

200. *Preparation and Properties of Bispentamethyldisilanylamine and Pentamethyldisilanyl Isocyanate.*

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Pentamethyldisilanyl chloride, $\text{Me}_3\text{Si}\cdot\text{SiMe}_2\text{Cl}$, has been found to react with ammonia and with silver cyanate to give the bis-disilanylamine and the disilanyl isocyanate, respectively. Physical properties of these compounds have been determined. The amine and the corresponding ether react with boron trifluoride, to give good yields of the fluorodisilane.

In a previous communication¹ we described the preparation and properties of some derivatives of disilane. In order to study the nature of the Si-Si linkage more fully we have synthesized new compounds containing the pentamethyldisilanyl, $\text{Me}_3\text{Si}\cdot\text{SiMe}_2$, group and have studied certain of their physical and chemical properties.

Bispentamethyldisilanylamine, $(\text{Me}_3\text{Si}\cdot\text{SiMe}_2)_2\text{NH}$, was prepared in good yield by the reaction of pentamethyldisilanyl chloride with ammonia. No evidence was obtained for the simultaneous formation of the primary or tertiary disilanylamine. Whether a primary, secondary, or tertiary amine is formed when a monohalogenosilane reacts with ammonia appears to depend primarily on the steric requirements of the other groups attached to the silicon. Thus silyl and methylsilyl chloride and disilanyl iodide give the corresponding tertiary silylamines²⁻⁴ as the only isolable species; trimethylsilyl chloride gives only the disilylamine as a stable species,^{5,6} while triphenylsilyl chloride gives the monosilylamine.⁷ Even though a more condensed amine may be sterically capable of existence, condensation of the primary amine first formed, or its further reaction with more halogenosilane, does not necessarily occur. Thus, although tristrimethylsilylamine cannot be formed directly by heating bistrimethylsilylamine even to 550° in the presence of trimethylsilyl chloride and

¹ Craig, Urenovitch, and MacDiarmid, *J.*, 1962, 548.

² Burg and Kuljian, *J. Amer. Chem. Soc.*, 1950, **72**, 3103.

³ Ebsworth and Emel us, *J.*, 1958, 2150.

⁴ Ward and MacDiarmid, *J. Inorg. Nuclear Chem.*, 1962, **21**, 287.

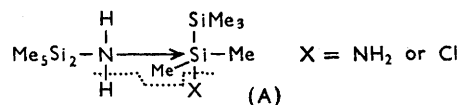
⁵ Sauer, *J. Amer. Chem. Soc.*, 1944, **66**, 1707.

⁶ Sauer and Hasek, *J. Amer. Chem. Soc.*, 1946, **68**, 241.

⁷ Kraus and Rosen, *J. Amer. Chem. Soc.*, 1925, **47**, 2739.

pyridine,^{6,8} it can be formed by reaction of the lithium⁹ or sodium⁸ salts of bistrimethylsilylamine with the chloride.

Since the ammonolysis of triethylsilyl chloride produces chiefly the monosilylamine as a stable species,^{6,10} the likelihood of obtaining a primary amine by the ammonolysis of pentamethylsilyl chloride appeared to be greater than in the case of trimethylsilyl chloride. However, the fact that none was obtained is not necessarily surprising since diethylmethylsilyl chloride produces only a secondary amine on treatment with ammonia.¹¹ Moreover, it appears likely that the increased steric requirements of the pentamethylsilyl group, which would tend to limit the ease of condensation of the primary amine, or its further reaction with pentamethylsilyl chloride, may be partly compensated by the presence of the Si-Si bond. The increased availability of vacant silicon *3d*-orbitals at



the Si-Si bond may assist in promoting condensation or further reaction with pentamethylsilyl chloride as shown in (A). The lone pair of electrons on the nitrogen might readily overlap the *3d*-orbitals of one silicon atom or the other, or even both simultaneously,¹ to give an intermediate complex which could then cleave at the dotted line as shown. That the presence of a Si-Si bond might favour such an interaction is indicated by the fact that liquid bispentamethylsilylamine is considerably associated (Trouton's constant, 28.1), whereas the Trouton's constant for bistrimethylsilylamine is only 23.5.¹²

Pentamethylsilyl isocyanate, $\text{Me}_3\text{Si-SiMe}_2\cdot\text{NCO}$, was prepared in good yield by the reaction of the chloride with silver cyanate. The isocyanate structure was confirmed by infrared and molar-refraction data.

The Si-Si bond in the pentamethylsilyl group has been found to be relatively non-reactive.¹ In an endeavour to ascertain whether boron trifluoride might cleave the Si-Si bond, it was bubbled through boiling bispentamethylsilyl ether and boiling bispentamethylsilylamine. It was believed that the Lewis acid-base interaction which would be expected to occur between boron trifluoride and the ether and amine might promote such a cleavage. However, if any did occur it was certainly only small since cleavage occurred preferentially at the Si-O and Si-N bonds, respectively, to give large yields of pentamethylsilyl fluoride in both cases. The reaction therefore appeared to proceed in an analogous manner to that between boron trifluoride and the corresponding trimethylsilyl ether¹³ or bistrimethylsilylamine.^{12,14}

EXPERIMENTAL

Fractional distillations were performed on a Podbielniak high-temperature distillation apparatus (Mini-Cal series 3400). Vapour-pressure data of new compounds were obtained by measuring the b. p. of a given material at different pressures on the Podbielniak distillation apparatus.

Bispentamethylsilylamine.—Freshly distilled pentamethylsilyl chloride (51.2 g., 0.307 mole) and anhydrous ether (450 ml.) were stirred in a 1-l. three-necked flask equipped with a mechanical stirrer, a water-jacketed condenser, and a gas inlet tube. A slow stream

⁸ Goubeau and Jiménez-Barberá, *Z. anorg. Chem.*, 1960, **303**, 217.

⁹ Wannagat and Niederprüm, *Angew. Chem.*, 1959, **71**, 574.

¹⁰ Bailey, Sommer, and Whitmore, *J. Amer. Chem. Soc.*, 1948, **70**, 435.

¹¹ Shostakovskii, Kochkin, Shikhiyev, and Vlasov, *Zhur. obshchei Khim.*, 1955, **25**, 622; *Chem. Abs.*, 1956, **50**, 3270.

¹² Sujishi, Final Report, Office of Ordnance Research, Contract No. DA-11-022-ORD-1264, Project No. TB 2-0001 (817), Control No. OOR-137-53, Aug. 1957.

¹³ Emeléus and Onyszchuk, *J.*, 1958, 604.

¹⁴ Becke-Goehring and Krill, *Chem. Ber.*, 1961, **94**, 1059.

of anhydrous ammonia was passed through the gas-inlet tube with constant stirring. Precipitation of ammonium chloride occurred immediately. After passage of the ammonia for ~5 hr. the solution was refluxed and filtered and the solid ammonium chloride was washed with ether. After removal of the ether by a rough bench-distillation the residue was fractionated on the Podbielniak distillation apparatus under an atmosphere of dry nitrogen. The initial distillate (b. p. 79—94°/6.2 mm.) upon further fractionation was found to consist of bispentamethylidisilanyl ether (6.1 g.) and crude *bispentamethylidisilanylamine* (29.2 g.) from which the pure amine (25.1 g.), b. p. 132.5—134°/40.5 mm., was isolated. After allowance for the formation of the ether by hydrolysis during handling, the yield of crude amine was 79.6% and that of pure amine was 68.5% [Found: C, 43.1; H, 11.2; N, 5.1; Si, 40.2%; *M* (cryoscopic in benzene) 276.3. $C_{10}H_{30}NSi_2$ requires C, 43.25; H, 11.25; N, 5.0; Si, 40.5%; *M*, 277.7]; the amine had d_4^{20} 0.8053, n_D^{30} 1.4556, $[R_L]_D$ 93.71 (calc., 93.33). Vapour pressures in the range

Vapour pressure (mm.) of bispentamethylidisilanylamine.

Temp.	105.7°	117.4°	124.8°	129.4°	134.4°	140.8°	146.8°	149.4°	152.4°	161.9°
V. p.: obs.	10.8	19.1	26.4	32.4	40.3	52.4	65.0	72.6	81.0	117.8
calc.	10.9	19.0	26.5	32.3	39.9	52.0	64.9	73.2	82.2	117.4

105.7—161.9° are represented by: $\log p(\text{mm.}) = 9.01378 - 3021.16/(273.18 + T)$ (T in °C). The extrapolated b. p. is 219.4°, the molar heat of vaporization is 13.83 kcal. mole⁻¹, and Trouton's constant is 28.1 cal. deg.⁻¹ mole⁻¹. No sign of thermal decomposition was observed during the above determinations.

Pentamethylidisilanyl Isocyanate.—Pentamethylidisilanyl chloride (34.1 g., 0.204 mole) was mixed with anhydrous ether (200 ml.) in a 500-ml. flask equipped with a water-jacketed condenser. To this was added, slowly and with stirring, silver cyanate (30.7 g., 0.205 mole). The reaction was slightly exothermic. The mixture was stirred at room temperature for ~10 hr. and then filtered and the precipitate was washed with anhydrous ether. The filtrate and washings were combined, the ether was removed by a rough distillation, and the residue was fractionated on the Podbielniak distillation apparatus in an atmosphere of dry nitrogen to give crude *pentamethylidisilanyl isocyanate* (24.0 g., 67.6%), b. p. 132—160°, from which the pure isocyanate (17.2 g., 48.5%), b. p. 159.4—160.0°, was isolated [Found: C, 41.6; H, 8.7; N, 8.1; Si, 32.4%; *M* (as above), 171.6. $C_6H_{15}NOSi_2$ requires C, 41.7; H, 9.0; N, 7.9; Si, 32.4%; *M*, 173.4], d_4^{30} 0.8537, n_D^{30} 1.4337, $[R_L]_D$ 52.86 (calc. for isocyanate, 52.76; for cyanate, 50.22). Vapour pressures are tabulated. Vapour pressures in the range 47.4—103.9° are represented

Vapour pressure (mm.) of pentamethylidisilanyl isocyanate.

Temp. ...	47.4°	58.7°	64.0°	68.9°	72.8°	76.6°	79.4°	81.8°	85.3°	88.0°	90.8°	93.1°	97.4°	103.9°
V. p.: obs.	10.9	17.5	25.4	31.3	37.3	44.4	50.5	55.6	64.7	72.1	79.8	87.8	103.5	133.3
calc.	11.1	17.6	25.1	31.4	37.4	44.2	49.9	55.3	64.0	71.5	80.0	87.7	103.8	133.0

by: $\log p(\text{mm.}) = 8.24711 - 2309.02/(273.18 + T)$. The extrapolated b. p. is 157.9°, the molar heat of vaporization is 10.57 kcal. mole⁻¹, and Trouton's constant is 24.5 cal. deg.⁻¹ mole⁻¹. No sign of thermal decomposition was observed during the above determinations.

Reaction of Bispentamethylidisilanyl Ether with Boron Trifluoride.—Boron trifluoride was passed into a 50-ml. round-bottomed flask equipped with a water-jacketed condenser and a magnetic stirrer, through a glass tube extending down the inside tube of the condenser. The excess of boron trifluoride passed out of the system through another glass tube extending from the top of the condenser to a trap held at -78° which in turn was connected to a mercury blow-off. The apparatus was flushed with dry nitrogen and then bispentamethylidisilanyl ether¹ (12.1 g., 0.044 mole) was placed in the flask and boron trifluoride was passed in while the contents were stirred. After a few minutes some white solid had been formed and the flask became warm. Boron trifluoride was passed in for 1 hr. at room temperature and then the flask was heated to the b. p. of the ether. Formation of white solid continued for ~3 hr. and then ceased. Heating was then discontinued. Distillation of the material in the flask, together with that which had collected in the -78° trap, produced crude pentamethylidisilanyl fluoride (11.0 g.), b. p. 90—101.5°, which afforded the pure fluoride (10.6 g.), b. p. 100—101.5° (lit.,¹⁵ 102°), the structure being confirmed by the infrared spectrum.¹⁶

¹⁵ Kumada, Yamaguchi, Yamamoto, Nakajima, and Shiina, *J. Org. Chem.*, 1956, **21**, 1264.

¹⁶ Pure fluoride was prepared by the method of Kumada *et al.*¹⁵ and its infrared spectrum was recorded.

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The white powdery residue in the flask had no infrared absorption characteristic of C-H or Si-Me linkages and it was believed to consist primarily of boron trioxide by analogy to the products of the reaction of bistrimethylsilyl ether with boron trifluoride.¹³ The crude disilanyl fluoride isolated, accounted for 84.4% of the pentamethyldisilanyl groups present in the starting material. It is believed that no other compounds except pentamethyldisilanyl fluoride and boron trioxide were formed in the reaction but that some of this fluoride was lost during the handling of the relatively small quantities of materials.

Reaction of Bis(pentamethyl)disilanylamine with Boron Trifluoride.—The apparatus was that described above. Bis(pentamethyl)disilanylamine (7.8 g., 0.028 mole) was stirred as boron trifluoride was passed in. The flask became hot immediately, solid began to be formed, and the liquid became somewhat yellow. After 1 hr. at room temperature the liquid was refluxed for 3 hr. while the passage of the trifluoride was continued. The small amount of liquid which had collected in the -78° trap was transferred to the reaction flask. Distillation gave crude pentamethyldisilanyl fluoride (6.1 g.), b. p. 71—101.5°, from which the pure fluoride (5.7 g.), b. p. 100—101.5° (correct infrared spectrum¹⁶), was isolated. The crude fluoride obtained accounted for 73.2% of the pentamethyldisilanyl groups present in the starting material. It is believed that the remainder were lost as fluoride during the handling of the relatively small quantities of materials since there was no evidence for the formation of any other organosilicon compound. A yellowish solid which had no infrared absorption characteristic of C-H or Si-Me linkages remained in the flask. By analogy with the final products of the reaction of bistrimethylsilylamine with boron trifluoride and with boron trichloride¹² it appears likely that this material was a polymeric *B*-fluoroborazen, (HNBF)_x.

Infrared Spectra.—Infrared spectra were taken with a Perkin-Elmer model 134 B Infracord double-beam recording spectrophotometer fitted with a sodium chloride optical system. The compounds were all dissolved in CCl₄ (~10% solution) and a 0.05 mm. cell equipped with sodium chloride windows was employed. The spectra are tabulated.

The infrared spectra of pentamethyldisilanyl compounds (cm.⁻¹).

(Me ₃ Si·SiMe ₂) ₂ NH	Me ₃ Si·SiMe ₂ NCO	Me ₃ Si·SiMe ₂ F	Interpretation	Ref.
	3775vw †		O-H stretch	19
3440vw			N-H stretch	8, a, b
3000s	3000m	3000m	C-H stretch	8, b, c, d
2950m	2950w	2950w	"	8, b, c, d
	2850sh		Unassigned	—
	2280vs		NCO stretch	17, 18
1500vw			N-H deformation	8, a, b
1430sh	1427w	1440w	CH ₃ deform. and/or NCO stretch	8, 17, 18, d
1400w	1395w	1400w	CH ₃ deformation	8, b, d
1305sh	1312vw	1312vw	Unassigned	—
1240vs	1250s	1250vs	CH ₃ deformation	8, 19, b, d
1180s			N-H deformation	8, a, b
1045vw †	1070vw †	1083w †	Si-O-Si stretch	19, b, d
928vs			Si-N-Si stretch	8, a, b
869s	878w	878sh	CH ₃ rock	8, b, d
		862vs	Si-F stretch	d
835vs	839s	837s	CH ₃ rock	8, 19, b
819—742vs *	819—742s *	810sh	Si-C stretch and/or CH ₃ rock	8, 19, b, d
		798vs		
		778sh		
		755sh		
718m	722w	715w	Unassigned	—
688m	695m	692w	Si-C stretch	8, b, d
	673m		Unassigned	—

† Impurity. * Transmittance constant between wavelengths given.

(a) Fessenden, *J. Org. Chem.*, 1960, **25**, 2191. (b) Kriegsmann, *Z. Elektrochem.*, 1957, **61**, 1088. (c) Bellamy, "The Infra-red Spectra of Complex Molecules," 2nd edn., John Wiley and Sons, New York, 1959, pp. 13—31. (d) Ebsworth, Onyszchuk, and Sheppard, *J.*, 1958, 1453.

The infrared spectrum of the isocyanate is similar to that of trimethylsilyl isocyanate¹⁷ and silicon tetrakisocyanate¹⁸ in that the symmetrical NCO stretching vibration falls at 1427 cm.⁻¹ [1435 cm.⁻¹ for Me₃Si·NCO and 1482 cm.⁻¹ for Si(NCO)₄] and the antisymmetrical at

¹⁷ Goubeau, Heubach, Paulin, and Widmaier, *Z. anorg. Chem.*, 1959, **300**, 194.

¹⁸ Miller and Carlson, *Spectrochim. Acta*, 1961, **17**, 977.

2280 cm^{-1} [2282 cm^{-1} for $\text{Me}_3\text{Si}\cdot\text{NCO}$ and 2284 cm^{-1} for $\text{Si}(\text{NCO})_4$]. This similarity, together with the absence of Si-O-C absorption in the 1050—1090 cm^{-1} region¹⁹ and the absence of normal cyanate absorption in the vicinity of 2250 and 1200 cm^{-1} (ref. 18) confirm the isocyanate structure of the compound.

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¹⁹ Bellamy, "The Infra-red Spectra of Complex Molecules," 2nd edition, John Wiley and Sons, New York, 1959, pp. 334—342.
