tetraborane consumed in Experiments P-1 through P-5 was 646.5 cc. The total pentaborane-11 produced was 361.1 cc., indicating a yield of 70%.

Since the first 15 min. of each of the latter two experiments was identical to P-1, it was believed that the actual effect of the diborane was probably greater than the figures indicated. A considerably longer series of experiments, P-6, in which the contribution of the first 15-min. segment is less significant and in which the diborane pressure was allowed to build up, illustrates this point. Therefore, it appears that the reaction given in eq. 3 is reversible and that P-6 represents the best conditions for the preparation of pentaborane-11.

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Trialkyl- and Triaryl(iso)cyanosilanes[1]

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Several new syntheses for trialkyl- and triaryl(iso)cyanosilanes have been developed. Infrared studies suggest that these compounds may be equilibrium mixtures of the cyanide and isocyanide forms. The previously unreported antimony tricyanide and germanium tetracyanide have been prepared by exchange reactions between trimethyl(iso)cyanosilane and the corresponding metal chloride.

Organo(iso)cyanosilanes have been prepared from the corresponding halosilanes and silver cyanide.[2–7] Satisfactory yields usually are obtained from bromo and iodo compounds but not from the chlorosilanes. A brief study of the reaction of trimethylchlorosilane with silver cyanide demonstrated that a significant improvement in yield could be achieved by conducting the reaction in an autoclave at elevated temperatures. For example, at 125°, trimethyl(iso)cyanosilane was obtained in about 40% yield, compared to 14% reported[4] from runs in refluxing benzene.

In a search for alternative methods[8] for preparing the (iso)cyanosilanes, four new syntheses were found. These are (1) reaction of a chlorosilane with potassium mercuricyanide in dimethylformamide, (2) reaction of a hexaalkyldisilazane with hydrogen cyanide, (3) replacement of a methoxyl group on silicon by reaction with trimethylacetyl cyanide in the presence of aluminum chloride and (4) exchange between an (iso)cyanosilane and a chlorosilane.

$$2\mathrm{R_3SiCl} \xrightarrow{\mathrm{K_2Hg(CN)_4}} 2\mathrm{R_3Si(CN)} + 2\mathrm{KCl} + \mathrm{Hg(CN)_2} \quad (1)$$

$$\mathrm{R_3SiNHSiR_3} + 3\mathrm{HCN} \longrightarrow 2\mathrm{R_3Si(CN)} + \mathrm{NH_4CN} \quad (2)$$

$$\mathrm{R_3SiOCH_3} + \mathrm{(CH_3)_3CCOCN} \xrightarrow{\mathrm{AlCl_3}} \mathrm{R_3Si(CN)} + \mathrm{(CH_3)_3CCOOCH_3} \quad (3)$$

$$\mathrm{R_3SiCl} + \mathrm{R'_3Si(CN)} \longrightarrow \mathrm{R_3Si(CN)} + \mathrm{R'_3SiCl} \quad (4)$$

Methods 1 and 2 are probably general although they have been used only to prepare trimethyl(iso)cyanosilane. Yields are comparable to the best results obtained with silver cyanide. The third method, which should be applicable in all cases where the boiling point of the methoxysilane is above that of methyl trimethylacetate (b.p. 102°), was used to prepare triethyl(iso)cyanosilane in 64% yield. Triphenyl(iso)cyanosilane also was prepared by this method, although a pure product was not obtained. Triphenyl(iso)cyanosilane was obtained in 66% yield by the exchange reaction between trimethyl(iso)cyanosilane and triphenylchlorosilane (method 4).

The structure of the (iso)cyanosilanes has not been conclusively established. Most recently, McBride and Beachell[5] have reported that the isocyanide structure is favored on the basis of their chemical and infrared studies. The principal infrared evidence was the presence of a strong band at $6.28\ \mu$ for both *t*-butyl isocyanide and trimethyl(iso)cyanosilane, and the absence of such a band in normal cyanides. These authors do, however, point out that the infrared spectrum in the region characteristic of the cyanide and isocyanide groups could be interpreted as favoring the cyanide form or a mixture of the two forms.

In our work, new infrared data suggest that the trialkyl(iso)cyanosilanes exist as equilibrium mixtures of the cyanide and isocyanide isomers with the former predominating at room temperature. For both trimethyl- and triethyl(iso)cyanosilane, the existence of two forms is indicated by the presence of a CN band at $4.76\ \mu$ in addition to the one at $4.58\ \mu$ that was reported by McBride and Beachell. This is shown for triethyl(iso)cyano of silane in Fig. 1. It has been observed[9a] that the

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[1] The nomenclature "(iso)cyanosilane" is used here in view of the uncertain structure of these compounds.

[2] H. Emeléus, A. G. Maddock and C. Reid, *J. Chem. Soc.*, 353 (1941).

[3] C. Eaborn, *ibid.*, 2755 (1949).

[4] C. Eaborn, *ibid.*, 3077 (1950).

[5] J. J. McBride and H. C. Beachell, THIS JOURNAL, **74**, 5247 (1952).

[6] H. Emeléus, M. Onyszchuk and W. Kuchen, *Z. anorg. allgem. Chem.*, **283**, 74 (1956).

[7] S. Sujishi, Paper 31P, Abstracts of the 119th A.C.S. Meeting, April, 1951.

[8] Trimethyl(iso)cyanosilane also has been obtained as a by-product in the reaction of trimethylchlorosilane, acetonitrile and sodium, M. Prober, THIS JOURNAL, **78**, 2274 (1956).

[9] (a) W. Gordy and D. Williams, *J. Chem. Phys.*, **4**, 85 (1936). (b) These authors, Gordy and Williams, also noted that the optical density of the CN band of an isocyanide is approximately double that of the corresponding cyanide. If this is true in the present case, then the equilibrium mixture contains 90% of the cyano form at room temperature because in the spectra of both trimethyl- and triethyl(iso)cyanosilanes the optical density of the $4.58\ \mu$ band is 4.5 times as great as that of the $4.76\ \mu$ band.

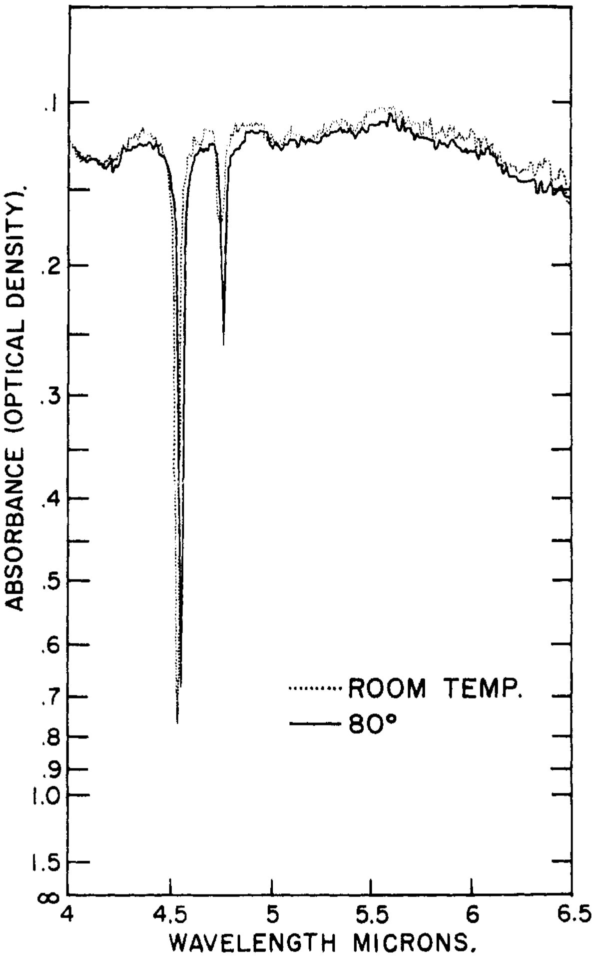

Fig. 1.—Infrared spectrum of triethyl(iso)cyanosilane (1.5 mil cell).

CN absorption band of an organic isocyanide usually occurs at about 0.2 μ longer wave length than that of the corresponding cyanide. This is in agreement with the wave length difference (0.18 μ) in the present case and would assign the 4.58 μ band to the cyanide and the 4.76 μ band to the isocyanide.

As shown in Fig. 1, the optical density of the 4.58 μ band of triethyl(iso)cyanosilane decreased as the temperature was increased from room temperature to 80°, while the optical density of the 4.76 μ band increased. This same behavior was also observed for these bands in the spectrum of trimethyl(iso)cyanosilane. This change was reversible, suggesting that the cyanide and isocyanide forms co-exist in a temperature-dependent equilibrium.[10] The relative intensities of these bands indicate that the cyanide isomer predominates at room temperature[9b] while higher temperatures favor an increase in the amount of the isocyanide isomer present. The band at 6.28 μ taken by McBride and Beachell as evidence for the isocyanide structure was present as a weak band in some of our spectra but was not present in the spectrum of pure material.

The spectrum of triphenyl(iso)cyanosilane shows only the CN band at 4.58 μ; however, the CN group comprises such a small part of this molecule that even this band is very weak and the normally weak band at 4.76 μ representing the second isomer might be undetectable. There is, accordingly, no evidence as to whether this compound is a mixture or exists in only one form. Triphenyl(iso)cyanosilane reacted readily with sulfur to give the same thiocyanate that has been obtained by reaction of triphenylchlorosilane with silver thiocyanate.[11] This reaction with sulfur also has been reported for trimethyl(iso)cyanosilane[5] and has been regarded as chemical evidence for the isocyanide form. However, it would be expected to occur with an equilibrium mixture as well as with a pure isocyanosilane and cannot be regarded as a proof of structure. An attempt to obtain other chemical evidence by reduction of trimethyl(iso)cyanosilane to trimethylsilylmethylamine or N-methyltrimethylsilylamine with lithium aluminum hydride gave only trimethylsilane.

The (iso)cyanosilanes have been found useful in the preparation of other cyanides by exchange reactions with the corresponding halides. For example, phosphorus trichloride reacted with trimethyl(iso)cyanosilane to give phosphorus tricyanide, identical to that prepared by reaction of phosphorus trichloride with silver cyanide,[12] and arsenic trichloride gave the previously reported[13] arsenic tricyanide.

In addition, the new antimony tricyanide and germanium tetracyanide were prepared from their chlorides by this method. Bismuth trichloride reacted incompletely to give a mixture of compounds containing both chloride and cyanide. All of these cyanides reacted rapidly with atmospheric moisture to evolve hydrogen cyanide. The arsenic, antimony, germanium and bismuth cyanides were insoluble in organic solvents, which suggests they may be polymeric in nature.

Attempts to extend this exchange reaction to the chlorides of aluminum, silicon, tin, titanium, zirconium and molybdenum gave complex halocyanides with which trimethyl(iso)cyanosilane appeared to be coördinated. These products were intractable, and analyses indicated them to be mixtures of compounds.

Experimental

Trimethyl(iso)cyanosilane. A. From Hydrogen Cyanide and Hexamethyldisilazane.—Hydrogen cyanide (34.5 g., 1.28 moles) was mixed with 200 ml. of ether and hexamethyldisilazane (34 g., 0.21 mole) was added slowly with stirring. A white suspension formed immediately. The addition of hexamethyldisilazane was completed in 30 minutes and the precipitated ammonium cyanide (4 g.,

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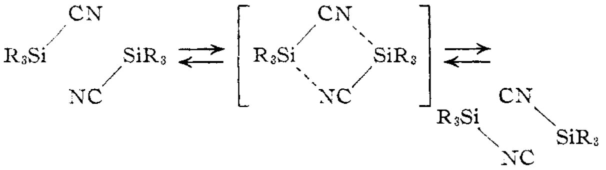
[10] In private conversation, Dr. Anton Burg suggested that this isomerization may occur *via* a bimolecular addition complex involving expansion of the silicon valence shell; for example



See, for example, N. Sidgwick, "The Electronic Theory of Valency," Oxford University Press, London, 1927, pp. 159–160.

[11] H. Gilman, *et al.*, THIS JOURNAL, **72**, 3045 (1950).

[12] G. Wehrbane and H. Hübner, *Ann.*, **128**, 254 (1863); **132**, 277 (1864).

[13] E. Guénez, *Compt. rend.*, **114**, 1186 (1892).

45.5%) was removed by inverse filtration. Distillation yielded 15.2 g. (36.7%) of trimethyl(iso)cyanosilane, b.p. 117°, n^{26}_{D} 1.3883 (lit.[4] b.p. 117.8°, n^{23}_{D} 1.3891).

B. From Potassium Mercuricyanide and Trimethylchlorosilane.—Potassium mercuricyanide (202 g., 0.53 mole) was dissolved in 270 ml. of anhydrous dimethylformamide. Trimethylchlorosilane (108.5 g., 1 mole) was added with rapid stirring over a 30-minute period. A fine white precipitate formed during this addition. The more volatile portion of the liquid was removed by distillation at reduced pressure to avoid reaction with the dimethylformamide.[14] Redistillation at atmospheric pressure gave trimethyl(iso)cyanosilane (31 g., 31.4% yield), b.p. 117°, n^{25}_{D} 1.3910, identical by infrared analysis to that prepared by the preceding method.

C. From Silver Cyanide and Trimethylchlorosilane.—Silver cyanide (70 g., 0.52 mole) and trimethylchlorosilane (55 g., 0.51 mole) contained in a vented glass liner were heated under autogenous pressure in a stainless steel bomb for 12 hr. at 125°. The resultant paste was slurried with anhydrous xylene and filtered. Distillation of the filtrate gave 19 g. (38% yield) of trimethyl(iso)cyanosilane, b.p. 117–118°. No variation in yield was noted when xylene was present during the heating cycle or when the reaction temperature was increased to 150°.

D. Reduction with Lithium Aluminum Hydride.—Trimethyl(iso)cyanosilane (15.4 g., 0.16 mole) was reduced with lithium aluminum hydride (5.95 g., 0.16 mole) in ether. Distillation of the products yielded 5 ml. of liquid, b.p. 5°, which was identified as trimethylsilane by infrared analysis.

Triethyl(iso)cyanosilane.—Trimethylacetyl cyanide[15] (56 g., 0.50 mole) and triethylmethoxysilane (70 g., 0.48 mole) were mixed and heated to reflux under a fractionating column. After several hours, only a few drops of material, b.p. 108–116°, were obtained (b.p. trimethylacetyl cyanide, 102°). The mixture was allowed to stand overnight and again brought to reflux. The head temperature was 120°, showing that little or no exchange was taking place. The mixture was allowed to cool and 1 g. of anhydrous aluminum chloride was added. Distillation was resumed and 45 g. (81%) of methyl trimethylacetate, b.p. 96–102°, was obtained in about 2 hr. Distillation of the remaining liquid gave 43 g. (64% yield) of triethyl(iso)cyanosilane, b.p. 181–183°, n^{26}_{D} 1.4270 (lit.[2] b.p. 181–182°).

Triphenyl(iso)cyanosilane.—Triphenylchlorosilane (4.3 g., 0.015 mole) was dissolved in triethyl(iso)cyanosilane (4 g., 0.028 mole) and the mixture was partially distilled. Triethylchlorosilane (1.7 ml.), b.p. 141° (lit. b.p. 143.5°) and 1.8 ml. of liquid, b.p. 141–166°, were obtained. The distillation was discontinued and the residue crystallized on cooling. Recrystallization of the residue from dichloromethane–petroleum ether gave 1.8 g. (43.3%) of triphenyl(iso)cyanosilane, b.p. 135–137°.

Anal. Calcd. for $C_{19}H_{15}SiN$: C, 80.0; H, 5.26; N, 4.91. Found: C, 80.16; H, 5.38; N, 4.35.

A similar reaction with trimethyl(iso)cyanosilane in place of triethyl(iso)cyanosilane gave a 66% yield of triphenyl(iso)cyanosilane. A sample exposed to the atmosphere for two weeks melted at 135–146° and contained only 0.75% nitrogen. These results suggest that the sample had been hydrolyzed by atmospheric moisture, presumably to triphenylsilanol, m.p. 155°.

The reaction of triphenylmethoxysilane with trimethylacetyl cyanide in the presence of aluminum chloride gave a 21% yield of impure triphenyl(iso)cyanosilane.

Triphenylsilyl(iso)thiocyanate.—A mixture of triphenyl(iso)cyanosilane (16.8 g., 0.059 mole) and sulfur (2 g., 0.062 mole) was heated in the melt for 1 hr. Attempted vacuum distillation gave a small amount of unreacted sulfur. Vacuum sublimation of the residue gave 3.8 g. of white solid (I), m.p. 98–101° after recrystallization from hexamethyldisiloxane.

Anal. Calcd. for $C_{19}H_{15}SiNS$: N, 4.61; S, 9.74. Found: N, 4.42; S, 10.01.

The melting point of triphenylsilyl(iso)thiocyanate prepared from silver thiocyanate and triphenylchlorosilane has variously been reported to be 76 ± 1°[16] and 100–101°.[11] A sample prepared by us by this method melted at 98–100° and the m.p. was undepressed on admixture with I.

Germanium Tetracyanide.—Trimethyl(iso)cyanosilane (11.0 g., 0.11 mole) was added under an atmosphere of nitrogen to a solution of freshly distilled germanium tetrachloride (5.7 g., 0.027 mole) in 50 ml. of dry xylene. The reaction mixture was heated to reflux temperature under an efficient fractionating column. As germanium tetracyanide formed, trimethylchlorosilane (b.p. 58°) was removed by distillation until a total of 7.7 g. (66% of theory) was collected. The insoluble germanium tetracyanide was removed from the xylene by filtration in a nitrogen-filled drybox. This product was washed with xylene and dried *in vacuo* at room temperature to give 3.0 g. (63%) of a buff-colored powder.

Anal. Calcd. for C_4N_4Ge: Ge, 41.4; equiv. wt. (CN), 44.1. Found: Ge, 40.41; equiv. wt. (CN), 44.6.

Antimony Tricyanide.—Reaction of sublimed antimony trichloride (4.8 g., 0.021 mole) and trimethyl(iso)cyanosilane (7.0 g., 0.07 mole) by the procedure described above gave 2.7 g. (64%) of antimony tricyanide. This compound was a white powder that decomposed when heated above 200°.

Anal. Calcd. for C_3N_3Sb: Sb, 61.0; equiv. wt. (CN), 66.7. Found: Sb, 62.59; equiv. wt. (CN), 67.0.

Arsenic Tricyanide.—Reaction of redistilled arsenic trichloride (6.5 g., 0.036 mole) and trimethyl(iso)cyanosilane (11.0 g., 0.11 mole) gave 3.5 g. (64%) of arsenic tricyanide as a white powder. As reported by Guénez[13] this compound decomposed upon heating.

Anal. Calcd. for C_3N_3As: C, 23.60; equiv. wt. (CN), 51.00. Found: C, 23.06; equiv. wt. (CN), 52.70.

Phosphorus Tricyanide.—By reaction of phosphorus trichloride (1.4 g., 0.01 mole) and trimethyl(iso)cyanosilane (3.0 g., 0.03 mole) there was obtained 0.60 g. (55%) of phosphorus tricyanide, m.p. 200°. A mixed melting point with authentic phosphorus tricyanide prepared from phosphorus trichloride and silver cyanide[12] showed no depression.

Bismuth Cyanide.—The product obtained from sublimed bismuth trichloride (3.1 g., 0.01 mole) and trimethyl(iso)cyanosilane (4.0 g., 0.04 mole) amounted to 2.0 g. and was either a bismuth chlorocyanide or a mixture of bismuth tricyanide and bismuth trichloride.

Anal. Calcd. for C_2N_2ClBi: C, 8.1; N, 9.4; Cl, 12.0. Calcd. for $CNCl_2Bi$: C, 3.9; N, 4.6; Cl, 23.2. Found: C, 6.54; N, 5.77; Cl, 15.94.

Acknowledgment.—The authors wish to express their thanks to Professor R. C. Lord for his valuable assistance in interpreting some of the infrared spectra.

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[14] E. G. Rochow and K. Gingold, THIS JOURNAL, **76**, 4852 (1954).

[15] N. Sperber and R. Fricano, *ibid.*, **72**, 2792 (1950).

[16] H. H. Anderson, *ibid.*, **70**, 1220 (1948).