.			(27, 131)
$Cl_3SiN(\text{iso-}C_3H_7)_2$		73–75/13 mm.			(31)
$Cl_3SiN(\text{iso-}C_4H_9)_2$		120–124/30 mm.			(131)
$Cl_3SiN(CH_2)_4CH_2$		101–106/17 mm.			(27)
$Br_3SiNCH_3(C_6H_5)$		140–145/12 mm.			(26)
$Cl_3SiNC_2H_5(C_6H_5)$		100–105/9 mm.			(31)
$Br_3SiNC_2H_5(C_6H_5)$		150–154/13 mm.			(26)
$[(C_6H_5)_3Ge]_3SiNH_2$	206–206.5				(137)
$(CH_3)_2(HS)SiNHCH_3$					(125)
Silanediamines:					
$(CH_3)_2Si(NHCH_3)_2$		66/165 mm.			(128)
$(CH_3)_2Si(NHC_2H_5)_2$		139			(128)
$(CH_3)_2Si(NHC_7H_{15})_2$		169–170/12 mm.	0.8297 (20°)	1.4425 (20°)	(128)
$(CH_3)_2Si[NHSi(CH_3)_3]_2$		192–195	0.8366 (20°)	1.4281 (20°)	(33)

TABLE 12 (*Continued*)

Compound	Melting Point	Boiling Point	d	n_D	References
	°C.	°C.			
Silanediamines:					
$(CH_3)_2Si[N(CH_3)_2]_2$	−98	128.4	0.809 (22°)		(3)
$(CH_3)_2Si[\underline{NCH_2CH_2}]_2$		99–100			(91)
$(CH_3)_2Si(NHC_6H_5)_2$	45	185–186/9 mm.	1.07 (30°)		(2)
$(CH_3)_2Si(NHCH_2C_6H_5)_2$		174–178/5 mm.	1.0090 (20°)	1.5409 (20°)	(128)
$(C_2H_5)_2Si[N(C_2H_5)_2]_2$		140–142/50 mm.	0.853 (20°)	1.4485 (20°)	(100)
$(C_2H_5)_2Si(NHC_6H_5)_2$	58	172–173/1 mm.			(2)
(*tert*-C_4H_9)$(CH_3)Si(NH_2)_2$	83	135			(186)
(*tert*-C_4H_9)$_2Si(NH_2)_2$		100/50 mm.		1.4534 (20°)	(186)
(*tert*-C_4H_9)$(C_{18}H_{37})Si(NH_2)_2$		199/7 mm.		1.4604 (20°)	(186)
(*tert*-C_4H_9)$(C_6H_5)Si(NH_2)_2$		149/37 mm.		1.5198 (20°)	(186)
$(C_6H_5)_2Si(NHCH_3)_2$		155–156/3 mm.			(121)
$(C_6H_5)_2Si(NHC_2H_5)_2$		120–122/1 mm.			(16)
$(C_6H_5)_2Si(NHC_3H_7)_2$		178–182/2 mm.			(121)
$(C_6H_5)_2Si(NHC_6H_{11})_2$		215/2 mm.			(121)
$(C_6H_5)_2Si(NHC_6H_5)_2$	153	413 (d.)			(2)
$(C_6H_5)_2Si(NHCH_2C_6H_5)_2$					(121)
$(C_6H_5CH_2)_2Si[\underline{NCH_2CH_2}]_2$		168–170			(91)
$(C_6H_5CH_2)_2Si[\underline{NCH_2CH}CH_3]_2$		173/1 mm.			(91)
$(1\text{-}C_{10}H_7)_2Si(NH_2)_2$	154–156				(44)
$(1\text{-}C_{10}H_7)_2Si(NHC_6H_5)_2$	184–186				(44)
$(CH_3O)_2Si[\underline{NCH_2CH_2}]_2$		49–50/11 mm.			(91)
(CH_3O)(*tert*-C_4H_9O)$Si(NH_2)_2$		62–65/12 mm.		1.4130 (20°)	(138)
(C_2H_5O)(*tert*-C_4H_9O)$Si(NH_2)_2$		63–66/9 mm.	0.961 (20°)	1.4185 (20°)	(138)
(iso-C_3H_7O)(*tert*-C_4H_9O)$Si(NH_2)_2$		64–66/8 mm.	0.934 (20°)	1.4170 (20°)	(138)
$(C_4H_9O)_2Si(NHCH_3)_2$		122–123/16 mm.			(118)
$(C_4H_9O)_2Si(NHC_2H_5)_2$		129–132/15 mm.			(116, 118)
$(C_4H_9O)_2Si[\underline{NCH_2CH_2}]_2$		93–94/2 mm.			(91)
$(C_4H_9O)_2(NHC_3H_7)_2$		150–151/15 mm.			(118)
$(C_4H_9O)_2Si(NHC_4H_9)_2$		170/15 mm.			(118)
$(C_4H_9O)_2Si(NHC_6H_5)_2$		183–184/30 mm.	0.9550 (20°)	1.4046 (25°)	(99, 118)
$(C_4H_9O)_2Si(NHCH_2C_6H_5)_2$		196/1 mm.			(118)
(C_4H_9O)(*tert*-C_4H_9O)$Si(NH_2)_2$		66–68/3 mm.	0.939 (20°)	1.4260 (20°)	(138)
(*sec*-C_4H_9O)(*tert*-C_4H_9O)$Si(NH_2)_2$		92–95/17 mm.	0.928 (20°)	1.4210 (20°)	(138)
(*tert*-C_4H_9O)$_2Si(NH_2)_2$		86/22 mm.	0.9294 (20°)	1.4188 (20°)	(68, 129, 138, 147)
$[ClCH_2C(CH_3)_2O]$(*tert*-C_4H_9O)$Si(NH_2)_2$		80–85/2 mm.			(147)
(*tert*-C_4H_9O)$_2Si(NHC_2H_5)_2$		108/22 mm.	0.8815 (20°)	1.4168 (20°)	(129)
(*tert*-C_4H_9O)$_2Si(NHC_7H_{15})_2$		212–214	0.8697 (20°)	1.4348 (20°)	(129)
(*tert*-C_4H_9O)$_2Si(NHC_6H_5)_2$	72				(129)
(*tert*-C_4H_9O)$_2Si(NHCH_2C_6H_5)_2$		217–219/11 mm.	1.0003 (20°)	1.4987 (20°)	(129)
(*tert*-$C_5H_{11}O$)$_2Si(NH_2)_2$		105–110/15 mm.	0.931 (20°)	1.4300 (20°)	(138, 147)
$HSiCl[NH($*tert*-$C_4H_9)]_2$		74–75/12 mm.	0.9201 (20°)	1.4379 (20°)	(202)
$HSiCl[N(C_2H_5)_2]_2$		77–78/12 mm.	0.9354 (20°)	1.4433 (20°)	(202)
$CH_3SiCl[NH($*tert*-$C_4H_9)]_2$		81–82/12 mm.	0.9259 (20°)	1.4419 (20°)	(202)
$CH_3SiCl[N(C_2H_5)_2]_2$		84–85/12 mm.	0.9343 (20°)	1.4453 (20°)	(202)
$C_2H_5SiCl[NH($*tert*-$C_4H_9)]_2$		95–96/12 mm.	0.9280 (20°)	1.4465 (20°)	(202)
$C_2H_5SiCl[N(C_2H_5)_2]_2$		100–101/12 mm.	0.9395 (20°)	1.4517 (20°)	(202)
$C_3H_7SiCl[NH($*tert*-$C_4H_9)]_2$		118–119/15 mm.	0.9153 (20°)	1.4468 (20°)	(200)
$C_3H_7SiCl[N(C_2H_5)_2]_2$		121/17 mm.	0.9323 (20°)	1.4530 (20°)	(200)
$C_3H_7SiCl[NCH_3(C_6H_5)]_2$		195–197/11 mm.		1.5675 (20°)	(200)
$C_3H_7SiBr[NCH_3(C_6H_5)]_2$		205/10 mm.	1.2126 (20°)	1.5770 (20°)	(202)
$Cl_2Si[NH($*tert*-$C_4H_9)]_2$	−9 to −6	98–101/14 mm.	1.0358 (20°)	1.4484 (20°)	(30, 32)
$Cl_2Si[N(CH_3)_2]_2$		59–61/20 mm.			(81)
$Cl_2Si[N(C_2H_5)_2]_2$		99–104/11 mm.	1.0324 (20°)	1.4514 (20°)	(27)
$Cl_2Si[N(\text{iso-}C_3H_7)_2]_2$	32–40	125–126/8 mm.			(31)
$Cl_2Si[\underline{NCH_2(CH_2)_3CH_2}]_2$		150–155/17 mm.			(27)
$Cl_2Si(NHC_6H_5)_2$					(85)
$Cl_2Si[NH(C_6H_4CH_3\text{-}o)]_2$					(85)
$Cl_2Si[NH(1\text{-}C_{10}H_7)]_2$					(85)
$Cl_2Si[NH(2\text{-}C_{10}H_7)]_2$					(85)
$Cl_2Si(NC_2H_3(C_6H_5)]_2$		185–187/9 mm.			(31)
$Br_2Si[NC_2H_3(C_6H_5)]_2$		221–224/15 mm.			(26)
Silanetriamines:					
$HSi(NHC_6H_5)_3$	114 (d.)				(165)
$HSi[\underline{NC_4}H_4]_3$		220/25 mm.			(157)
$CH_3Si[NH($*tert*-$C_4H_9)]_3$		96–97/12 mm.	0.8413 (20°)	1.4370 (20°)	(202)
$CH_3Si[N(CH_3)_2]_3$	−11	161	0.850 (22°)	1.4324 (22°)	(3)
$CH_3Si[N(C_2H_5)_2]_3$		115–116/12 mm.	0.8672 (20°)	1.4515 (20°)	(202)
$CH_3Si(NHC_6H_5)_3$		212/1 mm.	1.14 (30°)		(2)
$C_2H_5Si[NH($*tert*-$C_4H_9)]_3$		115–116/14 mm.	0.8459 (20°)	1.4414 (20°)	(202)

TABLE 12 (*Continued*)

Compound	Melting Point	Boiling Point	d	n_D	References
	°*C.*	°*C.*			
Silanetetramines:					
$C_2H_5Si[N(C_2H_5)_2]_3$		133–134/14 mm.	0.8773 (20°)	1.4595 (20°)	(202)
$C_2H_5Si(NHC_6H_5)_3$		232–234/1 mm.			(2)
$C_3H_7Si(NHCH_3)_3$		101/50 mm.	0.8884 (20°)	1.4427 (20°)	(200)
$C_3H_7SiNH_2[N(C_2H_5)_2]_2$		108–109/15 mm.	0.8684 (20°)	1.4489 (20°)	(200)
$C_3H_7Si(NHC_2H_5)_3$		90/12 mm.	0.8545 (20°)	1.4380 (20°)	(200)
$C_3H_7Si(NHC_3H_7)_3$		120/11 mm.	0.8545 (20°)	1.4436 (20°)	(200)
$C_3H_7Si[NH(\text{iso-}C_3H_7)]_3$		101–102/12 mm.	0.8332 (20°)	1.4339 (20°)	(200)
$C_3H_7Si[NH(\text{iso-}C_3H_7)][N(C_2H_5)_2]_2$		125–126/15 mm.	0.8595 (20°)	1.4494 (20°)	(200)
$C_3H_7Si[NH(\text{iso-}C_3H_7)]_2[N(C_2H_5)_2]$		111–112/13 mm.	0.8469 (20°)	1.4412 (20°)	(200)
$C_3H_7Si[NH(\text{iso-}C_3H_7)]_2[N(\text{iso-}C_3H_7)_2]$		131–132/15 mm.	0.8564 (20°)	1.4480 (20°)	(200)
$C_3H_7Si[NH(\text{iso-}C_3H_7)]_2[NH(\textit{tert}\text{-}C_4H_9)]$		105–107/11 mm.	0.8385 (20°)	1.4375 (20°)	(200)
$C_3H_7Si[NH(\text{iso-}C_3H_7)]_2[N(C_6H_{11})_2]$		188–189/8 mm.		1.494 (20°)	(200)
$C_3H_7Si[NH(\text{iso-}C_3H_7)]_2[NCH_3(C_6H_5)]$		153/10 mm.	0.9352 (20°)	1.5030 (20°)	(200)
$C_3H_7Si(NHC_4H_9)_3$		117–119/2 mm.	0.8527 (20°)	1.4474 (20°)	(200, 201)
$C_3H_7Si[NH(\text{iso-}C_4H_9)]_3$		140–141/12 mm.	0.8460 (20°)	1.4424 (20°)	(200)
$C_3H_7Si[NH(\textit{sec}\text{-}C_4H_9)]_3$		130–131/12 mm.	0.8473 (20°)	1.4436 (20°)	(200)
$C_3H_7SiNH_2[NH(\textit{tert}\text{-}C_4H_9)]_2$		104/15 mm.	0.8539 (20°)	1.4414 (20°)	(200)
$C_3H_7Si(NHC_2H_5)[NH(\textit{tert}\text{-}C_4H_9)]_2$		109–110/12 mm.	0.8471 (20°)	1.4415 (20°)	(200)
$C_3H_7Si[NH(\textit{tert}\text{-}C_4H_9)]_2[NH(\text{iso-}C_3H_7)]$		118–119/14 mm.	0.8430 (20°)	1.4404 (20°)	(200)
$C_3H_7Si[NH(\textit{tert}\text{-}C_4H_9)]_3$		119–120/11 mm.	0.8452 (20°)	1.4427 (20°)	(202)
$C_3H_7Si(NHC_5H_{11})_3$		164–165/3 mm.	0.8516 (20°)	1.4503 (20°)	(201)
$C_3H_7Si(NHC_6H_{13})_3$		182–183/2 mm.	0.8507 (20°)	1.4527 (20°)	(201)
$C_3H_7Si(NHC_6H_{11})_3$		187–189/2 mm.	0.9478 (20°)	1.4916 (20°)	(200, 201)
$C_3H_7Si[N(CH_3)_2]_3$		72–74/13 mm.	0.8695 (20°)	1.4423 (20°)	(200)
$C_3H_7Si[N(C_2H_5)_2]_3$		136–137/10 mm.	0.8752 (20°)	1.4599 (20°)	(202)
$C_3H_7Si(NHC_6H_5)_3$		235/3 mm.			(200, 201)
$C_3H_7Si[NCH_3(C_6H_5)]_2[NH(\text{iso-}C_3H_7)]$		204–205/10 mm.	1.0155 (20°)	1.5608 (20°)	(200)
$C_3H_7Si[NCH_3(C_6H_5)]_3$		227–229/2–3 mm.			(202)
$C_3H_7Si(NHCH_2C_6H_5)_3$		216–218/1 mm.	1.0503 (20°)	1.5665 (20°)	(201)
$C_3H_7Si[\underbrace{N(CH_2)_4CH_2}]_3$		172–175/2 mm.	0.9696 (20°)	1.5007 (20°)	(200)
$C_{18}H_{37}Si[N(C_2H_5)_2]_3$		211–216/0.16 mm.			(100)
$1\text{-}C_{10}H_7Si(NHC_6H_5)_3$	176–178				(44)
$C_4H_9OSi(NHCH_3)_3$		98–101/15 mm.			(119)
$C_4H_9OSi(NHC_2H_5)_3$		115–116/16 mm.			(116)
$C_4H_9OSi(NHC_3H_7)_3$		146–147/15 mm.			(119)
$C_4H_9OSi(NHC_4H_9)_3$		134–136/1.5 mm.			(119)
$C_4H_9OSi(NHC_6H_5)_3$		215–218/0.5 mm.			(119)
$C_4H_9OSi(NHCH_2C_6H_5)_3$	32	218–223/0.5 mm.			(119)
$\{[(C_2H_5)_2N]_3Si\}_2O$	−16	138–139/1 mm.	1.022 (23°)		(3)
$ClSi[N(CH_3)_2]_3$		62–63/12 mm.	0.9741 (20°)	1.4423 (20°)	(27)
$ClSi[N(C_2H_5)_2]_3$		131–136/13 mm.	0.9516 (20°)	1.4568 (20°)	(27)
$ClSi[NH(\textit{tert}\text{-}C_4H_9)]_3$	17–18	138–141/34 mm.	0.9309 (20°)	1.4460 (20°)	(30, 32)
$ClSi[\underbrace{N(CH_2)_4CH_2}]_3$		155–158/3 mm.			(27)
Silanetetramines:					
$Si[NH(\textit{tert}\text{-}C_4H_9)]_4$	45–46	127–131/12 mm.			(28)
$Si[N(CH_3)_2]_4$	−2	74–75/19 mm.	0.973 (22°)		(3)
	12–15	72–75/13 mm.	0.8881 (20°)	1.4436 (20°)	(27)
$Si[N(C_2H_5)_2]_4$	3–4	156–158/14 mm.	0.9026 (20°)	1.4670 (20°)	(29)
$Si[N(C_2H_5)_2][\underbrace{NCH_2CH_2}]_3$		100/10 mm.			(91)
$Si[\underbrace{N(CH_2)_4CH_2}]_4$	81–82	181–182/2 mm.			(27)
$Si(NHC_6H_5)_4$	136				(130, 155)
$Si[NH(C_6H_4CH_3\text{-}p)]_4$	131–132				(155)
$Si[NH(C_6H_4CH_3\text{-}o)]_4$					(155)
$Si[N(CH_2C_6H_5)_2]_4$					(130)
$Si[\underbrace{NC_4H_4}]_4$	173.4				(156, 157)
$Si[NH(1\text{-}C_{10}H_7)]_4$					(155)
$Si[NH(2\text{-}C_{10}H_7)]_4$					(155)
Disilazanes:					(155)
$(H_3Si)_2NCH_3$	−124.6 to −124.1				(198)
$(H_3Si)_2NBH_2$	−40 to −35				(37)
$(H_3Si)_2NB_2H_5$	−69.6 to −68.8				(37)
$(H_3Si)_2NBCl_2$	60–65 (d.)				(37)
$(H_3Si)_2NBF_2$					(199)
$(H_3SiCH_2)_2NCH_3$	−115	80			(55)
$[(CH_3)_3Si]_2NH$		125.7–126.2	0.7741 (20°)	1.4078 (20°)	(69, 79, 112, 181, 185)
$[(CH_3)_3Si]_2NCH_3$		148	0.794 (25°)	1.4190 (25°)	(143, 169)
		71			(79)
$[(CH_3)_3Si]_2NCH_2CH{=}CH_2$		179	0.820 (25°)	1.4363 (25°)	(193)
$[(CH_3)_3Si]_2N(CH_2)_3SiH_2C_6H_5$		184/25 mm.	0.896 (25°)	1.4900 (25°)	(193)
$[(CH_3)_3Si]_2NSO_2OSi(CH_3)_3$		78/0.05 mm.			(13)
$[C_2H_5(CH_3)_2Si]_2NH$		174–175	0.8014 (20°)	1.4295 (20°)	(33, 179)

TABLE 12 (*Continued*)

Compound	Melting Point	Boiling Point	d	n_D	References
	°C.	°C.			
Disilazanes:					
$[(C_2H_5)_2SiH]_2NH$		102–103/50 mm.	0.8035 (20°)	1.4340 (20°)	(178)
$[CH_3(C_2H_5)_2Si]_2NH$		111–112.5/40 mm.	0.8316 (20°)	1.4423 (20°)	(179)
$[(C_2H_5)_3Si]_2NH$		100/1 mm.			(8, 53, 105)
$[(CH_3)_3SiCH_2Si(CH_3)_2]_2NH$		93/2 mm.	0.8352 (20°)	1.4478 (20°)	(141)
$[(C_2H_5)_3SiCH_2Si(C_2H_5)_2]_2NH$		188/2 mm.	0.8860 (20°)	1.4809 (20°)	(141)
$[(C_3H_7)_3SiCH_2Si(C_3H_7)_2]_2NH$		214–216/2.5 mm.	0.8641 (20°)	1.4725 (20°)	(141)
$[(C_4H_9)_3SiCH_2Si(C_4H_9)_2]_2NH$		256–257/3.5 mm.	0.8622 (20°)	1.4731 (20°)	(141)
$[C_6H_5(CH_3)_2Si]_2NH$		128–129/2–3 mm.	0.9850 (20°)	1.5384 (20°)	(180)
$[(C_6H_5)_3Si]_2NH$	175				(154)
	235–236				(45)
$[(p\text{-}CH_3C_6H_4)_3Si]_2NH$	223–224				(45)
$\{[p\text{-}(CH_3)_2NC_6H_4]_3Si\}_2NH$					(205)
$[(CH_3O)_3Si]_2NH$		95–97/8 mm.			(162)
$[C_6H_5(CH_3O)_2Si]_2NH$		92–95/6 mm.	1.124 (15°)		(162)
$[(C_2H_5O)_3Si]_2NH$		115–116/10 mm.	1.003 (15°)		(162)
$[(iso\text{-}C_3H_7O)_3Si]_2NH$					(175)
$[(iso\text{-}C_3H_7O)_2SiNH_2]_2NH$					(175, 214)
$[(C_4H_9O)_3Si]_2NH$		210–211/14 mm.			(116, 117)
$[(tert\text{-}C_4H_9O)_2SiNH_2]_2NH$		162–163/22 mm.	0.9513 (20°)	1.4240 (20°)	(129)
$[(C_6H_5O)_3Si]_2NH$		261–265			(175, 214)
$[(CH_3)_3Si](Cl_3Si)NH$		70–72/24 mm.			(81)
$[(CH_3)_3Si](Cl_3Si)NCH_3$		75–77/27 mm.			(81)
$(Cl_3Si)_2NH$		34/3 mm.			(173)
Trisilylamines:					
$(H_3Si)_3N$	−105.7	52	0.895 (−106°)		(110, 160, 195, 198)
$(D_3Si)_3N$					(160)
$(H_3SiCH_2)_3N$	−107	108			(55)
$[(CH_3)_3Si]_3N$	70–71	76/12 mm.	0.8635 (20°)	1.4545 (20°)	(79, 210)
$(Cl_3Si)_3N$	44–48 (78)				(148)
Cyclosilazanes:					
$[(CH_3)_2SiNH]_3$	−10	188	0.9196 (20°)	1.4448 (20°)	(33, 34, 82, 109, 128)
$[(CH_3)_2SiNC_6H_5]_3$	249–250	190–193/11 mm.			(128)
$[(CH_3)C_2H_3SiNH]_3$		112–115/13 mm.		1.4564 (20°)	(92)
$[(C_2H_5)_2SiNH]_3$	−41	150/10 mm.	0.9287 (20°)	1.4670 (20°)	(33)
$[C_6H_5(CH_3)SiNH]_3$	115–116	218–220			(92)
$[(C_6H_5)_2SiNH]_3$	213.5				(121)
$[(iso\text{-}C_3H_7O)_2SiNH]_3$		147			(175, 214)
$[(C_4H_9O)_2SiNH]_3$		245–250/12 mm.			(116)
$[(tert\text{-}C_4H_9O)_2SiNH]_3$	189–190				(68, 129)
$[(C_6H_5O)_2SiNH]_3$					(175)
$[(CH_3)_2SiNH]_4$	97	225			(33, 34, 82, 128)
$[(C_2H_5)_2SiNH]_4$	16	190–192/10 mm.	0.9521 (20°)	1.4769 (20°)	(33)
$[(iso\text{-}C_3H_7O)_2SiNH]_4$		191			(175)
$[(C_6H_5O)_2SiNH]_4$	129				(175)
Silylamides:					
$(CH_3)_3SiNHCHO$		84–85/0.1 mm.			(95)
$(CH_3)_3SiNHCOCH_3$	52–54	185–186			(95)
$(CH_3)_3SiN(CH_3)COCH_3$		48–49/11 mm.		1.4379 (24°)	(95)
$(CH_3)_3SiNHCOC(CH_3){=}CH_2$	65–68				(95)
$(CH_3)_3Si\underbrace{NCO(CH_2)_3CH_2}$		77–81/6 mm.			(95)
$(CH_3)_3SiNHCOC_{17}H_{35}$					(95)
$(CH_3)_3SiNHCOC_6H_5$	118–120				(95)
$(CH_3)_3SiNHCONH_2$	160–171				(51)
$(CH_3)_3SiNCH_3CONHCH_3$	77–79				(51)
$(C_6H_5)_3SiNHCOCH_3$	159–163				(95)
$(i\text{-}C_3H_7O)_3Si\underbrace{NCO(CH_2)_4CO}$	65–67				(175)
Tetrakis(triethylsilyl)uric acid	43	200–205/0.04 mm.			(22)

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