

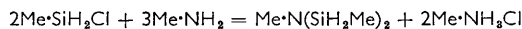
439. The Preparation and Donor Properties of Some Silylamines.

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Tri(methylsilyl)amine, $(\text{Me}\cdot\text{SiH}_2)_3\text{N}$, *N*-methyldi(methylsilyl)amine, $\text{Me}\cdot\text{N}(\text{SiH}_2\text{Me})_2$, and *NN*-dimethyl(methylsilyl)amine, $\text{Me}_2\text{N}\cdot\text{SiH}_2\text{Me}$, have been prepared and characterised. Physical properties of *NN*-dimethyl-(trimethylsilyl)amine, $\text{Me}_2\text{N}\cdot\text{SiMe}_3$, have been determined. The electron-donor properties of the nitrogen atoms in these compounds towards trimethylboron, methyl iodide, methylidosilane, hydrogen halides, and boron trifluoride have been studied; in some cases relatively stable adducts were formed. Equimolar addition compounds of trimethylamine with methyl-fluoro-, -chloro-, -bromo-, and -iodo-silane have been prepared.

TRISILYLAMINE, $(\text{SiH}_3)_3\text{N}$, was first prepared by Stock and Somieski¹ by the reaction of excess of silyl chloride with ammonia in the vapour phase. With excess of ammonia the main product was disilylamine, $(\text{SiH}_3)_2\text{NH}$; this decomposed at room temperature giving silane, trisilylamine, and solid polymers. *N*-Methyldisilylamine was made similarly from methylamine and silyl chloride;² *NN*-dimethylsilylamine, however, could not be isolated from the products of the reaction of silyl chloride and dimethylamine,² and was eventually made from silyl bromide and dimethylamine.³ Triorganosubstituted halogenosilanes also react with amines containing hydrogen bound to nitrogen to give silylamines,⁴ but the product depends on the size of the organic groups.⁵ In this way a few *Si*-trimethylsilylamines have been made from trimethylchlorosilane,⁶ but no attempt has been made to study systematically the effect of methyl-substitution in the silyl group on the donor properties of the nitrogen atom. This was the purpose of preparing the three new amines described below.

Tri(methylsilyl)amine was prepared from ammonia and excess of methylchlorosilane. The products included an unstable material, believed to be di(methylsilyl)amine, $(\text{Me}\cdot\text{SiH}_2)_2\text{NH}$; a similar substance was formed when an excess of ammonia was used. *N*-Methyldi(methylsilyl)amine, $\text{Me}\cdot\text{N}(\text{SiH}_2\text{Me})_2$, was prepared similarly from methylamine and methylchlorosilane:



In view of the difficulty of isolating *NN*-dimethylsilylamine,² *NN*-dimethyl(methylsilyl)amine was made from dimethylamine and methylidosilane rather than from methylchlorosilane; the products included the addition compound of the amine and methylidosilane, which was later prepared from its two components. *NN*-Dimethyl(trimethylsilyl)amine was made as described by Mjörne.⁷

Tri(methylsilyl)amine was decomposed at -78° by dry hydrogen chloride, giving ammonium chloride and methylchlorosilane:



The three other amines reacted similarly, and this behaviour is like that of most other silylamines.^{1,2,3} Only two compounds containing silicon bound to nitrogen are known to form adducts with a hydrogen halide;⁸ they are *NN*-dimethyl(trichlorosilyl)amine,

¹ Stock and Somieski, *Ber.*, 1921, **54**, 740.

² Emeléus and Miller, *J.*, 1939, 819.

³ Sujishi and Witz, *J. Amer. Chem. Soc.*, 1954, **76**, 4631.

⁴ Kraus and Rosen, *ibid.*, 1925, **47**, 2739; Larsson and Mjörne, *Trans. Chalmers Univ. Göttenburg*, 1949, No. 87, 29; Bailey, Sommer, and Whitmore, *J. Amer. Chem. Soc.*, 1948, **70**, 435.

⁵ Brewer and Haber, *ibid.*, 1948, **70**, 3888.

⁶ Sauer and Hasek, *ibid.*, 1946, **68**, 241.

⁷ Mjörne, *Svensk kem. Tidskr.*, 1950, **62**, 120.

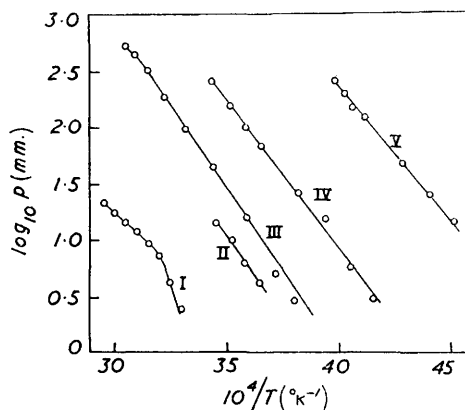
⁸ Cass and Coates, *J.*, 1952, 2347.

$\text{Me}_2\text{N}\cdot\text{SiCl}_3$, and tetra-*N*-methyl(dichlorosilyl)ene)diamine, $(\text{Me}_2\text{N})_2\text{SiCl}_2$. The structures of the adducts are not known.

One of the reasons why silylamines can be prepared from halogenosilanes and ammonia or amines is that they do not as a rule form quaternary compounds,^{1,2} although halogenosilanes give adducts with tertiary aliphatic amines.^{2,9,10} Tri(methylsilyl)amine and *N*-methyldi(methylsilyl)amine were found to conform to this pattern; when methyl iodide was mixed with either, it was recovered unchanged.¹¹ Methyl iodide reacted with both *NN*-dimethyl(methylsilyl)amine and *NN*-dimethyl(trimethylsilyl)amine, however, forming stable, solid 1 : 1 adducts. The last amine formed no adduct with methyl chloride. Similarly, methyliodosilane did not react with tri(methylsilyl)amine or *N*-methyldi(methylsilyl)amine; with *NN*-dimethyl(methylsilyl)amine it reacted violently at low temperatures to form a 1 : 1 adduct whose vapour density showed it to be completely dissociated in the vapour phase. The dissociation products were identified spectroscopically as methyliodosilane and the original amine. The dissociation was initially reversible at 0°, but the compound decomposed slowly at room temperature, probably because of disproportionation of the halide. Dissociation-pressure measurements (5–45°) gave an approximately

Dissociation pressures of addition compounds of methylhalogenosilanes.

- I, Trimethylamine–methyliodosilane.
 II, Trimethylamine–methylbromosilane.
 III, *NN*-Dimethyl(methylsilyl)amine–methyliodosilane.
 IV, Trimethylamine–methylchlorosilane.
 V, Trimethylamine–methylfluorosilane.



linear plot of $\log_{10} p$ against $1/T$, leading to a heat of dissociation of *ca.* 10 kcal. mole⁻¹. *NN*-Dimethyl(trimethylsilyl)amine also reacted with methyliodosilane, giving a solid equimolar adduct; this however gave complex products when vaporized. In view of the formation of definite adducts by *NN*-dimethylsilylamines, the behaviour of trimethylamine itself was examined. In this case equimolar compounds were formed with all of the four methylhalogenosilanes $\text{Me}\cdot\text{SiH}_2\text{X}$ ($\text{X} = \text{F}, \text{Cl}, \text{Br}, \text{or I}$). Dissociation-pressure measurements for the series are shown in the Figure as plots of $\log_{10} p$ against $1/T$; the fluoride and the bromide adduct were shown spectroscopically to dissociate to their original components in the vapour phase, and dissociation was shown by vapour-density measurements to be virtually complete.

Although the graphs for the fluoride and the chloride compound are almost linear, the dissociation pressures were not exactly reproducible with descending temperature. This is probably due to the rapid disproportionation of the methylhalogenosilanes.¹⁰ The results do, nevertheless, establish the order of stability of the adducts. They also lead to heats of dissociation of the order of 10 kcal. mole⁻¹.

With trimethylboron neither tri(methylsilyl)amine nor *N*-methyldi(methylsilyl)amine gave an adduct, and recovery of the boron compound was quantitative. With *NN*-dimethyl(methylsilyl)amine and *NN*-dimethyl(trimethylsilyl)amine, reaction occurred in

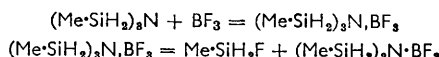
⁹ Aylett, Emeléus, and Maddock, *J. Inorg. Nuclear Chem.*, 1955, **1**, 187.

¹⁰ Miller, Ph.D. Thesis, London, 1939.

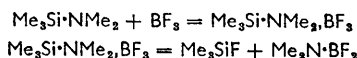
¹¹ For details of this and other negative experiments see Ebsworth, Ph.D. Thesis, Cambridge, 1957.

approximately equimolar ratios; the solid products melted at *ca.* -35° and -40° to -30° respectively.

The experiments on the formation of compounds between the silylamines and either boron trifluoride or trichloride showed that the adducts initially formed were unstable. Thus, with boron trifluoride, tri(methylsilyl)amine reacted at -78° , to give a crystalline solid; this decomposed rapidly in the presence of excess of boron trifluoride to give methylfluorosilane and *NN*-di(methylsilyl)aminoboron difluoride:



NN-Dimethyl(methylsilyl)amine similarly gave methylsilyl fluoride and *NN*-dimethylaminoboron difluoride, while *NN*-dimethyl(trimethylsilyl)amine gave trimethylfluorosilane and *NN*-dimethylaminoboron difluoride:



These reactions are very like those recently described between silylamines containing SiH_3 groups and boron trifluoride.¹² Tri(methylsilyl)amine reacted with boron trichloride at -78° to give a solid equimolar adduct, but this decomposed when warmed, forming a variety of products which included methylchlorosilane.

The above results show that the methylated silylamines, like those containing the SiH_3 group,^{1,13} are comparatively weak bases. The *NN*-dimethylsilylamines are appreciably stronger bases than the others,³ but no acceptor has yet been found which will differentiate between the *N*-methylsilylamines and the trisilylamines. These form only unstable adducts, and any attempt to assess relative base-strengths from the stabilities of such compounds must assume a knowledge of the mechanisms of decomposition which is not available.

This agrees with the theory of $d\pi$ -bonding between silicon and amino-nitrogen.^{14,15} According to the theory, the nitrogen's lone pair of electrons can pass partly into vacant $3d$ orbitals on the silicon atom, and thus becomes less readily available to external electron-acceptors. This cannot happen with carbon, which has no $3d$ orbitals in its outer shell; hence each successive substitution of silicon for carbon in the methylamines should lead to a drop in the basic properties of the resulting amine.

It is less easy to see how silicon-methylation affects the donor properties of the nitrogen atom. It is only possible to compare the base-strengths of the three *NN*-dimethylsilylamines, for only these form reasonably stable addition compounds. Towards trimethylboron, the dissociation pressures of the adducts suggest that silicon-methylation weakens the B-N bond; this would be expected for steric reasons, and is probably not an electronic effect. The other differences between the three amines can be put down to steric influences, and there is no evidence to suggest that silicon-methylation has any marked effect on the nitrogen atom's electron-donor properties.

EXPERIMENTAL

Preparation of Methylchlorosilane and Methylbromosilane.—Methyliodosilane (1 g.) was passed as vapour through a tube packed with dried powdered mercuric chloride (30 g.). Methylchlorosilane was isolated by fractionation, in 90% yield based on the equation $2\text{Me}\cdot\text{SiH}_2\text{I} + \text{HgCl}_2 = 2\text{Me}\cdot\text{SiH}_2\text{Cl} + \text{HgI}_2$ (Found: *M*, 81.5; v. p. 63 mm. at -45° ; m. p. -135° . Calc. for CH_5ClSi : *M*, 80.5; v. p. 63 mm. at -45° ; m. p. -135°).

¹² Sujishi and Witz, *J. Amer. Chem. Soc.*, 1957, **79**, 2447.

¹³ Burg and Kuljian, *ibid.*, 1950, **72**, 3103.

¹⁴ Craig, Maccoll, Nyholm, Orgel, and Sutton, *J.*, 1954, 332.

¹⁵ Hedburg, *J. Amer. Chem. Soc.*, 1955, **77**, 6491.

Methylchlorosilane (1.5 g.) was passed as vapour over dried powdered silver bromide (40 g.) mixed with glass wool (40 g.). From the volatile products *methylbromosilane* was isolated by fractional distillation at -96° (Found: Si-H, 1.60; Br, 63.0%; *M*, 126. CH_3BrSi requires Si-H, 1.60; Br, 63.6%; *M*, 125). The m. p. was -119° . The v. p. was given in the range -10° to 23° by $\log_{10} p$ (mm.) = $7.732 - 1490/T$. The extrapolated b. p. was $34^\circ \pm 0.5^\circ$, the latent heat of vaporization 6800 cal./mole, and Trouton's constant 21.8. The infrared spectrum is described elsewhere.¹⁶ The yield was 93% based on the equation $\text{Me}\cdot\text{SiH}_2\text{I} + \text{AgBr} = \text{Me}\cdot\text{SiH}_2\text{Br} + \text{AgI}$.

Preparation of Tri(methylsilyl)amine.—In a typical experiment methylchlorosilane (0.593 g.) was mixed with ammonia (0.163 g.) in the vapour phase at room temperature. The pressures of the reactants were controlled so as to keep an excess of halide in the reaction-vessel. *Tri(methylsilyl)amine* was isolated by fractional distillation and condensation of the products (Found: C, 24.2; H, total, 10.2; Si-H, 4.0; N, 9.5%; *M*, 149. $\text{C}_3\text{H}_{15}\text{NSi}_3$ requires C, 24.0; H, total, 10.0; Si-H, 4.04; N, 9.4%; *M*, 149). The m. p. was -107° . The v. p. was given in the range $50-105^\circ$ by $\log_{10} p$ (mm.) = $7.491 - 1760/T$. The extrapolated b. p. was $108.6^\circ \pm 0.2^\circ$, the latent heat of vaporization 8100 cal./mole, and Trouton's constant 20.7. The compound absorbed in the ultraviolet region below 2500 Å, and there was no maximum above 2000 Å. The infrared spectrum is described elsewhere.¹⁶ The yield was 65–70% based on the equation $3\text{Me}\cdot\text{SiH}_2\text{Cl} + 4\text{NH}_3 = (\text{Me}\cdot\text{SiH}_2)_3\text{N} + 3\text{NH}_4\text{Cl}$. A second product which decomposed slowly at room temperature to tri(methylsilyl)amine and other products was tentatively identified as *di(methylsilyl)amine* (Found: *M*, 112. $\text{C}_2\text{H}_{11}\text{NSi}_2$ requires *M*, 105).

Reaction of Tri(methylsilyl)amine with Hydrogen Chloride.—Hydrogen chloride (0.096 g.) and tri(methylsilyl)amine (0.059 g.), when mixed at -78° , formed a white solid. After 18 hr. hydrogen chloride (0.040 g.) was recovered (Found: *M*, 35.5; v. p. 10 mm. at -136° . Calc. for HCl: *M*, 36.5; v. p. 10 mm. at -136°), with methylchlorosilane (0.094 g.) (Found: *M*, 81; v. p. 51.9 mm. at -46° . Calc. for CH_3ClSi : *M*, 80.5; v. p. 56 mm. at -46°). The chloride in the residue corresponded with 0.020 g. of ammonium chloride.

Reaction of Tri(methylsilyl)amine with Boron Trichloride.—An equimolar mixture of boron trichloride (0.058 g.) and tri(methylsilyl)amine (0.074 g.) was solid at -78° , the m. p.s of both components being the same, -107° . The solid melted with gas evolution at -46° and did not freeze on re-cooling to -78° . The volatile products isolated were: hydrogen chloride (0.007 g.); an inseparable mixture of boron trichloride and methylchlorosilane (0.030 g.), shown to contain 0.023 g. of the latter by measurement of the hydrogen evolved on alkaline hydrolysis; and a heavy, barely volatile liquid which decomposed slowly at room temperature leaving a white involatile solid residue. When an initial excess of amine was taken, pure methylchlorosilane was recovered in place of the mixture with boron trichloride.

Reaction of Tri(methylsilyl)amine with Boron Trifluoride.—An equimolar mixture of boron trifluoride (0.048 g.) and tri(methylsilyl)amine (0.104 g.) solidified at -78° . The volatile products were a mixture of boron trifluoride and methylfluorosilane (0.044 g.), with a less volatile material which was probably a mixture of tri(methylsilyl)amine and *NN*-di(methylsilyl)aminoboron difluoride (see below).

A mixture of boron trifluoride (0.132 g.) and tri(methylsilyl)amine (0.146 g.) was liquid at -96° . After 18 hr. at -78° the products volatile at -96° were boron trifluoride (0.064 g.) (Found: *M*, 67.5; v. p. 31 mm. at -133° . Calc. for BF_3 : *M*, 67.8; v. p. 34 mm. at -133°) and methylfluorosilane (0.059 g.) (Found: *M*, 65; v. p. 27.2 mm. at -96° , 100 mm. at -78° . Calc. for CH_3FSi : *M*, 64; v. p. 28 mm. at -96° , 104 mm. at -78°). The residue, involatile at -96° , was *NN*-di(methylsilyl)aminoboron difluoride (Found: Si-H, 2.52; B, $\sim 7.3\%$; *M*, 152. $\text{C}_2\text{H}_{10}\text{F}_2\text{NBSi}_2$ requires Si-H, 2.61; B, 6.65%; *M*, 152). The compound was stable in glass at room temperature, but decomposed rapidly in the presence of tap-grease. The yield of methylfluorosilane was 95%, and of *NN*-di(methylsilyl)aminoboron difluoride 80%, based on the equation $(\text{Me}\cdot\text{SiH}_2)_3\text{N} + \text{BF}_3 = (\text{Me}\cdot\text{SiH}_2)_2\text{N}\cdot\text{BF}_2 + \text{Me}\cdot\text{SiH}_2\text{F}$; each mole of amine combined with 1.02 moles of boron trifluoride.

Preparation of N-Methyldi(methylsilyl)amine.—Methylamine (0.370 g.) and methylchlorosilane (0.790 g.) were mixed in the vapour phase, the halide being kept as far as possible in excess. From the volatile products *N-methyldi(methylsilyl)amine* (0.300 g.) was isolated by fractional distillation at -64° and condensation at -96° . It was purified by condensation at -78° (Found: Si-H, 3.36; N, 12.0%; *M*, 119. $\text{C}_3\text{H}_{13}\text{NSi}_2$ requires Si-H, 3.38; N, 11.8%;

¹⁶ Ebsworth, Onyszchuk, and Sheppard, *J.*, 1958, 1453.

M, 119). The m. p. was -115° . The v. p. at 0° was 27.5 mm., and between 30° and 78° was expressed by $\log_{10} p$ (mm.) = $7.646 - 1683/T$. The extrapolated b. p. was $80.1^{\circ} \pm 0.2^{\circ}$, the latent heat of vaporization 7700 cal./mole, and Trouton's constant 21.7. The yield was 65% based on the equation $2\text{Me}\cdot\text{SiH}_2\text{Cl} + 3\text{Me}\cdot\text{NH}_2 = \text{Me}\cdot\text{N}(\text{SiH}_2\text{Me})_2 + 2\text{Me}\cdot\text{NH}_2\text{Cl}$.

Reaction of N-Methyldi(methylsilyl)amine with Hydrogen Chloride.—Hydrogen chloride (0.101 g.) and *N*-methyldi(methylsilyl)amine (0.065 g.) when mixed at 78° formed a white solid. After 18 hr. hydrogen chloride (0.039 g.) was recovered (Found: *M*, 35; v. p. 373 mm. at -96° . Calc. for HCl : *M*, 36.5; v. p. 390 mm. at -96°), with methylchlorosilane (0.089 g.) (Found: *M*, 82; v. p. 51 mm. at -47° . Calc. for CH_3ClSi : *M*, 80.5; v. p. 52 mm. at -47°). The chloride in the solid residue corresponded with 0.038 g. of methylamine hydrochloride.

Preparation of NN-Dimethyl(methylsilyl)amine.—Dimethylamine (0.345 g.) and methyl-iodosilane (0.730 g.) were mixed in the vapour phase at room temperature, the amine being kept as far as possible in excess. From the products, *NN*-dimethyl(methylsilyl)amine (0.310 g.) was isolated by fractionation (Found: *Si*-H, 2.26; *N*, 15.3%; *M*, 89. $\text{C}_3\text{H}_{11}\text{NSi}$ requires *Si*-H, 2.24; *N*, 15.7%; *M*, 89). The compound solidified to a clear glass which softened at -150° to -160° . The v. p. at 0° was 127 mm. and in the range $0-44^{\circ}$ was given by $\log_{10} p$ (mm.) = $7.505 - 1474/T$. The extrapolated b. p. was $45.3^{\circ} \pm 0.2^{\circ}$, the latent heat of vaporization 6750 cal./mole, and Trouton's constant 21.3. The yield was 90% based on the equation $\text{Me}\cdot\text{SiH}_2\text{I} + 2\text{Me}_2\text{NH} = \text{Me}_2\text{N}\cdot\text{SiH}_2\text{Me} + \text{Me}_2\text{NH}_2\text{I}$. An unstable volatile white solid was also formed in the reaction: it was involatile at -64° , and was identified as the adduct $\text{Me}_2\text{N}\cdot\text{SiH}_2\text{Me}, \text{Me}\cdot\text{SiH}_2\text{I}$, described below.

Reaction of NN-Dimethyl(methylsilyl)amine with Hydrogen Chloride.—Hydrogen chloride (0.089 g.) and *NN*-dimethyl(methylsilyl)amine (0.073 g.) formed a white solid at -78° . After 18 hr. hydrogen chloride (0.035 g.) was recovered (Found: *M*, 38; v. p. 13 mm. at -134° . Calc. for HCl : *M*, 36.5; v. p. 13 mm. at -134°), with methylchlorosilane (0.065 g.) (Found: *M*, 80; v. p. 61 mm. at -46° . Calc. for CH_3ClSi : *M*, 80.5; v. p. 56 mm. at -46°). The chloride in the solid residue corresponded with 0.065 g. of dimethylamine hydrochloride.

Reaction of N-Dimethyl(methylsilyl)amine with Trimethylboron.—An equimolar mixture of *NN*-dimethyl(methylsilyl)amine (0.052 g.) and trimethylboron (0.031 g.) was solid at -64° ; the m. p.s of the components are -100° and $\sim -150^{\circ}$ and neither component could be recovered at -96° , showing that neither was in excess. The vapour density at 20° of a completely vaporized sample gave *M*, 73 (a completely dissociated adduct requires *M*, 72). The dissociation pressures, measured with a dead space of ~ 50 ml., were:

<i>p</i> (mm.)	6.5	11.0	15.5	20.5	26.5	43.0	180
Temp.	-64°	-46°	-39°	-35°	-30°	-23°	0°

The solid melted at $\sim -35^{\circ}$.

Reaction of NN-Dimethyl(methylsilyl)amine with Methyl Iodide.—Methyl iodide (0.158 g.) and *NN*-dimethyl(methylsilyl)amine (0.039 g.) were mixed at room temp. White crystals were formed gradually, and the material appeared solid after 3 days. Methyl iodide (0.089 g.) was recovered (Found: *M*, 135; v. p. 142 mm. at 0° . Calc. for CH_3I : *M*, 142; v. p. 141 mm. at 0°). This methyl iodide could not be fully purified from what was probably a decomposition product of the amine. If the methyl iodide recovered is assumed to be pure, the molar combining ratio was 0.91 : 1. The solid was involatile in a vacuum (Found: *I*, 54.5. $\text{C}_4\text{H}_{14}\text{NISi}$ requires *I*, 55.0%).

Reaction of NN-Dimethyl(methylsilyl)amine with Methyliodosilane.—*NN*-Dimethyl(methylsilyl)amine (0.028 g.) and methyliodosilane (0.389 g.) reacted vigorously at -50° , forming a white solid. Excess of methyliodosilane (0.333 g.) was recovered (Found: *M*, 167; v. p. 49.0 mm. at 1° . Calc. for CH_3ISi : *M*, 172; v. p. 46.0 mm. at 1°). The molar reacting ratio was 0.97 : 1. The solid was involatile at -46° (Found: *Si*-H, 1.48; *I*, 48.9%. $\text{C}_4\text{H}_{16}\text{Si}_2\text{N}$ requires *Si*-H, 1.53; *I*, 48.7%). The dissociation was initially reversible, the infrared spectrum of the vapour being identical with that expected of a mixture of the two reactants. The vapour density showed the dissociation to be virtually complete (Found: *M*, 127, 135. A completely dissociated adduct requires *M*, 130). Slow decomposition occurred at room temperature and a liquid was formed. Methylsilane (0.023 g.) was recovered after three weeks (Found: *M*, 44; 76 mm. at -96° . Calc. for CH_3Si : *M*, 46; v. p. 84 mm. at -86°).

Reaction of NN-Dimethyl(methylsilyl)amine with Boron Trifluoride.—An equimolar mixture of *NN*-dimethyl(methylsilyl)amine (0.075 g.) and boron trifluoride (0.057 g.) was solid at -78° .

The solid melted below room temperature and, after warming to about 60°, methylfluorosilane (0.040 g.) was recovered (Found: *M*, 64; v. p. 98 mm. at -78°. Calc. for CH₅FSi: *M*, 64; v. p. 104 mm. at -78°). A crystalline residue remained, which was shown spectroscopically to be *NN*-dimethylaminoboron difluoride.

Preparation of NN-Dimethyl(trimethylsilyl)amine.—Mjörne's method⁷ was used. The product was purified by fractional distillation at -64° (Found: C, 50.3; H, 12.7; N, 11.8%; *M*, 117. Calc. for C₅H₁₅NSi: C, 51.2; H, 12.8; N, 11.9%; *M*, 117). The v. p. was 22.5 mm. at 0°, and in the range 40–84° was given by log₁₀ *p* (mm.) = 7.491 - 1657/*T*. The b. p. was 86.2° ± 0.2°, the latent heat of vaporization 7600 cal./mole, and Trouton's constant 21.1.

Reaction of NN-Dimethyl(trimethylsilyl)amine with Hydrogen Chloride.—*NN*-Dimethyl(trimethylsilyl)amine (0.063 g.) and hydrogen chloride (0.074 g.) gave a white solid at -78°. After 18 hr., hydrogen chloride (0.035 g.) was recovered (Found: *M*, 37; v. p. 82.5 mm. at -117°. Calc. for HCl: *M*, 36.5; v. p. 80 mm. at 117°), with trimethylchlorosilane (0.052 g.) (Found: *M*, 109; v. p. 72 mm. at 0°. Calc. for C₃H₉ClSi: *M*, 109; v. p. 74 mm. at 0°). The solid residue contained chloride corresponding with 0.065 g. of dimethylamine hydrochloride.

Reaction of NN-Dimethyl(trimethylsilyl)amine with Hydrogen Iodide.—*NN*-Dimethyl(trimethylsilyl)amine (0.074 g.) and hydrogen iodide (0.228 g.) formed a solid at -78°, which decomposed at room temperature. Hydrogen iodide (0.063 g.) was recovered (Found: *M*, 126; v. p. 154 mm. at -65°. Calc. for HI: *M*, 128; v. p. 162 mm. at -65°) and trimethyliodosilane (0.100 g.) (Found: I, 60.5%; *M*, 200. Calc. for C₃H₉ISi: I, 63.5%; *M*, 200).

Reaction of NN-Dimethyl(trimethylsilyl)amine with Trimethylboron.—*NN*-Dimethyl(trimethylsilyl)amine (0.092 g.) and trimethylboron (0.106 g.) gave a product which was solid at -64°. Trimethylboron (0.063 g.) was recovered by distillation at -96° (Found: *M*, 56; v. p. 30 mm. at -79°. Calc. for C₃H₉B: *M*, 56; v. p. 31 mm. at -79°). The combining ratio was 1.02 : 1. A sample when completely vaporized at 20° had *M* 84 (a completely dissociated adduct requires *M* 86.5). The dissociation pressures, measured in a dead space of 50 ml., were:

<i>p</i> (mm.)	6.0	11.3	40.4	108.0	141.5	183.5	218
Temp.	-64°	-45°	-34°	-23°	-18°	-11°	0°

Reaction of NN-Dimethyl(trimethylsilyl)amine with Methyl Iodide.—The amine (0.101 g.) and methyl iodide (0.258 g.) reacted slowly at room temperature, forming white crystals. After 3 days the residual volatile material was methyl iodide (0.136 g.) (Found: *M*, 139; v. p. 139 mm. at 0°. Calc. for CH₃I: *M*, 142, v. p. 141 mm. at 0°). The molar combining ratio was 1.01 : 1. The white solid was involatile in a vacuum at room temperature (Found: I, 49.7. C₆H₁₈NISi requires I, 49.0%). The solid was unchanged after 18 hr. at 110°.

Reaction of NN-Dimethyl(trimethylsilyl)amine with Methyliodosilane.—The amine (0.035 g.) and methyliodosilane (0.224 g.) reacted at -46°, to form a white solid. Methyliodosilane (0.174 g.) was recovered (Found: *M*, 174; v. p. 43 mm. at 0°. Calc. for CH₃ISi: *M*, 172; v. p. 43 mm. at 0°). The molar reacting ratio was 1.00 : 1. The solid had a v. p. of ~10 mm. at 20°, but decomposition occurred on sublimation at room temperature and a white involatile solid residue remained.

Reaction of NN-Dimethyl(trimethylsilyl)amine with Boron Trifluoride.—The amine (0.053 g.) and boron trifluoride (0.140 g.) formed a white solid at room temperature. Boron trifluoride (0.109 g.) was recovered (Found: *M*, 68; v. p. 191 mm. at -118°. Calc. for BF₃: *M*, 67.8; v. p. 173 mm. at -118°). The solid was involatile at room temperature; it vaporized at 100°, producing trimethylfluorosilane (0.035 g.) (Found: *M*, 93; v. p. 125 mm. at -23°. Calc. for C₃H₉FSi: *M*, 92; v. p. 124 mm. at -23°), while crystals of *NN*-dimethylaminoboron difluoride were deposited (Found: C, 25.8; H, 6.7. Calc. for C₂H₈NF₂B: C, 25.9; H, 6.7%). The infrared spectrum of the crystals was identical with that of the sample prepared from *NN*-dimethyl(methylsilyl)amine (see above). For each mole of amine taken, 0.99 mole of boron trifluoride was consumed and 0.82 mole of trimethylfluorosilane was produced.

Reactions of Trimethylamine.—(a) *With methylfluorosilane.* Trimethylamine (0.188 g.) and methylfluorosilane (0.326 g.) gave a solid product at -96°; methylfluorosilane (0.214 g.) was recovered (Found: *M*, 65; v. p. 106 mm. at -78°. Calc. for CH₅FSi: *M*, 64; v. p. 100 mm. at -78°). The molar combining ratio was 0.96 : 1. The solid was volatile at -64°, and dissociated reversibly up to -46°. The extrapolated dissociation pressure was 1 atm. at -16°. The vapour density showed the compound to be completely dissociated in the vapour

phase (Found: M , 62. A completely dissociated *adduct* requires M , 62.5); the dissociation products were identified spectroscopically as trimethylamine and methylfluorosilane.

(b) *With methylchlorosilane.* Trimethylamine (0.032 g.) and methylchlorosilane (0.065 g.) formed a white *solid* at -46° (Found: Si-H, 1.35; Cl, 25.3. $C_4H_{14}NClSi$ requires Si-H, 1.43; Cl, 25.4%); methylchlorosilane (0.021 g.) was recovered (Found: M , 78; v. p. 60 mm. at -45° . Calc. for CH_5ClSi : M , 80.5; v. p. 63 mm. at -45°). The molar combining ratio was 1.00 : 1. Dissociation pressures of the solid were measured: there was some decomposition above 0° . The vapour had M 70 (a completely dissociated adduct requires M 70.5).

(c) *With methylbromosilane.* Trimethylamine (0.053 g.) and methylbromosilane (0.261 g.) formed a white *solid* at 0° (Found: Si-H, 1.08; Br, 43.0. $C_4H_{14}NBrSi$ requires Si-H, 1.09; Br, 43.4%); methylbromosilane (0.154 g.) was recovered at -46° (Found: M , 125; v. p. 191 mm. at 0° . Calc. for CH_5BrSi : M , 125; v. p. 196 mm. at 0°). The molar combining ratio was 1.04 : 1. The solid had a dissociation pressure of 4 mm. at 0° ; dissociation was not reversible between 0° and 10° ; the dissociation products were identified spectroscopically as the original reactants.

(d) *With methyliodosilane.* Trimethylamine (0.026 g.) and methyliodosilane (0.167 g.) reacted vigorously together at -50° , forming white crystals. Methyliodosilane (0.092 g.) was recovered (Found: M , 169; v. p. 46 mm. at 1° . Calc. for CH_5ISi : M , 172; v. p. 46 mm. at 1°). Vapour pressures were recorded up to 110° , but the graph of $\log p$ against $1/T$ was not linear, nor was the dissociation reversible. The dissociation pressure at 20° was *ca.* 1 mm.

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