945. *The Preparation and Properties of Silyl Isocyanate.*

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Silyl isocyanate has been prepared for the first time, and some of its physical properties have been determined. Its reactions with acid, alkali, methanol, hydrogen chloride, ammonia, phosphines, diborane, and silver salts have been investigated; in the reaction with boron trifluoroide, the very unstable difluoroisocyanatoboron is formed at low temperatures.

MANY silyl compounds have been prepared by allowing iodosilane vapour to pass over the silver, mercury(II), or lead(II) salts of the appropriate anions,[1] but the product may be unstable in the presence of the metal compound, so that yields are sometimes low.[2] We have found that dilution of the iodosilane vapour with nitrogen leads to substantially greater yields; by using this modification we have obtained silyl isocyanate from silver cyanate and iodosilane in yields of up to 25%, though previous attempts to prepare the compound by using undiluted iodosilane vapour had been unsuccessful.[3]

Silyl isocyanate is a colourless volatile liquid which, when pure, is stable for at least two weeks in a sealed apparatus at room temperature. The normal Trouton constant shows that there is little or no association in the liquid phase; in the proton resonance spectrum the chemical shift and the ^{29}SiH coupling constant are very close to those of silyl isothiocyanate.[4] The vapour-phase infrared bands show the characteristic contours associated with the parallel and the perpendicular bands of a symmetric top molecule in which one moment of inertia is small, and the " strong, weak, weak, strong " rotational detail in the perpendicular bands is consistent with a linear arrangement of the heavy atoms, as in silyl isothiocyanate; [5] detailed studies of the high-resolution infrared and the microwave spectrum are in progress.

In the presence of impurities the compound is unstable at room temperature. Polymerization is catalysed by diborane and by cyanic acid, and decomposition in the presence of silver cyanate is rapid at room temperature; this accounts for the previous failure to obtain the compound. Decomposition is also rapid in the presence of triethylphosphine at room temperature; no sign was detected of the formation of a dimer such as aryl isocyanates give under these conditions.[6] Phosphine itself, however, did not induce decomposition within one hour at room temperature. This extreme sensitivity to traces of impurity makes it very difficult to assess the relative stabilities of silyl isocyanate and silyl isothiocyanate. Reaction with an excess of ammonia at −78° gives monosilane and an involatile solid product.

The compound reacts quantitatively with alkali, to give hydrogen and a solution of sodium cyanate; hydrolysis with acid gives carbon dioxide quantitatively, presumably from cyanate ion, together with some hydrogen. With an excess of methanol there is a complex reaction; the Si–N and the Si–H bonds are attacked, giving methyl carbamate, hydrogen, and a mixture of methoxysilanes. Even with equimolar amounts of the two reactants the Si–H as well as the Si–N bonds are attacked. Hydrogen chloride breaks the Si–N bond, forming silyl chloride and cyanic acid, but an excess is required for complete reaction, probably because the cyanic acid formed reacts with hydrogen chloride.

Despite the decomposition of silyl isocyanate in the presence of diborane at room temperature, the two compounds do not combine either at room temperature or at −78°.

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[1] Emeléus, MacDiarmid, and Maddock, *J. Inorg. Nuclear Chem.*, 1955, **1**, 194.
[2] Ebsworth and Mays, *J.*, 1961, 4879.
[3] MacDiarmid, *J. Inorg. Nuclear Chem.*, 1955, **2**, 88.
[4] Ebsworth and Turner, unpublished work.
[5] Ebsworth, Mould, Taylor, Wilkinson, and Woodward, *Trans. Faraday Soc.*, 1962, **58**, 1069.
[6] Saunders and Slocombe, *Chem. Rev.*, 1943, **43**, 211.

With boron trifluoride, the reaction at −78° is described by the equation:

$$SiH_3\cdot NCO + BF_3 = SiH_3F + [BF_2\cdot NCO]$$

When the reaction products are allowed to warm to room temperature, boron trifluoride is obtained, with small amounts of a very unstable volatile liquid. This decomposes rapidly at room temperature to give boron trifluoride and a solid; its infrared spectrum contains bands at frequencies (1390, 1320, and 1310 cm.$^{-1}$) that are observed in the spectra of a number of BF_2X derivatives,[7] besides bands characteristic of the isocyanate group, and the liquid has therefore been identified as difluoroisocyanatoboron. The decomposition to boron trifluoride and polymeric boron isocyanate is rapid and complete at room temperature:

$$3BF_2\cdot NCO = 2BF_3 + B(NCO)_3$$

Several reactions between silyl compounds and silver salts were studied to try to determine the position of cyanate in the conversion series proposed by MacDiarmid[8] for silyl compounds. Silyl isocyanate forms little or no silyl isothiocyanate when allowed to pass over solid silver thiocyanate, while the reverse reaction leads to extensive formation of the cyanate; from these and other observations we have concluded that isocyanate comes after isothiocyanate in the series: Cl, CN, NCS, NCO. This is in agreement with Eaborn's series for trialkylsilyl compounds.[9]

EXPERIMENTAL

Preparation.—In a typical experiment, a slow stream of nitrogen, dried by passage through concentrated sulphuric acid and a molecular sieve, was bubbled through iodosilane (1·5 g.) at −46°, and then over a mixture of silver cyanate (8 g.) and powdered glass (16 g.). The volatile products were condensed at −196° and the non-condensable gases were pumped away continuously. During the reaction, a hot band travelled slowly along the reaction tube and the solid turned grey-black; cyanic acid, silicon tetraisocyanate, and a trace of silyl isocyanate (all identified spectroscopically) were the volatile products at this stage. When the hot zone reached the end of the tube, the proportion of silyl isocyanate in the products increased, and some unchanged iodosilane was recovered. The volatile products were allowed to warm to room temperature at which cyanic acid (which cannot be separated from silyl isocyanate by fractional distillation) forms an involatile adduct with some of the unchanged iodosilane; the mixture was then passed over silver thiocyanate, and the unchanged iodosilane was converted into silyl isothiocyanate which can be separated without difficulty from the isocyanate. By repeated distillation at −78° and condensation at −112°, pure *silyl isocyanate* (0·150 g.) was obtained (Found: C, 16·3; H, 4·1; N, 19·1%; *M*, 73. CH_3NOSi requires C, 16·4; H, 4·1; N, 19·2%; *M*, 73). The yield, based on the amount of silyl iodide taken, was 20%. Cooling of the reaction tube to −46° improved the yield but substantially reduced the extent of reaction with the silver salt, and so was not generally employed.

Physical Properties.—Silyl isocyanate is a colourless liquid (m. p. −88·6° ± 0·5°). The b. p. (extrapolated over 2°) is 18·1° ± 0·2°; between −10° and the b. p., the vapour pressure is related to the temperature by the expression: $\log_{10} p$ (mm.) = $-1428/T + 7{\cdot}783$ and is 362 mm. at 0°. Over the same range the latent heat of vaporization is 6540 ± 50 cal./mol., and Trouton's constant is 22·5. Infrared bands were observed at 2300—2200, 1450, 960, and 710 cm.$^{-1}$.

The nuclear magnetic resonance spectrum was recorded on a Varian Associates V4300B spectrometer with flux stabiliser and sample spinning, operating at 40 Mc./sec. The proton resonance spectrum of the compound dissolved in cyclohexane consisted of the expected single sharp peak with satellites due to ^{29}SiH groups; in 15% solution in cyclohexane as internal standard and solvent ($\tau = 8{\cdot}56$), $\tau = 5{\cdot}58 \pm 0{\cdot}005$ p.p.m., and $J(^{29}\text{SiH}) = 231{\cdot}5 \pm 0{\cdot}7$.

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[7] Brinckman and Stone, *J. Amer. Chem. Soc.*, 1960, **82**, 6218; Ebsworth, Ph.D. Thesis, Cambridge, 1957.

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

[9] Eaborn, *J.*, 1950, 3077.

The ultraviolet spectrum of the compound in the vapour phase showed no maxima between 200 and 360 mμ. The spectrum of methyl isocyanate, recorded under the same conditions, showed $\lambda_{max.}$ 280 mμ (log ε 1·52), with marked and extensive vibrational fine structure in which at least two series of peaks could be distinguished.

Stability.—After 2 weeks at room temperature in a sealed glass apparatus, the vapour pressure of a pure sample of the compound (36·2 mg.) had dropped from 362 to 337 mm., and a small amount (0·1 ml.) of non-condensable gas had formed; 95% of the sample, however, was recovered unchanged (*M*, 72; identification confirmed spectroscopically). A sample contaminated with a large proportion of cyanic acid polymerized almost completely in 12 hr. under the same conditions. When a mixture of silyl isocyanate (26·8 mg.) and silver cyanate (1 g.) was allowed to warm to room temperature, the silver salt blackened rapidly; after 5 min., 10·8 ml. of non-condensable gas had been evolved. A small amount of silyl isocyanate was recovered (identified spectroscopically); 1·3 moles of non-condensable gas were evolved for each mole of silyl isocyanate taken in two such experiments.

Reactions.—(*a*) *With diborane and phosphine.* The compound neither reacted with, nor was decomposed by, diborane or phosphine at −78° during 12 hr., the starting materials being recovered. No reaction was observed between silyl isocyanate and phosphine at room temperature during 1 hr. When a mixture of diborane (1·31 mmoles) and silyl isocyanate (0·596 mmole) was kept at room temperature for 1 hr., the diborane was recovered, with silyl isocyanate (0·485 mmole); the white solid which remained effervesced when treated with alkali.

(*b*) *With triethylphosphine.* Silyl isocyanate (0·0359 g.) and triethylphosphine (0·016 g.) were kept at room temperature for 5 min.; the mixture bubbled vigorously and became cloudy. No non-condensable gas was formed; monosilane (0·0054 g.) was recovered, with silyl isocyanate (~0·006 g.) (both identified spectroscopically), and a product, barely volatile at −46°, whose infrared spectrum indicated the presence of triethylphosphine, SiH, and NCO groups, though there was no absorption between 2000 and 1500 cm.$^{-1}$ where the CO groups of an isocyanate dimer would be expected. Traces of a viscous liquid and an involatile solid remained in the reaction tube.

(*c*) *With ammonia.* Silyl isocyanate (0·456 mmole) and ammonia (1·465 mmoles) were kept at −78° for 1 hr.; monosilane (0·2 mmole) (identified spectroscopically) was recovered at this temperature. When the system warmed to room temperature, more monosilane (~0·05 mmole) was evolved, together with ammonia (0·906 mmole) (Found: *M*, 17·6; v. p. 49·7 mm. at −78°. Calc. for H_3N: *M*, 17; v. p. 44 mm. at −78° [10]). The white solid remaining in the reaction tube was shaken with water and filtered; the filtrate was shown qualitatively to contain cyanate ion, while the white solid residue effervesced on treatment with alkali and gave ammonia without heating.

(*d*) *Hydrolysis.* These reactions were used to analyse the compound. (i) With alkali. Silyl isocyanate (0·594 mmole) was shaken vigorously with 40% sodium hydroxide solution (15 ml.). Non-condensable gas (1·79 mmoles) was liberated. The hydrolysate effervesced on acidification and when an excess of 40% sodium hydroxide was added to the acidified solution, ammonia (0·597 mmole) was liberated, collected in a saturated solution of boric acid, and titrated against standard hydrochloric acid (Methyl Red).

(ii) With acid. Silyl isocyanate (0·556 mmole) was hydrolysed with 30% sulphuric acid (9 ml.). Much non-condensable gas was evolved, together with carbon dioxide which was collected in standard barium hydroxide solution, the excess of hydroxide being titrated against standard acid (0·551 mmole of CO_2 evolved). The hydrolysate gave ammonia (0·547 mmole) when made alkaline.

(*e*) *With methanol.* Silyl isocyanate (0·393 mmole) and methanol (1·387 mmoles) were mixed and kept at room temperature for 18 hr. Colourless needles appeared in the liquid; 0·662 mmole of non-condensable gas was collected, with monosilane (~0·05 mmole) (identified spectroscopically). The remaining volatile product, barely volatile at −46° (*M*, 110; v. p. 18·4 mm. at 0°), was shown spectroscopically to be a mixture of trimethoxysilane (*M*, 122; v. p. 18·7 mm. at 0° [11]) with a little tetramethoxysilane (*M*, 152; m. p. 2° [12]) and unchanged methanol (*M*, 32; v. p. 28 mm. at 0° [13]). The colourless crystals were identified as methyl carbamate, m. p.

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[10] Stock, Henning, and Kuss, *Ber.*, 1921, **54**, 1119.

[11] MacDiarmid, *J. Amer. Chem. Soc.*, 1959, **81**, 5109.

[12] Sternbach and Rochow, *J. Amer. Chem. Soc.*, 1948, **70**, 2170.

[13] Richardson, *J.*, 1886, **59**, 762.

55° (lit.,[14] 56°) (Found: C, 32·3; H, 6·9; N, 18·4. Calc. for $C_2H_5NO_2$: C, 32·0; H, 6·7; N, 18·7%). In a second experiment, silyl isocyanate (0·426 mmole) and methanol (0·422 mmole) were allowed to react under the same conditions as before; non-condensable gas (0·20 mmole) was evolved, with monosilane (0·21 mmole) (Found: *M*, 32·2; identification confirmed spectroscopically). The infrared spectrum of the remaining volatile material (11·5 mg.) gave bands characteristic of methoxy- and cyanato-groups, with weak SiH-absorption; the material contained 10·8% of nitrogen. A small amount of non-volatile solid was also formed.

(*f*) *With hydrogen chloride.* Silyl isocyanate (0·0301 g.) and hydrogen chloride (0·0512 g.) were kept at −78° for 18 hr. Hydrogen chloride (0·0303 g.) was recovered (Found: *M*, 37·0; v. p. 120 mm. at −112°. Calc. for HCl: *M*, 36·5; v. p. 117 mm. at −112° [15]), with chlorosilane (0·0252 g.) (Found: *M*, 68; v. p. 49 mm. at −80°. Calc. for H_3ClSi: *M*, 66·5; v. p. 48 mm. at −80° [16]) and cyanic acid (0·010 g.) (Found: *M*, 46. Calc. for CHNO: *M*, 43); all identifications were confirmed spectroscopically. Traces of white solid remained in the reaction tube. The molar ratio (isocyanate consumed : hydrogen chloride consumed : chlorosilane recovered : cyanic acid recovered) is 1 : 1·39 : 0·92 : 0·57.

(*g*) *With boron trifluoride.* Silyl isocyanate (0·475 mmole) was kept with boron trifluoride (1·840 mmoles) at −78° for 18 hr. Volatile material (1·781 mmoles) recovered at −112° was shown to be a mixture of boron trifluoride and fluorosilane, which could not be separated by fractional distillation; alkaline hydrolysis of the mixture gave hydrogen (1·333 mmoles), corresponding to 0·444 mmole of fluorosilane (if all the Si–H bonds in the mixture are assumed to be present as fluorosilane); by difference, the amount of boron trifluoride in the mixture was 1·34 mmoles, giving a molar ratio (boron trifluoride consumed : silyl isocyanate consumed : fluorosilane recovered) of 1·06 : 1·00 : 0·94. On warming to room temperature, the white residue in the reaction vessel melted to a colourless liquid, and when distilled at room temperature left a white involatile solid. On distillation, a liquid was obtained, barely volatile at room temperature, that deposited a white solid each time it was distilled. The infrared spectrum of its vapour showed absorption characteristic of boron trifluoride and a trace of fluorosilane, with additional peaks at 2300s, 1380m, 1320ms, and 1310ms $cm.^{-1}$; the first of these is associated with isocyanates and the other three with BF_2-compounds.[7] These additional peaks disappeared from the spectrum after two more distillations, at which stage an involatile white solid residue remained, the only other product being boron trifluoride (0·309 mole) (Found: *M*, 67·8. Calc. for BF_3: *M*, 67·8) (identification confirmed spectroscopically). The molar ratio (silyl isocyanate consumed: boron trifluoride recovered from adduct) was 1 : 0·65. The white solid remaining in the reaction tube and the vacuum line was shown qualitatively to contain boron and cyanate.

(*h*) *With silver salts.* Silyl isocyanate was recovered unchanged after passing as vapour over silver thiocyanate at room temperature. When silyl isothiocyanate was allowed to distil over solid silver cyanide, no silyl cyanide was recovered; the volatile material consisted of silyl isothiocyanate (Found: *M*, 90; v. p. 15·8 mm. at 0°. Calc. for CH_3NSSi: *M*, 89; v. p. 16 mm. at 0° [3]), with a trace of monosilane (identified spectroscopically). When silyl cyanide was allowed to distil over solid silver thiocyanate, a mixture of silyl cyanide and silyl isothiocyanate was recovered (identified spectroscopically).

Preparation of Starting Materials.—Iodosilane was prepared from monosilane and hydrogen iodide in the presence of aluminium iodide; [17] silver salts were prepared by precipitation from neutral solution.

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[14] Wagner, *Z. phys. Chem.*, [B], 1939, **43**, 336.
[15] Giaque and Wiebe, *J. Amer. Chem. Soc.*, 1928, **50**, 101.
[16] Stock and Somieski, *Ber.*, 1919, **52**, 695.
[17] Emeléus, Maddock, and Reid, *J.*, 1941, 353.