

**650.** *Dimethylamino-derivatives of Monosilane. Preparation, Some Physical and Chemical Properties, and Pyrolysis.*

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Dimethylamine reacts with di-iodosilane and with trichlorosilane to give the compounds  $\text{SiH}_{4-n}(\text{NMe}_2)_n$ , where  $n = 2$  or  $3$ , respectively. Some physical properties of these compounds and of  $\text{Si}(\text{NMe}_2)_4$  are reported. Their reactions with air, water, bromine, hydrogen chloride, and lithium aluminium hydride have been studied; the Si-N bond is generally cleaved. These amino-silanes, in contrast to *NN*-dimethylaminosilane, are stable thermally *in vacuo*. The main products of their pyrolysis at temperature up to  $400^\circ$  have been identified, and a mechanism is suggested.

AMINO-DERIVATIVES of silane,  $\text{SiH}_{4-n}(\text{NH}_2)_n$ , appear to be unstable,<sup>1</sup> and have not been isolated. The corresponding dimethylamino-derivatives,  $\text{SiH}_{4-n}(\text{NMe}_2)_n$ , are known however when  $n = 1$  or  $4$ . *N*-Silyldimethylamine was prepared by Sujishi and Witz<sup>2</sup> by the gas-phase reaction of bromosilane and dimethylamine. Anderson<sup>3</sup> obtained the tetrakis-compound ( $n = 4$ ) from silicon tetrachloride and dimethylamine in light petroleum, but Breederveld and Waterman<sup>4</sup> found that it was necessary to heat  $\text{SiCl}_2(\text{NMe}_2)_3$  with a large excess of dimethylamine at  $100^\circ$  in benzene in order to complete the reaction. In the absence of solvent,  $\text{SiCl}_2(\text{NMe}_2)_2$  and dimethylamine do not react<sup>5</sup> at  $100^\circ$ . The compound  $\text{SiH}(\text{NMe}_2)_3$  was briefly mentioned by Burg<sup>6</sup> as an intermediate in the preparation of trifluorosilane, while the ethyl analogue,  $\text{SiH}(\text{NEt}_2)_3$ , was prepared<sup>7</sup> as a possible

<sup>1</sup> Stock and Somieski, *Ber.*, 1921, **54**, 740.

<sup>2</sup> Sujishi and Witz, *J. Amer. Chem. Soc.*, 1954, **76**, 4631.

<sup>3</sup> Anderson, *J. Amer. Chem. Soc.*, 1952, **74**, 1421.

<sup>4</sup> Breederveld and Waterman, *Research*, 1952, **5**, 537.

<sup>5</sup> Cass and Coates, *J.*, 1952, 2347.

<sup>6</sup> Burg, "Fluorine Chemistry," Academic Press, New York, 1950, Vol. I, p. 109.

<sup>7</sup> Pike and Schank, *J. Org. Chem.*, 1962, **27**, 2190.

catalyst for the reaction of trichlorosilane with acrylonitrile. In neither case were any chemical properties given. Cass and Coates<sup>5</sup> attempted to prepare  $\text{SiH}_2(\text{NMe}_2)_2$  and  $\text{SiH}(\text{NMe}_2)_3$  by reduction of the corresponding Si-Cl compounds with lithium aluminium hydride alone or in ether solution. Both Si-N and Si-Cl bonds were cleaved.

### EXPERIMENTAL

*Apparatus and Materials.*—Volatile compounds were handled in a vacuum system<sup>8</sup> in the absence of mercury; solids and liquids of low volatility were manipulated in a dry-box filled with oxygen-free nitrogen. Di-iodosilane was prepared from silane and hydrogen iodide,<sup>9</sup> purified by repeated fractional condensation at  $-46^\circ$  (v. p., 4.0 mm./0°; lit.,<sup>9</sup> 4.2 mm./0°), and stored at  $-196^\circ$ . Trichlorosilane was fractionated *in vacuo* until tensiometrically homogeneous (v. p., 69 mm./ $-23^\circ$ ; lit.,<sup>10</sup> 68 mm./ $-23^\circ$ ). Dimethylamine was dried ( $\text{CaH}_2$ ) and fractionated (v. p., 171 mm./ $-23^\circ$ ; lit.,<sup>11</sup> 172 mm./ $-23^\circ$ ).

*Bisdimethylaminosilane.*—*Preparation.* Di-iodosilane (0.5817 g., 2.05 mmole) reacted with dimethylamine (11.9 mmole) in the gas phase. The apparatus has been described.<sup>12</sup> Immediately the vapours mixed, a white solid was produced as a smoke. After 1 hr. at room temperature, the volatile products were: hydrogen (<1 ml. at N.T.P.), excess of dimethylamine (4.3 mmole; reacting ratio  $\text{SiH}_2\text{I}_2:\text{NHMe}_2$ , 1:3.7), crude bisdimethylaminosilane (held at  $-96^\circ$ ), and a substance of low volatility, held at  $-23^\circ$ . Repeated fractional condensation at  $-84^\circ$  gave the compound [Found: H (as Si-H), 1.5; Si, 20.8;  $\text{NMe}_2$ , 75.1%; *M*, 116, 117.  $\text{C}_4\text{H}_{14}\text{N}_2\text{Si}$  requires H (as Si-H), 1.7; Si, 23.7;  $\text{NMe}_2$ , 74.6%; *M*, 118.]

*Physical properties.* The m. p. was  $-105$  to  $-103^\circ$  (six samples, in a Stock<sup>13</sup> apparatus); *d* 0.788 g./ml. at  $20^\circ$ . Saturated vapour pressures were measured with a sensitive spoon gauge below room temperature and with an all-glass tensimeter up to about  $70^\circ$  with the annexed results. Between  $15$  and  $71^\circ$ , these pressures are expressed by  $\log_{10} P(\text{mm.}) = 7.499 -$

Temp. ....	11.4°	15.2°	20.1°	25.1°	31.0°	35.4°	39.4°	44.6°
V. p. (mm.).....	38.9	42.9	52.9	67.2	87.0	104	122	155
Temp. ....	44.6°	48.8°	50.0°	53.6°	55.6°	57.2°	66.7°	69.5°
V. p. (mm.).....	162	176	185	212	226	240	334	366
Temp. ....	71.1°	58.4°	46.0°	29.0°	25.6°	22.2°		
V. p. (mm.).....	386	272 *	185 *	100 *	90 *	79 *		

\* Decreasing temperature.

$1691/T$  with a maximum error of 1.6 mm. The extrapolated b. p. is therefore  $93^\circ$ , the heat of vaporization is 7710 cal./mole, and Trouton's constant is 21.1. Some decomposition had occurred, indicated by increased vapour pressures on cooling.

*Trisdimethylaminosilane.*—*Preparation.* Chlorine could not be completely eliminated from trichlorosilane by gas-phase reaction with dimethylamine. For example, trichlorosilane (0.1951 g., 1.44 mmole) reacted with 8.45 mmole of an approximately ten-fold excess of dimethylamine (combining ratio 1:5.87). After 1 hr. at room temperature, the volatile products were: excess of dimethylamine, crude trisdimethylaminosilane (held at  $-64^\circ$ ), and a liquid of low volatility held at  $-23^\circ$ . Hydrogen was absent. Alkaline hydrolysis of a small sample of the crude product gave  $\text{Cl}^-$ . The rest of the fraction was therefore sealed with further dimethylamine in a small tube for 24 hr. at room temperature. Repeated fractional condensation of the product at  $-64^\circ$  gave the compound [Found: H (as Si-H), 0.61;  $\text{NMe}_2$ , 81.4%; *M*, 160.  $\text{C}_6\text{H}_{18}\text{N}_3\text{Si}$  requires H (as Si-H), 0.62;  $\text{NMe}_2$ , 82.0%; *M*, 161].

*Physical properties.* The m. p. was  $-91$  to  $-89^\circ$ , *d* 0.850 g./ml. at  $20^\circ$ . Saturated vapour pressures were as annexed. Between  $36$  and  $114^\circ$ , these pressures are expressed by  $\log_{10} P(\text{mm.}) = 8.052 - 2147/T$  with a maximum error of 2.9 mm. The extrapolated b. p. is therefore  $142^\circ$ , the latent heat of vaporization is 9830 cal./mole, and Trouton's constant is 23.7. Values of vapour pressure on cooling show that negligible decomposition had occurred.

<sup>8</sup> Aylett, Emelús, and Maddock, *J. Inorg. Nuclear Chem.*, 1955, **1**, 187.

<sup>9</sup> Emelús, Maddock, and Reid, *J.*, 1941, 353.

<sup>10</sup> Jenkins and Chambers, *Ind. Eng. Chem.*, 1954, **46**, 2367.

<sup>11</sup> Stull, *Ind. Eng. Chem.*, 1947, **39**, 536.

<sup>12</sup> Aylett, *J. Inorg. Nuclear Chem.*, 1956, **2**, 325.

<sup>13</sup> Stock, *Ber.*, 1917, **50**, 156.

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Temp. ....	36.0°	38.2°	47.4°	55.0°	62.0°	69.0°	74.6°	82.0°
V. p. (mm.).....	13.0	14.1	23.2	32.9	46.3	60.8	77.8	102.2
Temp. ....	89.8°	94.0°	99.0°	104.0°	110.0	114.5°	117.5°	120.5°
V. p. (mm.).....	135.5	163.4	192.5	230	280	324	349	390
Temp. ....	124.0°	125.5°	90.0°	72.0°	63.6°	34.6°		
V. p. (mm.).....	422	448	146 *	76.0 *	52.0 *	12.2 *		

\* Decreasing temperature.

*Tetrakisdimethylaminosilane.*—*Preparation.* Silicon tetrachloride (4.12 g., 24.2 mmole) and dimethylamine (247 mmole) reacted exothermally in the gas phase; a white smoke formed at once. After 1 hr. the volatile products were: unused dimethylamine, a liquid held at  $-46^{\circ}$  [neutralization equivalent, 95. Calc. for  $\text{SiCl}_2(\text{NMe}_2)_2$ , 93.5], and traces of less volatile liquids.

In another experiment, silicon tetrachloride (4.40 g., 25.9 mmole) and dimethylamine (276 mmole) in isopentane solution (10 ml.) reacted for 30 min. at  $-45^{\circ}$  and then for 30 min. at room temperature. A liquid of low volatility resulted [neutralization equivalent, 59. Calc. for  $\text{Si}(\text{NMe}_2)_4$ , 51; for  $\text{SiCl}(\text{NMe}_2)_3$ , 65]. Further heating of this liquid with dimethylamine (140 mmole) in isopentane (10 ml.) for 1 hr. at  $120^{\circ}$  reduced the neutralization equivalent to 55. This product was finally treated with water (50 mg.) at room temperature for 1 hr. Fractionation yielded pure tetrakisdimethylaminosilane (Found: Cl, 0.0%. Neutralization equivalent, 51.6).

*Physical properties.* The m. p. was  $16-18^{\circ}$  (lit.,<sup>4</sup>  $12-15^{\circ}$ ),  $d$  0.910 g./ml. at  $20^{\circ}$  (lit.,<sup>4</sup> 0.885 g./ml.). Saturated vapour pressures are as annexed. These values determine the equation  $\log P$  (mm.) =  $7.330 - 2087/T$ ; the maximum observed deviation from this is 4 mm. The extrapolated b. p. is therefore  $196^{\circ}$ , the latent heat of vaporization is 9520 cal./mole and Trouton's constant is 20.3.

Temp. ....	91.0°	98.5°	107°	111°	116°	120°	126°	130.5°
V. p. (mm.).....	42	53	68	81	91	106	126	148
Temp. ....	142°	138°	124°	87.5°				
V. p. (mm.).....	201	174 *	119 *	40 *				

\* Decreasing temperature.

*Infrared Spectra.*—Measurements in the gas phase, made with a Hilger H800 double-beam instrument (NaCl and KBr prisms, 10 and 50 cm. path lengths), gave the following band centres (in  $\text{cm}^{-1}$ ): (a)  $\text{SiH}_2(\text{NMe}_2)_2$ : 2975vs, 2879vs, 2790vs, 2136vs, 1461s, 1304vs, 1195vs, 1162sh, 1081m, 1004vs, 953s, 918vs, 744m, 692m, 650s; (b)  $\text{SiH}(\text{NMe}_2)_3$ : 2974s, 2860vs, 2794vs, 2162w, 2108s, 1479sh, 1463s, 1380m, 1296vs, 1189vs, 1144sh, 1075m, 996vs, 865vs, 846vs, 811sh, 697m, 660w, 619m, 523m, 460w.

*Chemical Properties.*—*Reaction with air and water.* Bisdimethylaminosilane at room temperature was exposed to air. After several minutes, a white solid began to form on the sides of the tube, dimethylamine could be smelt strongly, and the liquid slowly became more viscous.

In another experiment, bisdimethylaminosilane (0.0234 g., 0.198 mmole) reacted *in vacuo* with a deficit of conductivity water at room temperature for 12 hr. The mixture effervesced, a white solid was formed, and hydrogen (0.156 mmole) and dimethylamine (0.314 mmole) were the volatile products.

Trisdimethylaminosilane (0.0451 g., 0.280 mmole) reacted with water (0.0776 g., 4.31 mmole) at room temperature for 30 min. with intermittent shaking. The products were: hydrogen (0.275 mmole), dimethylamine (0.587 mmole), excess of water, and a white solid, part of which was slightly volatile. The residue was treated with 20% sodium hydroxide solution, but no further evolution of amine occurred. In a series of experiments, not more than 77.5% of dimethylamine was recovered.

Tetrakisdimethylaminosilane (0.0725 g., 0.355 mmole) and water (1.310 mmole) reacted for 65 hr. at room temperature. Dimethylamine (0.170 mmole, 12% of possible) was then present. The aqueous residue was transferred to a tube containing potassium hydroxide; it effervesced vigorously after melting, and all the dimethylamine was liberated.

*Reaction with potassium hydroxide.* Trisdimethylaminosilane (0.0121 g., 0.075 mmole) reacted with anhydrous potassium hydroxide for 2 hr. at room temperature. 87% of silane-triamine was recovered; other volatile products were: hydrogen (0.003 mmole) and dimethylamine (0.016 mmole). Proportion of bonds cleaved: Si-H, 4; Si-N, 7%.

*Reaction with bromine.* Bisdimethylaminosilane (0.2750 g., 2.33 mmole) and bromine (0.1990 g., 1.25 mmole) reacted at room temperature *in vacuo* for 1 hr. Incondensable gases were absent; volatile products were: bisdimethylaminosilane (0.317 mmole) and a mixture of liquids (*A*) that was difficult to transfer and to separate. The white solid residue slowly became brown. The most volatile part of *A* (0.1300 g.) was hydrolysed with 20% potassium hydroxide solution [Found: Si, 13.6; H, 0.3; NMe<sub>2</sub>, 42.6; Br, 43.5. Calc. for SiH<sub>0.88</sub>Br<sub>1.12</sub>(NMe<sub>2</sub>)<sub>2</sub>: Si, 13.6; H, 0.4; NMe<sub>2</sub>, 42.7; Br, 43.3%].

*Reaction with hydrogen chloride.* Trisdimethylaminosilane (0.0306 g., 0.190 mmole) reacted with anhydrous hydrogen chloride (5.53 mmole) at room temperature for 12 hr. The products were: trichlorosilane (0.120 mmole, 63%; v. p., 67 mm./-22°), excess of hydrogen chloride (4.56 mmole; v. p., 118 mm./-112°; lit.,<sup>11</sup> 120 mm./-112°), and a white solid (41.7 mg.), soluble in alcohol-water.

*Reaction with lithium aluminium hydride.* Di-isopropyl ether (5 ml., dried with LiAlH<sub>4</sub>), lithium aluminium hydride (0.3 g.), and bisdimethylaminosilane (0.0532 g., 0.451 mmole) were warmed together from -196° to room temperature. After 30 min., the volatile products were: hydrogen (4.4 ml.), silane (0.451 mmole. Found: *M*, 31.4. Calc. for SiH<sub>4</sub>: *M*, 32.1), dimethylamine (0.598 mmole. Found: *M*, 44.8. Calc. for C<sub>2</sub>H<sub>7</sub>N: *M*, 45.0), and the ether.

*Pyrolysis of Bisdimethylaminosilane.*—Reactions were performed in sealed, thick-walled Pyrex tubes (~20 ml.). Volatile products were identified by vapour density and infrared measurements. Results are shown in Table 1.

TABLE 1.

SiH <sub>2</sub> (NMe <sub>2</sub> ) <sub>2</sub> (mmole)	Temp.	Time (hr.)	Yield *			SiH <sub>4</sub> /NHMe <sub>2</sub>
			H <sub>2</sub>	SiH <sub>4</sub>	NHMe <sub>2</sub>	
0.708	190°	6	0	0.01	0.03	0.3
0.697	300	5	0	0.04	0.03	1.3
0.265	380	8	0.15	0.17 (0.25) †	0.10	1.7 (2.5) †

\* In mmole/mmole of SiH<sub>2</sub>(NMe<sub>2</sub>)<sub>2</sub>. † Based on formation of H<sub>2</sub> from SiH<sub>4</sub> (see text).

Hydrogen was formed only at temperatures (above *ca.* 350°) where silane decomposes. Values (marked †) in Table 1 show the total yield of silane, assuming that all hydrogen derives from the decomposition SiH<sub>4</sub> → Si + 2H<sub>2</sub>. A liquid of low volatility and a solid residue were also formed; the latter was colourless and crystalline in the first two experiments, but brown and apparently amorphous in the last. Two fractions of the liquid were hydrolysed with 20% sodium hydroxide solution; a small quantity of white solid was formed which did not dissolve on heating. Hydrogen was estimated with a Toepler pump, and amine was distilled into an excess of standard acid and determined by back-titration. A more volatile fraction gave hydrogen (0.24%) and amine (17.9 mequiv./g.) while a less volatile portion evolved 0.13% and 16 mequiv./g., respectively.

*Pyrolysis of Trisdimethylaminosilane.*—Reactions carried out as before gave the results in Table 2.

TABLE 2.

SiH(NMe <sub>2</sub> ) <sub>3</sub> (mmole)	Temp.	Time (hr.)	Yield *				SiH <sub>4</sub> /NHMe <sub>2</sub>
			H <sub>2</sub>	SiH <sub>4</sub>	NHMe <sub>2</sub>	CH <sub>4</sub>	
1.12	260°	6.5	0	0.004	0.02	0	0.2
0.91	360	3	0.01	0.004 (0.009) †	0.04	0	0.1 (0.2) †
0.79	350	11	0.02	0.003 (0.013) †	0.07	0	0.04 (0.2) †
0.91	400	24	2.63	0.30 (1.61) †	0.44 ‡	0.47	—

\* In mmole/mmole of SiH(NMe<sub>2</sub>)<sub>3</sub>. † Based on formation of H<sub>2</sub> from SiH<sub>4</sub>. ‡ Mixture of ammonia and methylamines (see text).

No unchanged starting material was recovered from the last run, which alone produced methane (estimated by infrared intensity measurements, when pressure-broadened by nitrogen). A red-brown deposit was formed on the walls of the tube, while the "amine" fraction was

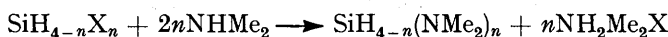
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mainly ammonia (Found:  $M$ , 20.3. Calc. for  $\text{NH}_3$ :  $M$ , 17.0. V. p., 64 mm./ $-73.5^\circ$ ; lit.,<sup>14</sup> 65 mm./ $-73.5^\circ$ ). No intermediate products were formed. In the first three runs, liquids of low volatility were isolated, separated into two fractions, and hydrolysed: (a) more volatile fraction: H, 0.28%; amine, 18.4 mequiv./g.; (b) less volatile fraction: H, 0.11%; amine, 18.1 mequiv./g. Alkaline hydrolysis up to  $100^\circ$  in a closed tube gave an insoluble oil that floated on the surface. All dissolved in acid.

## RESULTS AND DISCUSSION

Dimethylaminosilanes were prepared by the general reaction:



where  $\text{X} = \text{I}$  ( $n = 2$ ) or  $\text{Cl}$  ( $n = 3$  or  $4$ ). Substitution of halogen was much more difficult with increasing  $n$ : bisdimethylaminosilane was formed readily by a gas-phase reaction, but the tris-compound's production required prolonged reaction and a large excess of dimethylamine. Where  $n = 4$ , reactions in the gas phase or in the liquid phase without solvent gave mainly  $\text{SiCl}_2(\text{NMe}_2)_2$ . This compound slowly reacted with a large excess of dimethylamine in solution under forcing conditions to give a crude product; dimethylamine hydrochloride was insoluble in successful solvents. It was essential finally to add a little water to the crude tetrakisdimethylaminosilane. Remaining Si-Cl bonds were hydrolysed in preference to Si-N bonds, thereby forming less volatile compounds with Si-O-Si bonds. These could be separated easily from the tetrakis-compound by fractionation. The observed order of ease of substitution is probably due chiefly to overcrowding in reaction intermediates. Models suggest that 5-co-ordinate adducts such as  $\text{SiHCl}(\text{NMe}_2)_2, \text{NHMe}_2$  and, especially,  $\text{SiCl}(\text{NMe}_2)_3, \text{NHMe}_2$  are seriously hindered sterically. Substitution of H or Cl by  $\text{NMe}_2$  will also alter the electron-accepting power of silicon, as a result of changed  $\sigma$ -abstraction and  $\pi$ -donation. In the reaction of  $\text{SiCl}_3(\text{NMe}_2)$  or  $\text{SiCl}_2(\text{NMe}_2)_2$  with dimethylamine, where steric effects are not expected to be decisive, the latter reacts less readily.

Physical properties of silane and its dimethylamino-derivatives are collected in Table 3.

TABLE 3.

	$M$	M. p.	B. p.	$\Delta H_{\text{vap}}$ (cal./mole)	$\Delta S_{\text{vap}}$ (cal./ $^\circ\text{C}$ /mole)	$d_{20}$
$\text{SiH}_4$ <sup>15</sup> .....	32	$-185^\circ$	$-111^\circ$	2980	18.4	0.68 †
$\text{SiH}_3\text{NMe}_2$ <sup>2</sup> .....	75	+3	—	14,000 *	—	—
$\text{SiH}_2(\text{NMe}_2)_2$ <sup>a</sup> .....	118	$-104$	93	7710	21.1	0.788
$\text{SiH}(\text{NMe}_2)_3$ <sup>a</sup> .....	161	$-90$	142	9830	23.7	0.850
$\text{Si}(\text{NMe}_2)_4$ <sup>a</sup> .....	204	+17	196	9520	20.3	0.910

\* Heat of sublimation. † At m. p. <sup>a</sup> This work.

The anomalous position of *N*-silyldimethylamine is obvious; intermolecular association by  $\text{N} \longrightarrow \text{Si}$  dative  $\sigma$ -bonding has been suggested<sup>2,16</sup> as its cause. Substitution of one hydrogen (attached to silicon) by a dimethylamino-group lowers the melting point markedly. This fact, the normal value of Trouton's constant, and the relatively low boiling point (only  $10^\circ$  higher than that of the lighter bisdimethylaminomethane<sup>17</sup>) all suggest that bisdimethylaminosilane is not significantly associated. Similar considerations apply to the tris- and tetrakis-derivatives. The relatively high melting point of the last compound is characteristic of nearly spherical molecules.<sup>18</sup>

<sup>14</sup> Stock, Henning, and Kuss, *Ber.*, 1921, **54**, 1119.

<sup>15</sup> Gmelin, "Handbuch der anorganischen Chemie; Silicium Teil B," Verlag Chemie, Weinheim, 1959, p. 238—240.

<sup>16</sup> Ebsworth and Sheppard, *J. Inorg. Nuclear Chem.*, 1959, **9**, 95.

<sup>17</sup> Aylett and Peterson, unpublished observations.

<sup>18</sup> Cf.  $\text{Si}(\text{OMe})_4$ , m.  $+2^\circ$ .

TABLE 4.

Si-H Stretching frequencies (cm.<sup>-1</sup>) in the molecules SiH<sub>4-n</sub>X<sub>n</sub>, where X is NMe<sub>2</sub>, F, Cl, or Me.

	<i>n</i> = 1	<i>n</i> = 2	<i>n</i> = 3
X = NMe <sub>2</sub> .....	2150, 2094 <sup>a</sup>	2136 <sup>b</sup>	2108 <sup>b</sup>
• F .....	2206, 2196 <sup>c</sup>	—	2315 <sup>d</sup>
Cl .....	2201, 2195 <sup>c</sup>	2200 <sup>e</sup>	2274 <sup>e</sup>
Me .....	2160 <sup>f</sup>	2145 <sup>g</sup>	2123 <sup>h</sup>

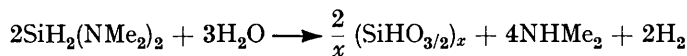
Cf. SiH<sub>4</sub>,<sup>26</sup> 2175 cm.<sup>-1</sup>.

<sup>a</sup> Ref. 19. <sup>i</sup>This work. <sup>c</sup> Ref. 20. <sup>d</sup> Ref. 21. <sup>e</sup> Ref. 22. Ref. 23. <sup>g</sup> Refs. 24 and 25. <sup>h</sup> Ref. 25.

The Si-H stretching frequencies of various substituted silanes are in Table 4. Increasing alkyl or aryl substitution usually produces progressively lower absorption frequencies,<sup>27</sup> while the reverse is true of halogen or alkoxy-substituents.<sup>28</sup> On the basis of known correlations between Si-H stretching frequency and electronegativity,<sup>28,29</sup> the dimethylamino-group should produce similar effects to chlorine. Experimentally, the frequency varies irregularly along the series and falls, in the tris-compound, to a value lower than that of most other SiHX<sub>3</sub> compounds. If (as has been suggested<sup>29a</sup>) highly electronegative ligands normally enhance the δ<sup>+</sup>Si-Hδ<sup>-</sup> dipole, *d*<sub>π</sub>-*p*<sub>π</sub> interaction in the Si-N bond may oppose this effect and lower the frequency.

The C-H stretching frequencies and CH<sub>3</sub> asymmetric and symmetric deformation frequencies are normal (2790—2975, 1461—1463, and 1296—1304 cm.<sup>-1</sup>, respectively). Below 1300 cm.<sup>-1</sup>, strong absorptions near 1195 and 1000 cm.<sup>-1</sup> are probably due to SiN<sub>2</sub> or SiN<sub>3</sub> skeletal stretching modes. In accordance with a recent analysis of SiH<sub>2</sub>XX' compounds,<sup>24</sup> the strong bands of bisdimethylaminosilane at 953 and 918 cm.<sup>-1</sup> are assigned to the SiH<sub>2</sub> bending and wagging modes, respectively. The tris-compound's band at 811 cm.<sup>-1</sup> is probably a Si-H bending vibration; trichlorosilane<sup>22</sup> and triorganosilanes<sup>30</sup> absorb in the region 805—820 cm.<sup>-1</sup>

The bis-, tris-, and tetrakis-dimethylaminosilanes are less reactive than the first member of the series, *N*-silyl-dimethylamine. Their decomposition when stored at room temperature for some months *in vacuo* is negligible, and they slowly evolve dimethylamine in air (*N*-silyl-dimethylamine explodes). They all react with air-free water, the rate decreasing with increasing substitution. Thus SiH<sub>2</sub>(NMe<sub>2</sub>)<sub>2</sub> with a deficit of water rapidly gave hydrogen and dimethylamine in the mole ratio 1 : 2.01 and a solid residue of approximate empirical composition SiH<sub>1.2</sub>(NMe<sub>2</sub>)<sub>0.4</sub>O<sub>1.2</sub>. Removal of all the dimethylamino-groups would therefore yield the compound (SiHO<sub>3/2</sub>)<sub>x</sub> by the reaction:



<sup>19</sup> McKean, personal communication.

<sup>20</sup> Newman, O'Loane, Polo, and Wilson, *J. Chem. Phys.*, 1956, **25**, 855; Hawkins, Polo, and Wilson, *ibid.*, 1953, **21**, 1122.

<sup>21</sup> Newman, Polo, and Wilson, *Spectrochim. Acta*, 1959, **15**, 793.

<sup>22</sup> Gibian and McKinney, *J. Amer. Chem. Soc.*, 1951, **73**, 1431.

<sup>23</sup> Randić, Ph.D. Thesis, Cambridge, 1957; Kaye and Tannenbaum, *J. Org. Chem.*, 1953, **18**, 1750; Kovalev, *Optika i Spektroskopiya*, 1960, **8**, 315.

<sup>24</sup> Ebsworth, Onyszchuk, and Sheppard, *J.*, 1958, 1453.

<sup>25</sup> Ball, Goggin, McKean, and Woodward, *Spectrochim. Acta*, 1960, **16**, 1358.

<sup>26</sup> Batuev, Petrov, Ponomarenko, and Matveeva, *Izvest. Akad. Nauk S.S.S.R., Otdel. khim. Nauk*, 1956, 1243.

<sup>27</sup> Kniseley, Fassel, and Conrad, *Spectrochim. Acta*, 1959, **15**, 651.

<sup>28</sup> Smith and Angelotti, *Spectrochim. Acta*, 1959, **15**, 412.

<sup>29</sup> (a) Kriegsmann, *Z. anorg. Chem.*, 1959, **299**, 138; (b) Webster, *J.*, 1960, 5132; Thompson, *Spectrochim. Acta*, 1960, **16**, 238.

<sup>30</sup> Kaplan, *J. Amer. Chem. Soc.*, 1954, **76**, 5880.

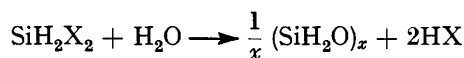


[1964]

*Dimethylamino-derivatives of Monosilane.*

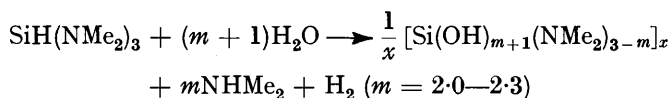
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When hydrolysis produces an acidic solution, as with halogenosilanes, disubstituted compounds react<sup>31</sup> in the following way:



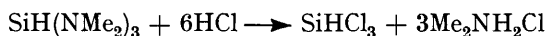
while  $(\text{SiHO}_{3/2})_x$  is produced by hydrolysis<sup>32</sup> of  $\text{SiHX}_3$  compounds. The composition of the oxyhydride thus depends on the pH produced by the leaving group in the solution.

Trisdimethylaminosilane reacted slowly with a large excess of water to give quantitative elimination of hydrogen. Recovery of dimethylamine corresponded to about three-quarters of that required for complete hydrolysis. This may be due in part to difficulty of separation, but is more probably because the oxygen-containing hydrolysis product becomes insoluble and unwettable before all the dimethylamino-groups have been removed. The reaction may therefore be written:



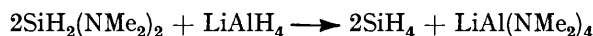
With aqueous alkali, dimethylamino-groups were completely removed and this reaction was used for analysis. Trisdimethylaminosilane reacted very slowly with solid potassium hydroxide in the absence of water; after 2 hours at room temperature, 4% of the Si-H bonds and 7% of the Si-bonds were cleaved. It has been noted that organosilicon hydrides do not react with alkali metal hydroxides alone or in inert media.<sup>33</sup>

Bromine and bisdimethylaminosilane gave a white solid and a mixture of volatile products. The latter contained excess of bisdimethylaminosilane, a less volatile liquid of overall composition  $\text{SiH}_{0.88}\text{Br}_{1.12}(\text{NMe}_2)_2$ , and a little liquid of very low volatility. Bromine therefore replaces hydrogen more readily than dimethylamino-groups; the reverse was true for water. The fate of hydrogen bromide necessarily evolved is uncertain; the white solid may contain dimethylammonium bromide formed by abstraction of dimethylamine from the silicon compound. All Si-N bonds in trisdimethylaminosilane were cleaved by excess of hydrogen chloride, and trichlorosilane was formed:



This reaction is essentially the reverse of that used for synthesis of trisdimethylaminosilane.

When a mixture of lithium aluminium hydride, bisdimethylaminosilane, and di-isopropyl ether was allowed to warm from  $-196^\circ$ , a vigorous reaction ensued below room temperature. The theoretical quantity of silane required by the equation:



was rapidly liberated, together with a little hydrogen. After 30 minutes, dimethylamine was present; this presumably arose by the reaction of lithium tetrakisdimethylaminoaluminate<sup>34</sup> with excess of hydride in the presence of solvent. This rapid cleavage of the Si-N bond explains the failure of Cass and Coates<sup>5</sup> to prepare dimethylaminosilanes by the reduction of the corresponding chlorides.

The extensive work of Stokland<sup>35</sup> shows that decomposition of silane in a static system is slow at  $350^\circ$  but rapid at  $450^\circ$ . *N*-Silyldimethylamine decomposes above its melting point of  $+3^\circ$  to give unknown products, with an accompanying increase in vapour pressure.

<sup>31</sup> Stock, Somieski, and Wintgen, *Ber.*, 1917, **50**, 1764.

<sup>32</sup> Schwarz, *Ber.*, 1919, **52**, 601; Wiberg and Simmler, *Z. anorg. Chem.*, 1956, **283**, 401.

<sup>33</sup> Eaborn, "Organosilicon Compounds," Butterworths, London, 1960, p. 203.

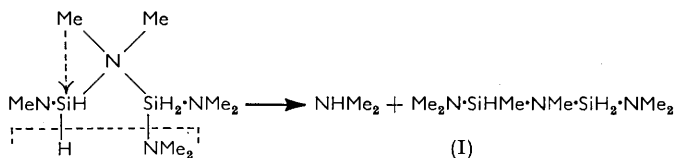
<sup>34</sup> Ruff, *J. Amer. Chem. Soc.*, 1961, **83**, 2835.

<sup>35</sup> Stokland, *Kgl. norske Videnskab. Selskabs Skrifter*, 1948 (3), 1.

In this study it was shown that bisdimethylaminosilane begins to decompose appreciably above 300°, while trisdimethylaminosilane must be heated to 400° before breakdown is rapid. In both cases, the products more volatile than the starting materials were: (a) silane, (b) dimethylamine, also (c) hydrogen when the temperature was high enough to decompose silane readily, and (d) methane, ammonia, and possibly methylamine in one experiment. Trimethylamine or hydrocarbons other than methane were not detected. The ratio of silane to dimethylamine was generally higher for the bis-compound than the tris. The other products were all less volatile than the starting material and consisted of a mixture of colourless liquids and a solid. The colour of the solid varied with the temperature of preparation; as the temperature increased it became darker and more metallic-looking. Pyrolysis of  $\text{SiH}_2(\text{NMe}_2)_2$  at 380° and  $\text{SiH}(\text{NMe}_2)_3$  at 400° gave solids of composition  $\text{SiN}_{2.3}\text{C}_{4.6}\text{H}_{11.6}$  and  $\text{SiN}_{3.7}\text{C}_{7.7}\text{H}_{13.0}$ , respectively. In each, silane evolution has made the Si : N ratio less than that of the starting material. The original C : N ratio is approximately maintained, but C : H has fallen. This implies that hydrogen is lost from the methyl groups, and that new C-N, C-Si, or C-C bonds are formed to produce a highly cross-linked structure.

A free-radical mechanism has been used to interpret the pyrolysis of silane<sup>35</sup> and disilane,<sup>36</sup> and also some additions<sup>37</sup> of silicon hydrides to alkenes and alkynes. In the present work, the small number of products observed makes this type of process a little unlikely; for this reason, a mechanism involving an intermediate bimolecular complex is preferred. Other reactions of silicon hydride derivatives have been interpreted in this way.<sup>38</sup>

The observed order of decomposition temperatures can then be understood in terms of ease of complex formation. Steric effects will increase and  $\text{N} \rightarrow \text{Si}$  intermolecular association will be more difficult as the number of dimethylamino-groups increases. In addition, the less hindered compounds may undergo base-catalysed reactions<sup>39</sup> catalysed by themselves. Two possible reaction paths of a bimolecular complex  $[\text{SiH}_2(\text{NMe}_2)_2]_2$  are: (a) disproportionation, and (b) elimination of dimethylamine with simultaneous migration of a methyl group



Similar processes could occur, less readily, with  $[\text{SiH}_2(\text{NMe}_2)_2, \text{SiH}(\text{NMe}_2)_3]$  and  $[\text{SiH}(\text{NMe}_2)_3]_2$  to give silane, dimethylamine,  $\text{Si}(\text{NMe}_2)_4$ , and compounds analogous to the silazane (I). Hydrolysis of the less volatile products gave results that were consistent with this formulation.

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<sup>36</sup> Emeléus and Reid, *J.*, 1939, 1021.

<sup>37</sup> White and Rochow, *J. Amer. Chem. Soc.*, 1954, **76**, 3897; Benkeser and Hickner, *ibid.*, 1958, **80**, 5298; Curtice, Gilman, and Hammond, *ibid.*, 1957, **79**, 4754.

<sup>38</sup> MacDiarmid, *Adv. Inorg. Chem. Radiochem.*, 1961, **3**, 207.

<sup>39</sup> Schaeffer and Wells, Technical Report No. 2, Office of Naval Research, Contract Nonr-908 (14), August 1961.