959. *The Preparation and Properties of Disilylcyanamide.*

By E. A. V. Ebsworth and M. J. Mays.

Disilylcyanamide, $(SiH_3)_2N{\cdot}CN$, has been obtained by interaction of silver cyanamide and bromo- or iodo-silane, and some of its physical properties have been determined. The silicon–nitrogen bonds are broken almost quantitatively by hydrogen chloride; an unstable addition compound is formed with boron trifluoride. The reactions with certain silver salts have also been investigated.

Iodosilane reacts with a number of salts of silver, mercury(II) and lead(II) to give the iodide of the heavy metal and the silyl derivative of the anion;[1] we have prepared disilylcyanamide, $(SiH_3)_2N{\cdot}CN$, from silver cyanamide and iodosilane: $2SiH_3I + Ag_2N{\cdot}CN = (SiH_3)_2N{\cdot}CN + 2AgI$. Iodosilane vapour is allowed to pass over a mixture of silver cyanamide and glass wool, initially at room temperature: yields are never greater than 25% and are often less, but attempts to improve them by varying the conditions of the reaction have so far proved unsuccessful. Since it has been shown that disilylcyanamide decomposes in the presence of silver cyanamide, the low yields are perhaps not surprising.

Disilylcyanamide is a colourless liquid which is stable at room temperature for days in sealed apparatus, but decomposes slightly if heated to about 80° for some hours. Its Trouton constant shows that there is little association in the liquid phase. The infrared

---

[1] Emeléus, MacDiarmid, and Maddock, *J. Inorg. Nuclear Chem.*, 1955, **1**, 194; MacDiarmid, *ibid.*, 1955, **2**, 88; Downs and Ebsworth, *J.*, 1960, 3516.

spectrum has been recorded, but no vibrational assignments have yet been made—these are under study. The nuclear magnetic resonance shows chemical shifts of the protons very close to those obtained for trisilylamine, *N*-methylsilylamines, and silyl isothiocyanate, suggesting that this parameter is largely determined by the nature of the other atom bound to silicon; the ^{29}SiH coupling constant is closer to the values obtained for disiloxane and disilyl sulphide (see Table).

Nuclear magnetic resonance couplings and SiH chemical shifts in disilylcyanamide and related compounds.

	τ ($\pm$0·01)	$J_{^{29}\mathrm{SiH}}$		τ ($\pm$0·01)	$J_{^{29}\mathrm{SiH}}$
$(SiH_3)_2N{\cdot}CN$	5·55	225 ± 1	$SiH_3{\cdot}NCS$ [b]	5·55	240 ± 2
$(SiH_3)_3N$ [a]	5·56	212 ± 2	$(SiH_3)_2O$ [b]	5·39	221·5 ± 0·2
$(SiH_3)_2N{\cdot}CH_3$ [a]	5·56	212 ± 2	$(SiH_3)_2S$ [b]	5·66	224·0 ± 0·3
$SiH_3{\cdot}N(CH_3)_2$ [a]	5·66 (±0·04)	208 ± 2			

[a] Ebsworth and Sheppard, *J. Inorg. Nuclear Chem.*, 1959, **9**, 95. [b] Ebsworth and Turner, unpublished work.

None of the physical properties so far studied indicates whether the compound has the structure $(SiH_3)_2N{\cdot}CN$, as so far assumed, or $SiH_3{\cdot}N{:}C{:}N{\cdot}SiH_3$, which is also possible in principle; the vibrational spectrum may help to decide this point.

The compound reacts with hydrogen chloride according to the equation $(SiH_3)_2N{\cdot}CN + 4HCl = 2SiH_3Cl + H_2N{\cdot}CCl_2{\cdot}NH_2$. It reacts with silver thiocyanate and with silver chloride at room temperature, forming the silyl derivative of the anion; though neither reaction is quantitative, none of the disilylcyanamide was recovered in either case. Unchanged disilylcyanamide, however, was recovered after passage over silver bromide, and no bromosilane was detected among the products of the reaction; in a subsequent experiment, bromosilane was found to react with silver cyanamide, to give disilylcyanamide, so it seems that cyanamide should be included in MacDiarmid's conversion series [2] between bromide and chloride.

The reaction between disilylcyanamide and boron trifluoride is complex. When an excess of boron trifluoride is kept with disilylcyanamide for 18 hours at —78°, the volatile products consist of a mixture of boron trifluoride and fluorosilane; analysis suggest that the combining ratio (BF_3 : cyanamide) approaches 2 : 1 at low temperatures. When the solid residue attains room temperature, more boron trifluoride and fluorosilane are evolved, leaving a white solid which when heated gives off fluorosilane but no boron trifluoride. These observations may be interpreted in terms of the following reactions:

$$\begin{array}{ll}
(SiH_3)_2N{\cdot}CN + BF_3 \rightleftharpoons (SiH_3)_2N(BF_3){\cdot}CN \quad . \; . \; . \; . \; . \; . \; . \; . \; . & (1) \\
(SiH_3)_2N(BF_3){\cdot}CN \longrightarrow SiH_3F + SiH_3{\cdot}N(BF_2){\cdot}CN \quad . \; . \; . \; . \; . \; . \; . & (2) \\
SiH_3{\cdot}N(BF_2){\cdot}CN + BF_3 \rightleftharpoons [SiH_3{\cdot}N(BF_2){\cdot}CN]BF_3 \quad . \; . \; . \; . \; . \; . \; . & (3) \\
\qquad\Big\downarrow \text{Heat} & \\
SiH_3F + (BFCN_2) \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . & (4)
\end{array}$$

About 80% of the silyl groups present initially in the disilylcyanamide are evolved as fluorosilane after 18 hours at —78°, showing that reaction (4) occurs slowly even at this low temperature. This complex reaction is in keeping with those of silylamines and silyl cyanides with boron trifluoride.[3]

EXPERIMENTAL

Preparation of Disilylcyanamide.—In a typical experiment, iodosilane (1·0 g.) was allowed to pass as vapour over a mixture of silver cyanamide (6 g.) and powdered glass wool (12 g.). The solid became grey-black and hot, while a little hydrogen was produced. From the volatile products *disilylcyanamide* (0·065 g.) was obtained (Found: SiH, 5·8; N, 27·4%; *M*, 102.

[2] MacDiarmid, *Quart. Rev.*, 1956, **10**, 208.

[3] Sujishi and Witz, *J. Amer. Chem. Soc.*, 1957, **79**, 2447; Ebsworth and Emeleus, *J.*, 1958, 2150; Evers, Freitag, Kriner, MacDiarmid, and Sujishi, *J. Inorg. Nuclear Chem.*, 1959, **13**, 239.

$CH_6N_2Si_2$ requires SiH, 5·9; N, 27·4%; *M*, 102). The other volatile products included silane, disiloxane, and hydrogen cyanide (identified spectroscopically and from molecular-weight measurements). In other experiments, disilylcyanamide was obtained from the reactions between iodosilane and lead(II) cyanamide, and from bromosilane and silver cyanamide, but the yield was 10—20% in each case; when iodosilane was allowed to react with undiluted silver cyanamide, the mixture exploded.

Physical properties of the product were determined for samples which had been repeatedly distilled at −46° and condensed at −64°. The compound melts at −74·8° ± 0·5°; the b. p. (extrapolated over 4° from a vapour-pressure curve) is 84·7° ± 0·5°, and the vapour pressures between 50° and the boiling point are given by the equation $\log_{10} p(\text{mm.}) = 7{\cdot}800 - 1761/T$. The vapour pressure at 0° is 18·5 mm.

The latent heat at the b. p. is 8100 ± 50 cal./mole^{-1} and Trouton's constant is 22·6. The vapour pressures obtained on cooling showed that there had been slight decomposition during the experiment.

The proton resonance spectrum of the compound dissolved in cyclohexane consisted of the expected single sharp peak, with satellites due to ^{29}SiH groups; the chemical shift τ in 10% solution measured relative to cyclohexane as solvent is 5·55 ± 0·01 p.p.m., and is unchanged for a 3% solution in the same solvent. The ^{29}SiH coupling constant is 225 ± 1 c/s. Strong infrared absorption bands appear at 2200, 950, 800, and 740 cm.$^{-1}$.

The compound was stable at room temperature in sealed apparatus for several days, but decomposed slightly during 3 hr. at 80°. The infrared spectrum of the decomposition products suggests that a trace of silane had been formed.

In the presence of solid silver cyanamide, decomposition is rapid and almost explosive at room temperature, being complete in a few minutes. The yellow silver salt becomes grey, and the volatile material recovered includes silane, hydrogen cyanide, and a non-condensable gas.

Reactions.—(a) *With hydrogen chloride.* Disilylcyanamide (0·0448 g.) and hydrogen chloride (0·0788 g.) were mixed and kept at −78° for 18 hr. The volatile products consisted of hydrogen chloride (0·0132 g.) (Found: *M*, 36·7; v. p. at −112°, 122 mm. Calc.: *M*, 36·5; v. p.[4] at −112°, 117 mm.) and chlorosilane (0·0613 g.) (Found: *M*, 66·6; v. p. at −64°, 131 cm. Calc.: *M*, 66·5; v. p.[5] at −64°, 137 mm.); an involatile white solid remained, soluble in water (Found, in a subsequent experiment: C, 10·7; H, 3·4; N, 24·4. Calc. for $CCl_2H_4N_2$: C, 10·5; H, 3·5; N, 24·4%); the aqueous solution was boiled with sodium hydroxide; and treatment with nitric acid and silver nitrate then gave 0·1256 g. of silver chloride. The molar ratio, cyanamide consumed : HCl consumed : SiH_3Cl formed : chloride in residue is 1·00 : 4·09 : 1·04 : 2·00.

(b) *With boron trifluoride.* Disilylcyanamide (0·33 mmole) was kept with boron trifluoride (1·78 mmoles) at −78° for 18 hr. The volatile material recovered at −96° (*M*, 63) was shown spectroscopically to be a mixture of boron trifluoride (*M*, 68) and fluorosilane (*M* 50); these compounds cannot be separated by distillation. A white solid residue evolved a mixture of boron trifluoride and fluorosilane when warmed to room temperature, and gave off fluorosilane alone when heated to 100° for 15 min.; 2·0 mmoles of volatile material were recovered in all. The solid residue left after heating was shown qualitatively to contain Si–H bonds (Found: C, 13·8; H, 1·8; N, 31·7. Calc. for $BFCN_2$: C, 17·1; N, 40·1%).

In a second experiment, disilylcyanamide (0·63 mmole) and boron trifluoride (2·63 mmole) were kept together at −78° for 18 hr.; 2·45 mmoles of volatile material were recovered at −96°, and when hydrolysed gave 3·32 mmoles of hydrogen. On the assumptions that all the Si–H bonds in the products were originally present as fluorosilane, and that no other volatile product was formed initially, the amount of boron trifluoride recovered is found by difference to be 1·29 mmoles, giving a molar combining ratio under the stated conditions of 1·86 : 1 [BF_3 : $(SiH_3)_2N{\cdot}CN$]. In a further experiment, disilylcyanamide (0·39 mmole) was kept with a 2 : 1 molar excess of boron trifluoride at −78° for 15 min.; a mixture of fluorosilane and boron trifluoride (1·66 mmoles) was recovered at −96°. When disilylcyanamide was kept with a large excess of boron trifluoride at −78° for 5 min., the volatile products recovered at −96° contained appreciable amounts of fluorosilane.

(c) *With silver chloride.* Disilylcyanamide (0·0175 g.) was allowed to pass as vapour over a 2 : 1 mixture of glass wool and silver chloride; chlorosilane was recovered (0·0078 g.) (Found:

---

[4] Giaque and Wiebe, *J. Amer. Chem. Soc.*, 1928, **50**, 101.

[5] Stock and Somieski, *Ber.*, 1919, **51**, 695.

M, 67; v. p. at $-85°$, 28 mm. Calc.: *M*, 66·5; v. p.[5] at $-85°$, 35 mm.); the identification was confirmed spectroscopically.

(d) *With silver thiocyanate.* When disilylcyanamide (0·016 g.) was allowed to pass as vapour over a 2 : 1 mixture of glass wool and silver thiocyanate, only 0·003 g. of volatile material was recovered. This had an infrared spectrum identical with that of silyl isothiocyanate, and when hydrolysed gave thiocyanate ion.

(e) *With silver bromide.* When disilylcyanamide (0·020 g.) was allowed to pass as vapour over a 2 : 1 mixture of powdered glass wool and silver bromide, volatile material was recovered [(0·014 g.) (v. p. at 0°, 31 mm. Calc. for SiH_3Br: v. p. at 0°, 710 mm.)]. The infrared spectrum showed that no bromosilane was present, and that the main component was disilylcyanamide. It was concluded that some decomposition of the starting material had occurred in the presence of the silver salt.

Starting Materials.—Iodosilane was prepared by treating silane with hydrogen iodide in the presence of aluminium iodide at 100°.[6] A solution of cyanamide was obtained from calcium cyanamide and sulphuric acid,[7] and on neutralization with quicklime and treatment with silver nitrate solution gave silver cyanamide.

We are grateful to Mr. S. Frankiss for help in recording the nuclear magnetic resonance spectra, to the Wellcome Foundation for lending the nuclear magnetic resonance spectrometer to the Department, and to the Department of Scientific and Industrial Research for a maintenance grant (to M. J. M.).

INORGANIC CHEMISTRY LABORATORY,
THE UNIVERSITY, CAMBRIDGE.

[*Received, May* 18*th*, 1961.]

---

[6] Emeléus, Maddock, and Reid, *J.*, 1941, 353.

[7] Nowak, *Przemysl Chem.*, 1957, **13**, 688; *Chem. Abs.*, 1958, **52**, 9625.