[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF DELAWARE]

Methylisocyanosilanes[1]

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The preparation, infrared absorption spectra, physical properties and some reactions of trimethylisocyanosilane and dimethyldiisocyanosilane are given.

In spite of the rather extensive work in the field of organosilicon chemistry, particularly in the last ten years, there still remain whole classes of compounds in classical organic chemistry which have no counterpart in organosilicon chemistry. Some of these are apparently incapable of existence, others are probably of a very low order of stability. Among these classes of compounds not represented in the silicon field until the present work are the isocyanides.[3]

This paper presents the results of a study of the products obtained by the reaction of silver cyanide with methyl silicon halides. This type of reaction has been employed by Forbes and Anderson[4] and by Anderson[5] to prepare organosilicon isocyanates and isothiocyanates.

Trimethylchlorosilane was found to be considerably less reactive with silver cyanide than were trimethylbromo- and trimethyliodosilanes, which were of about equal reactivity.

The reactions of silver cyanide with the methyl silicon halides and with silicon tetrabromide were investigated but only two isocyanides were obtained, namely, trimethylisocyanosilane (I) and dimethyldiisocyanosilane (II).

Experimental

Preparation of Starting Materials: Phenyltrimethylsilane.—One mole (108.6 g.) of trimethylchlorosilane was added dropwise and with stirring over a period of three hours to a solution of 1.2 moles of phenylmagnesium bromide in 300 ml. of ether. After addition was complete, the mixture was refluxed gently with stirring for two hours longer. The precipitate of magnesium salts was filtered off, washed with ether and the product and washings distilled at atmospheric pressure until all the ether was stripped off. The product was then distilled under diminished pressure from the precipitate which had formed during removal of the ether, and redistilled at atmospheric pressure. There was obtained 122.6 g. of phenyltrimethylsilane, b.p. 169–171°, $n^{25}\text{D}$ 1.4886, a yield of 81.5%.

This method gives a slightly better yield in much less time than that of Bygden.[6]

Dimethyldiphenylsilane.—This material was prepared in the same manner as phenyltrimethylsilane using dimethyldichlorosilane and phenylmagnesium bromide. The yield of product, b.p. 176–178° (45 mm.), $n^{28}\text{D}$ 1.5573, was 73%.

Trimethyliodosilane.—The method used was that of Pray[7] with important modifications. One mole (254 g.) of iodine and one mole (150 g.) of trimethylphenylsilane were heated in a 500-ml. flask fitted with reflux condenser for 12 hours on a steam-bath. Then, instead of adding antimony and distilling, the mixture was first distilled through a long Vigreux column. In this way the product could be separated from the greater part of the unreacted iodine. The distillate, up to 120°, was redistilled over powdered antimony. The yield of trimethyliodosilane obtained in this manner was 107 g., b.p. 107–108°, 85% of the theoretical.

Trimethylbromosilane.—A modification of the method of Pray[7] was also used here. Two moles (320 g.) of bromine was added dropwise with stirring to two moles (300 g.) of phenyltrimethylsilane in a 500-ml. 3-neck flask fitted with a reflux condenser. The flask was kept in an ice-bath. After all the bromine had been added, 2-methyl-2-butene was added dropwise until the bromine color had just disappeared (about 3 ml.). Fractionation gave 295 g. of trimethylbromosilane, b.p. 79.5–80.5° (760 mm.), a yield of 96%.

Dimethyldibromosilane.—No reference could be found to the preparation of this compound by the reaction of dimethyldiphenylsilane with bromine. However, it was found that the reaction will take place, although it is much slower and the yield is not nearly as good as in the corresponding reaction with trimethylphenylsilane. The reaction was run as above (*cf.* trimethylbromosilane) except that, after addition of the bromine, the mixture was kept at 50–60° for 40 hours before adding olefin and distilling. A yield of 55% of dimethyldibromosilane, b.p. 110–112° (760 mm.), was obtained.

Methylisocyanosilanes. (1) **Trimethylisocyanosilane** (I). (a) **From Trimethyliodosilane.**—One hundred sixty-five grams (0.825 mole) of freshly distilled trimethyliodosilane was added to 250 ml. of dry benzene in a 3-neck flask. One hundred fifty grams (1.12 moles) of dry silver cyanide was added with stirring in 25-g. portions over a period of 1.5 hours. The silver salts turned a bright yellow immediately and there was noticeable heat of reaction. After the addition of silver cyanide was complete, the mixture was refluxed with stirring for 2.5 hours. Fifty milliliters of cumene was added as a chaser, and the product was distilled directly from the reaction mixture. The colorless distillate gave, on fractionation, 66.0 g. of I, b.p. 115–120°, $n^{27}\text{D}$ 1.3888, a yield of 80%.

(b) **From Trimethylbromosilane.**—Using the same procedure (a), a yield of 79.5% of I was obtained.

(c) **From Trimethylchlorosilane.**—A yield of 14% of I was obtained using procedure (a).

(2) **Dimethyldiisocyanosilane** (II).—Fifty-four and one-half grams (0.25 mole) of dimethyldibromosilane in 100 ml. of benzene was treated with 73 g. (0.50 mole + 10% excess) of silver cyanide added to the stirred solution over a period of 1.5 hours. The white solid became canary yellow on addition and there was noticeable warming of the mixture after each addition of silver cyanide. The mixture was refluxed gently with stirring for 2.5 hours. The solvent was then distilled directly from the reaction flask. The silver salts from the reaction mixture were washed with hot benzene and the mixture distilled. There was obtained 15.0 g. (0.136 mole) of II, b.p. 165–170°, m.p. 80–83°, a yield of 54.5%.

Methyltriisocyanosilane and Tetraisocyanosilane.—Attempts to prepare these compounds were unsuccessful. Each preparation was attempted under a variety of conditions. It was found that with methyltribromosilane and

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[3] Since this work was completed, C. Eaborn has reported the preparation and some reactions of four organosilicon isocyanides, including trimethylisocyanosilane: (a) *J. Chem. Soc.*, 2757 (1949); (b) 3077 (1950). No chemical evidence for the isocyanide rather than the normal cyanide structure is given; the iso structure is "tentatively" assigned (by analogy with organic compounds) on the basis of the fact that these compounds (with the exception of trimethylisocyanosilane) boil slightly lower than the corresponding iodides.

[4] G. S. Forbes and H. H. Anderson, THIS JOURNAL, **62**, 761 (1940); **70**, 1222 (1948).

[5] H. H. Anderson, *ibid.*, **69**, 3049 (1947); **70**, 1220 (1948); **71**, 1801 (1949).

[6] A. Bygden, *Ber.*, **45B**, 707 (1912).

[7] B. O. Pray, *et al.*, THIS JOURNAL, **70**, 433 (1948).

silicon tetrabromide there was very little or no reaction with silver cyanide in benzene solution since the silver salts did not take on the yellow color of silver bromide. When higher boiling solvents such as cumene and Dowtherm A (b.p. 260°) were used, there was evidence of reaction, since there was some yellowing of the solid and the characteristic odor was present. However, attempts to isolate the products were unsuccessful.

Physical Properties of the Methylisocyanosilanes.—The compounds have a characteristic and very disagreeable odor and a rather high vapor pressure. They are apparently quite toxic, since inhalation of the vapors for even a short time causes headache. They are very easily hydrolyzed, the susceptibility of the diisocyanide to hydrolysis being greater than that of the monoisocyanide.

Trimethylisocyanosilane.—A sample of carefully fractionated material gave the following constants: b.p. 117.8° (uncor.) at 760 mm., m.p. 10.5–11.5°, $n^{23}\text{D}$ 1.3891, d^{30}_4 0.7834.[8]

Dimethyldiisocyanosilane.—A sample of this material was recrystallized three times from ether in an atmosphere of dry air to prevent hydrolysis by atmospheric moisture which occurs rapidly with this compound. The material so obtained was used for analysis and determination of physical constants. These constants are: b.p. 168–169° (uncor.) at 762 mm.; m.p. 84–85°.

Analyses.—The compounds hydrolyze to give HCN and siloxanes (see below), so that both the Liebig and the Volhard titrations are applicable for the determination of the CN group in these compounds. The Volhard method was used for analysis of I and the Liebig method for II.

Anal. Calcd. for $(CH_3)_3SiNC$: CN, 26.24. Found: CN, 26.07. Calcd. for $(CH_3)_2Si(NC)_2$: CN, 47.23. Found: CN, 46.82.

The low result in the second case is attributed to slight hydrolysis by atmospheric moisture during transfer of the sample.

Reactions. A. Reaction with Water.—When a few milliliters of I were poured into an excess of water an exothermic reaction of moderate vigor occurred. The organic layer was separated and dried. Distillation gave hexamethyldisiloxane, b.p. 100.5° at 768 mm., $n^{25}\text{D}$ 1.3775, as the only product. In dilute acid or alkaline solutions the reaction was much more vigorous.

II, when dropped into water, reacts immediately on contact and then slowly forms an oil. If the water is made acidic or alkaline, reaction is much more vigorous and is accompanied by a hissing sound. When a limited amount of water is used, a white gummy material is formed.

These reactions may be written

$$(CH_3)_3SiNC + H_2O \longrightarrow [(CH_3)_3Si]_2O + 2HCN$$

$$n(CH_3)_2Si(NC)_2 + nH_2O \longrightarrow [(CH_3)_2SiO]_n + 2nHCN$$

B. **Reaction with the Grignard Reagent.**—To an excess of phenylmagnesium bromide in ether solution, there was added 10 g. (0.10 mole) of I in the usual manner. Reaction began immediately. On distillation there was obtained 10 g. (0.076 mole) of trimethylphenylsilane, b.p. 169–172°, $n^{20}\text{D}$ 1.4935, a yield of 76%.[9]

To a solution of 1.7 g. (0.015 mole) of II in 10 ml. of ether, there was added an ethereal solution of 0.045 mole of phenylmagnesium bromide as above. Distillation gave 2.8 g. (0.013 mole) of dimethyldiphenylsilane, b.p. 150–160° (20 mm.), $n^{25}\text{D}$ 1.5575, a yield of 87%.

These reactions can be summarized

$$(CH_3)_3SiNC + C_6H_6MgBr \longrightarrow (CH_3)_3SiC_6H_5 + Mg(CN)Br$$

$$(CH_3)_2Si(NC)_2 + 2C_6H_5MgBr \longrightarrow (CH_3)_2Si(C_6H_5)_2 + 2Mg(CN)Br$$

C. **Reaction with Halogens.**—I alone, or in solution, reacts rapidly with bromine in the cold. When an equimolar amount of bromine is added to this compound, the bromine color disappears immediately at first, more slowly toward the end. As soon as an equivalent of bromine has been added, the bromine color persists. Attempts to isolate the reaction product were unsuccessful. Reaction with chlorine is similar to that with bromine. The reaction product in chloroform solution is strongly lachrymatory. As with the bromine addition product, attempts at isolation were unsuccessful. II reacts with bromine in the same manner.

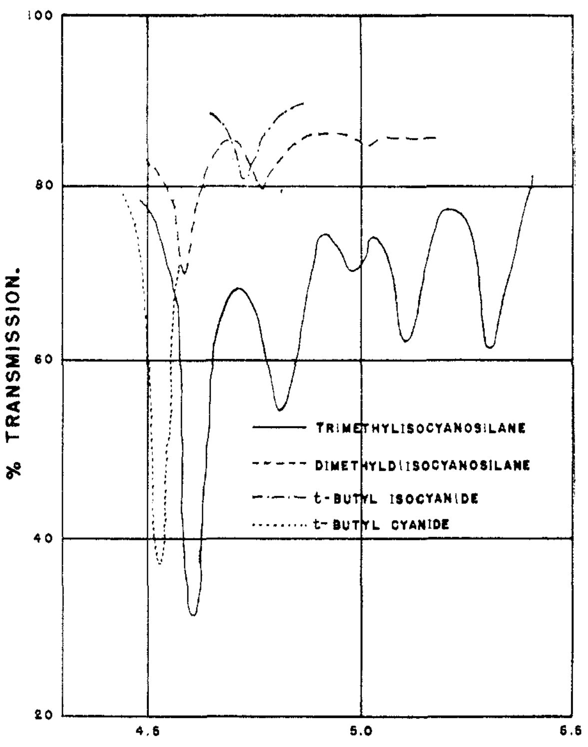

Fig. 1.—Infrared absorption bands.

D. **Reaction with Sulfur.**—Eleven grams (0.11 mole) of I in a test-tube fitted with reflux condenser was heated to gentle reflux. Powdered sulfur was added in small portions, so that each portion completely reacted before the next was added. A total of 3.13 g. (0.10 mole) of sulfur was absorbed. The small excess of sulfur was filtered off and the filtrate distilled. There was obtained 9.0 g. (0.07 mole) of trimethyl silicon isothiocyanate, b.p. 140–145°, $n^{20}\text{D}$ 1.4821, d^{24}_4 0.9302. The constants given by Anderson for this compound are (4): b.p. 143.1°, $n^{20}\text{D}$ 1.4820, d^{20}_4 0.931. As a further check on the identity of this material, its ultraviolet absorption spectra were compared with a sample of trimethyl silicon isothiocyanate prepared by the method of Anderson. The spectra were identical. The reaction then is

$$(CH_3)_3SiNC + S \longrightarrow (CN_3)_3SiN{=}C{=}S$$

The compound, as prepared by the reaction of I with sulfur, was found to deposit an amorphous orange solid on standing which was insoluble in common organic solvents and slowly soluble in concd. sulfuric acid. It is apparently a polymerization product. The solid leaves a white residue on ignition, presumably silica, and the liquid is found to be unchanged. Anderson makes no mention of such behavior, it may be that polymerization is induced by traces of sulfur.

E. **Reaction with Mercuric Oxide.**—When I is dropped on yellow mercuric oxide, a violent reaction occurs accompanied by liberation of sufficient heat to vaporize the liquid. If, however, the reaction is carried out in an ice-bath, and with stirring, it can be controlled. The products are hexamethyldisiloxane, and a white solid which consists of tetrahedral crystals and gives a positive test for CN^-. This must be mercuric cyanide.

This reaction appears to be

$$2(CH_3)_3SiNC + HgO \longrightarrow [(CH_3)_3Si]_2O + Hg(CN)_2$$

F. **Reduction.**—Various methods to reduce I under mild conditions were unsuccessful. Among these were sodium in absolute ethanol (apparently esterification occurred here, and sodium cyanide was isolated), hydrogenation with Raney nickel at fifty pounds pressure and room temperature, and hydrogenation with Adams catalyst under the same conditions. Reduction was finally accomplished by subjecting an ethereal solution of I to 1800 lb. pressure at 140° in the

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(8) C. Eaborn (ref. 3) gives b.p. 114–117°, m.p. 11 ± 0.5°.

(9) C. Eaborn (ref. 3) reports this reaction with similar results.

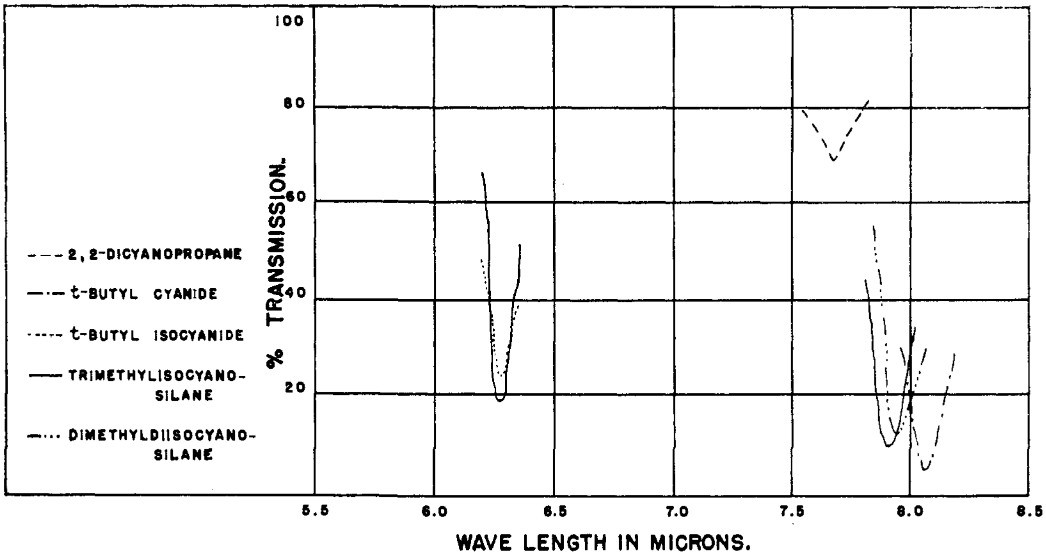

Fig. 2.—Infrared absorption bands.

presence of Raney nickel, for 2.5 hours. The only reduction product obtained was hexamethyldisilazane, no evidence of the presence of the expected reduction product, N-methyltrimethylsilylamine, was found. The hydrogenation mixture had a strong ammonia odor.

G. **Isomerization.**—In an attempt to isomerize I to the normal cyanide, 19.7 g. of the material was heated to 200–250° for three hours. After cooling, 19.2 g. of product was recovered. On distillation, all boiled below 120°, by far the greatest portion at 116–118°. There was a small amount of tarry residue which is probably oxidation product. The refractive indices of the starting and recovered material were 1.3888 and 1.3891 at 25°, respectively.

H. **Absorption Spectra.**—As a further aid in elucidating the structure of the reaction products of silver cyanide and methyl silicon halides, the infrared absorption spectra of these compounds were studied. In order to compare these spectra with the spectra of compounds whose structure is well established, a number of known organic cyanides and isocyanides were prepared and their spectra examined in a parallel manner. When feasible, similar compounds were examined at equal concentrations and in the same solvent. The infrared spectra were run on the pure compounds in the case of trimethylisocyanosilane and *t*-butyl cyanide. *t*-Butyl isocyanide and dimethyldiisocyanosilane were examined in methylcyclohexane solution.

The infrared spectra are shown in Figs. 1 and 2. The characteristic vibrational frequency of the cyanide group falls in the range 4.2–4.7 μ and that of the isocyanide group in the range 4.5–4.8 μ so that between 4.5 and 4.7 μ the bands overlap. Figure 1 shows that the two silicon isocyanides have their bands at 4.59 and 4.61 μ, while the band for *t*-butyl isocyanide falls at 4.27 μ. The normal cyanides, *t*-butyl cyanide and 2,2-dicyanopropane have their characteristic frequencies at 4.52 and 4.48 μ, respectively. On the basis of the masses of the groups (*e.g.*, trimethylsilyl- *vs.* *t*-butyl-) the characteristic band in the silicon compounds would be expected to fall toward the upper end of the isocyanide range (*i.e.*, closer to 4.7 μ) since the normal effect of a heavy group is to shift the band toward the longer wave lengths. This is illustrated by the following table in which a number of organic cyanides and isocyanides and their characteristic bands are listed in order of increasing weight of **R** groups.

R	Cyanides, μ	Isocyanides, μ
CH_3	4.38	4.58
C_2H_5	4.43	4.63
n-C_4H_9	4.45	4.65
C_6H_5	4.48	4.71

The trimethylsilyl group has nearly the same mass as the phenyl group (73 as compared with 77) so that trimethylisocyanosilane would be expected to absorb at about 4.69 μ if this effect holds with organosilicon compounds. The same argument may be applied to the diisocyanide.

At 6.28 μ, however, there is a band in the spectra of the isocyanides which does not appear in the normal cyanides (Fig. 2). This band seems to be little affected since the peaks for I and for *t*-butyl isocyanide fall in almost the same place.

The bands in the region 7.68–8.06 μ give no information by which a differentiation between the normal cyanide and the isocyanide structure can be made. It is interesting to note, however, that here, too, the bands of the methylisocyanosilanes fall very close together.

Figure 3 shows the complete spectra for trimethylisocyanosilane in the range 2–16 μ.

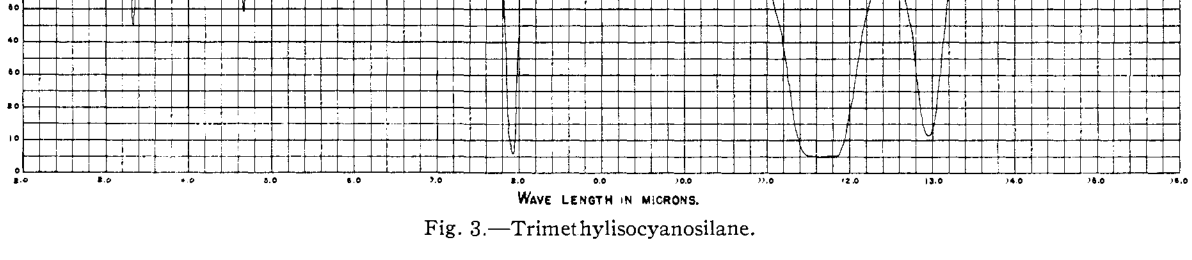

Fig. 3.—Trimethylisocyanosilane.

Discussion

The properties of the methylisocyanosilanes have been found to differ in several important respects from those of the organic isocyanides. As a result, the classical method of distinguishing between organic cyanides and isocyanides, namely, hydrolysis to an acid or an amine, respectively, has been found inapplicable in this case since hydrolysis results in cleavage of the linkage between the silicon atom and the functional group, so that the nature of the products gives no direct indication of the structure of the original compound. Similarly, the Grignard reagent, instead of adding to the nitrogen or the carbon atom, adds directly to the silicon atom so that again no differentiation can be made on the basis of this reaction.

The reaction with sulfur is positive for the isocyanide structure, since this reaction does not take place with normal cyanides.

The reaction with halogens appears to be direct addition of the type investigated by Nef[10] and by Tschermak[11]; it is characteristic of isocyanides and may be written

$$\text{R—N} \rightleftarrows \text{C} + \text{X}_2 \longrightarrow \text{R—N=CX}_2$$

These workers found the compounds to be quite unstable; the addition product of bromine and methyl isocyanide was a heavy unstable oil that could not be further studied nor purified. The product from phenyl isocyanide and chlorine was a strong lachrymator. This reaction with halogens is another typical reaction of isocyanides that does not take place with normal cyanides.

The products obtained from the reaction of mercuric oxide with I are not the expected ones. Instead of oxidation to the isocyanate, the reaction appears to be a simple metathesis, hexamethyldisiloxane and mercuric cyanide being formed. The explanation for this behavior is perhaps to be found in the great affinity of silicon for oxygen, with the silicon atom being more readily oxidized. The reaction resembles the corresponding reaction of organic isocyanides in its violence.[10]

The fact that no evidence of isomerization was found on heating I to 250° indicates either that the isocyanide structure is the thermodynamically stable one in this system, or that a very high activation energy is required to affect the change. If the latter be true, it may well be that, if, as is the case in carbon chemistry, the normal cyanide is the more stable, the difference in thermodynamic stability is much less in silicon compounds.

The hydrolysis of these compounds can be considered as proceeding by nucleophilic attack of hydroxyl on silicon, followed by elimination of the cyanide ion.

The reaction of the organosilicon isocyanides with the Grignard reagent is similar to the reaction of organic or organosilicon halides with this reagent and undoubtedly proceeds by the same mechanism.

The mechanism of the formation of hexamethyldisilazane by catalytic hydrogenation of I is not so easily explained. The only plausible mechanism which seems to explain this reaction is that hydrogenolysis of the nitrogen–carbon bond occurs either with or without the formation of N-methyltrimethylsilylamine as an intermediate

$$\begin{aligned}
&\text{(a)}\quad (\text{CH}_3)_3\text{SiNC} \xrightarrow{\text{H}_2} (\text{CH}_3)_3\text{SiN=CH}_2\\
&\qquad (\text{CH}_3)_3\text{SiN=CH}_2 \xrightarrow{\text{H}_2} (\text{CH}_3)_3\text{SiNH}_2 + \text{CH}_4\\
&\qquad 2(\text{CH}_3)_3\text{SiNH}_2 \longrightarrow [(\text{CH}_3)_3\text{Si}]_2\text{NH} + \text{NH}_3\\
&\text{(b)}\quad (\text{CH}_3)_3\text{SiNC} \xrightarrow{\text{H}_2} (\text{CH}_3)_3\text{SiN=CH}_2\\
&\qquad (\text{CH}_3)_3\text{SiN=CH}_2 \xrightarrow{\text{H}_2} (\text{CH}_3)_3\text{SiNHCH}_3\\
&\qquad (\text{CH}_3)_3\text{SiNHCH}_3 \xrightarrow{\text{H}_2} (\text{CH}_3)_3\text{SiNH}_2 + \text{CH}_4\\
&\qquad 2(\text{CH}_3)_3\text{SiNH}_2 \longrightarrow [(\text{CH}_3)_3\text{Si}]_2\text{NH} + \text{NH}_3
\end{aligned}$$

Hydrogenolysis of a carbon–nitrogen bond, while unusual, has been observed many times, and has been used as a preparative method. In most of these cases, one of the other groups attached to the nitrogen atom is an activating or electronegative group such as an aryl group.[12] Whitmore and Sommer place the trimethylsilyl group close to the phenyl group in electronegativity.[13]

The physical properties of the compounds are indicative of the isocyanide structure. They have extremely disagreeable odors and are apparently quite toxic.

The infrared data in the region of the characteristic vibration frequency of the cyanide and isocyanide groups could be interpreted as favoring the normal cyanide structure or a mixture of the two isomers. There has been no chemical evidence to indicate the existence of two forms. The bands for the methylisocyanosilanes lie toward the upper end of the range for the normal cyanide structure and at the lower end of the isocyanide range. The normal effect of a heavy R group is to cause a slight shift of the characteristic band toward the longer wave lengths. In the absence of the other information obtained in this work, this would appear to be evidence in favor of the normal cyanide structure, the relatively heavy trimethylsilyl group causing a shift into the longer wave lengths. In view of the chemical evidence and the other physical data, however, the only conclusion that can be drawn is that the magnitude of the shift is less than would be predicted by comparison with the behavior of carbon compounds. Further, if the data on the increase in the wave length of the characteristic bands of the organic cyanides are considered, it will be seen that the absorption peak of trimethylcyanosilane should fall between those for butyl cyanide (4.45 μ) and phenyl cyanide (4.48 μ) since the mass of the trimethylsilyl group is intermediate. The value found for the peak is considerably higher than this.

The presence of a strong band at 6.28 μ for both *t*-butyl isocyanide and trimethylisocyanosilane and the absence of such a band in normal cyanides supports the isocyanide structure.

Acknowledgment.—The authors are indebted to Mrs. William C. Meisenhelder for the infrared data.

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(10) J. Nef, *Ann.*, **270**, 267 (1892).

(11) A. Tschermak, *Bull. soc. chim.*, **80**, 185 (1890).

(12) H. Adkins, "Reactions of Hydrogen," Wisconsin Press, Madison, Wisconsin, 1937, Chaps IV and V.

(13) F. C. Whitmore and L. H. Sommer, This Journal, **68**, 481 (1946).