

from a mixture of benzene and ethanol to give 0.18 g. (39%) of tetraphenylsilane, m.p. 230–233°, identified by mixed melting point and infrared spectra. No other product was isolated from the mother liquor.

Triphenyl(1,1-diphenylethyl)silane. An ethereal solution of 0.015 mole of *n*-butyllithium¹⁴ was added at once to a solution of 5.0 g. (0.012 mole) of triphenyl(diphenylmethyl)silane, dissolved in 25 ml. of tetrahydrofuran. Heat was evolved and the solution turned deep red immediately. After stirring for 40 min. at room temperature, an excess of methyl sulfate was added. The color of the solution was discharged immediately. Hydrolysis and the usual work-up of the organic layer gave an oily residue, which gradually solidified. Two recrystallizations from a mixture of benzene and ethanol gave 3.0 g. (58%) of triphenyl(1,1-diphenylethyl)silane, m.p. 193–195°.

Anal. Calcd. for C₃₂H₂₈Si: Si, 6.37. Found: Si, 6.34, 6.47.

Triphenyl(1,2,2-triphenylethyl)silane. A solution of 0.020 mole of triphenylsilyllithium¹¹ in tetrahydrofuran was added with stirring to 5.12 g. (0.020 mole) of triphenylethylene. A deep red color developed immediately and heat was evolved. After stirring for 1 hr. at room temperature, the mixture was hydrolyzed. Subsequent to the usual work-up of the organic layer, an oily residue was obtained, which partially solidified. Two recrystallizations from a mixture of benzene and ethanol gave 6.4 g. (62%) of triphenyl(1,2,2-triphenylethyl)silane, m.p. 171–172°.

Anal. Calcd. for C₃₈H₃₂Si: Si, 5.45. Found: Si, 5.42, 5.59.

Triphenyl(1,1,2-triphenylethyl)silane. An ethereal solution of 0.015 mole of *n*-butyllithium¹⁴ was added at once to a solution of 5.0 g. (0.012 mole) of triphenyl(diphenylmethyl)silane, dissolved in 25 ml. of tetrahydrofuran. After stirring for 40 min. at room temperature, an excess of benzyl chloride was added. The color of the solution was discharged after a few minutes. Hydrolysis and the usual work-up of the organic layer gave a yellow oil, which partially solidified on standing with 10 ml. of petroleum ether (b.p. 60–70°). The crystalline product was recrystallized three times from a mixture of benzene and ethanol to give 1.5 g. (25%) of triphenyl(1,1,2-triphenylethyl)silane, m.p. 198–200°.

Anal. Calcd. for C₃₈H₃₂Si: Si, 5.45. Found: Si, 5.58, 5.60.

(14) H. Gilman, J. A. Beel, C. G. Brannen, M. W. Bullock, G. E. Dunn, and L. S. Miller, *J. Am. Chem. Soc.*, **71**, 1499 (1949).

Reaction of triphenylsilyllithium with tetraphenylethylene. A solution of 0.015 mole of triphenylsilyllithium in tetrahydrofuran was added to 5.0 g. (0.015 mole) of tetraphenylethylene. Apparently no reaction took place. The mixture was stirred for 6 hr. at room temperature, at which time the solution had turned deep brown. After stirring for one additional hour at 50°, the mixture was hydrolyzed with dilute acid. The work-up of the organic layer gave oily crystals, which were washed with 25 ml. of petroleum ether (b.p. 60–70°) and recrystallized from ethyl acetate to give 4.2 g. (84%) of tetraphenylethylene, m.p. 222–224° (mixed melting point). The filtrate was chromatographed on alumina. With petroleum ether as an eluent, 2.2 g. (56%) of triphenylsilane was obtained, m.p. 43–45° (after recrystallization from methanol).

Attempted reactions of triphenylsilylpotassium with other olefins. All reactions were carried out in the same manner. The triphenylsilylpotassium suspension was mixed with an equimolar amount of the olefinic compound and the mixture stirred for a certain period of time. Then water was added, the layers separated, the organic layer dried, and the solvent removed. The residue was recrystallized from petroleum ether (b.p. 60–70°) to give triphenylsilanol as the chief product. The results are given in Table I. In two experiments using 1,2-dimethoxyethane as the solvent in place of ether, a mixture of tetraphenylsilane and hexaphenyldisiloxane also was obtained.

In the reaction of $\Delta^{9,9}$ -bifluorene with triphenylsilylpotassium in ether, heat was evolved and the reaction mixture became very dark. The work-up gave a tar-like material, from which no pure product has been isolated.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, SAN JOSE STATE COLLEGE]

Synthesis and Cleavage of *N*-Trimethylsilylpyrrole¹

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N-Trimethylsilylpyrrole has been synthesized by the reaction of potassium pyrrole and trimethylchlorosilane and by an exchange reaction between hexamethyldisilazane and pyrrole. *N*-Trimethylsilylpyrrole has been found to be stable in ethanol; however, it undergoes cleavage to pyrrole and silicon derivatives (trimethylsilanol, hexamethyldisiloxane, or trimethylethoxysilane, depending upon the conditions of the reaction) in boiling water and in refluxing aqueous ethanol. The cleavage reaction is catalyzed by either acid or base. *N*-Trimethylsilylpyrrole undergoes decomposition when heated in a sealed tube at 225°. No evidence for the formation of 2-trimethylsilylpyrrole in this reaction could be obtained. Infrared spectra are given for *N*-trimethylsilylpyrrole and tetrapyrrolylsilane.

Although a number of compounds containing the silazane linkage are known, there appears to be no reported study of the stability of such a linkage in which the nitrogen of the silazane is in an aromatic

(1) This work was supported by a Frederick Gardner Cottrell grant from Research Corporation.

heterocyclic system. In view of the known susceptibility of the silazane linkage to cleavage by water, alcohols, and other reagents,² this investigation has been directed toward preparation of such a compound and a study of its cleavage reactions.

Silazane compounds undergo solvolysis and

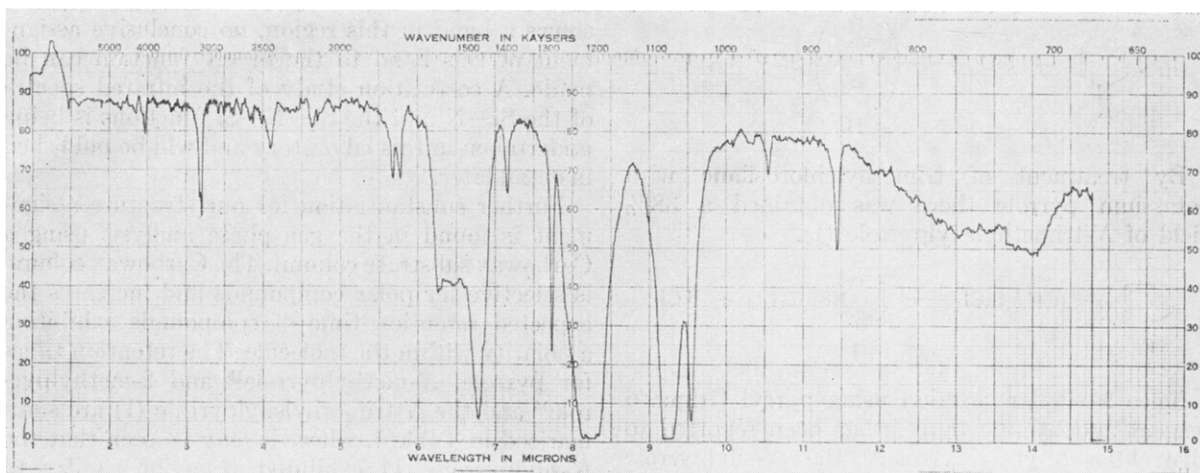


Fig. 1. Infrared spectrum of tetrapyrrolylsilane (II). Carbon tetrachloride.

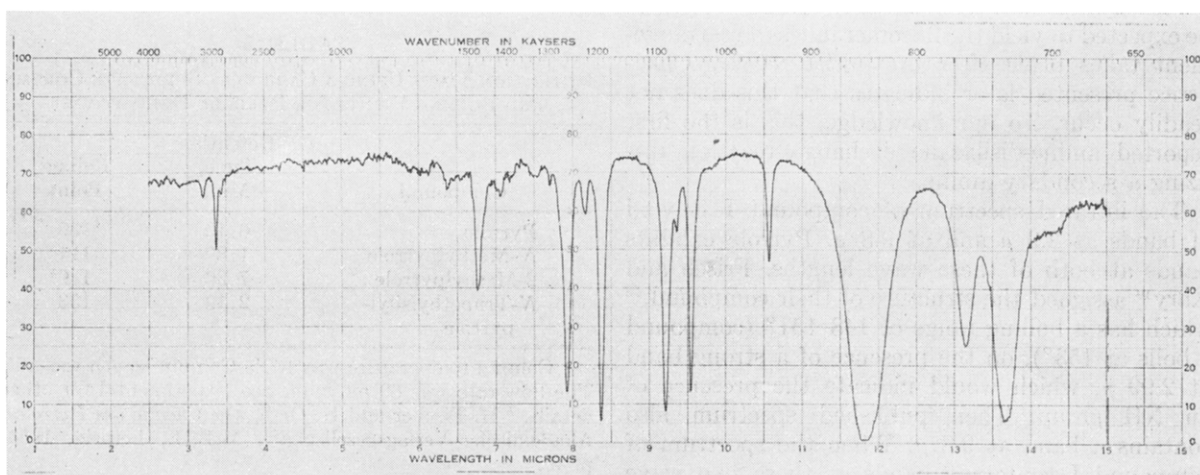


Fig. 2. Infrared spectrum of *N*-trimethylsilylpyrrole (I). Thin film

cleavage in the presence of either acids or bases. Andrianov³ has reported that ethereal solutions of triethylaminosilane, *N*-methyltriethylaminosilane, and *N,N*-dimethyltriethylaminosilane yield triethylsilanol when treated with water for one hour. Under similar conditions, the *N,N*-diethyltriethylaminosilane failed to cleave, but when homogeneous conditions (acetone solution) were used, the silanol was obtained. Kraus and Nelson⁴ report that triethylsilanol was obtained from the steam distillation of *N*-ethyltriethylaminosilane.

The instability of the silazane and the disilazane bonds have been utilized to synthesize other silicon compounds. Sulfur and phosphorus silicon com-

pounds have been obtained by the cleavage of silazanes and disilazanes by the appropriate reagents.⁵ Halosilanes,⁶ hydroxysilanes,⁷ and alkoxy-silanes⁸ can be obtained from silazanes or disilazanes.

For our work we have chosen to prepare and study *N*-trimethylsilylpyrrole (I). A few silylpyrroles have been synthesized. Reynolds⁹ has prepared tetrapyrrolylsilane (II), dichloropyrrolylsilane, and tripyrrolylsilane from potassium pyrrole and the appropriate chlorosilane. He reports that these compounds decompose in acid, base, water or alcohols.

(5) Ref. 2(d).

(6) D. L. Bailey, L. H. Sommer, and F. C. Whitmore, *J. Am. Chem. Soc.*, **70**, 435 (1948).

(7) C. S. Miner, I. A. Bryan, R. P. Holysz, and G. W. Pedlow, *Ind. Eng. Chem.*, **39**, 1368 (1947).

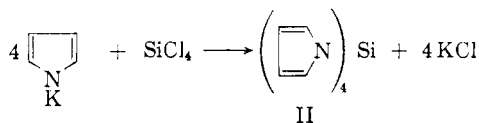
(8) (a) Ref. 7; (b) P. A. Di Giorgio, L. H. Sommer, and F. C. Whitmore, *J. Am. Chem. Soc.*, **71**, 3254 (1949); (c) A. P. Kreshkov, L. V. Myshlyaeva, and L. M. Khananashvili, *Zhur. Obshchei Khim.*, **28**, 2112 (1958); *Chem. Abstr.*, **53**, 2074g (1959).

(9) (a) J. E. Reynolds, *J. Chem. Soc.*, 505 (1909); (b) J. E. Reynolds, *J. Chem. Soc.*, 508 (1909).

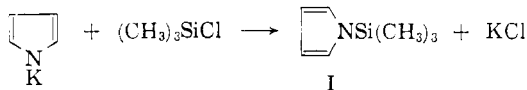
(2) (a) F. S. Kipping, *Proc. Chem. Soc.*, **23**, 8 (1907); (b) P. A. Di Giorgio, L. H. Sommer, and F. C. Whitmore, *J. Am. Chem. Soc.*, **71**, 3254 (1949); (c) P. D. George, L. H. Sommer, and F. C. Whitmore, *J. Am. Chem. Soc.*, **75**, 6308 (1953); (d) von M. Becke-Goehring and G. Wunsch, *Ann.*, **618**, 43 (1958).

(3) K. A. Andrianov, S. A. Golubtsov, and E. A. Semenova, *Izvest. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk* (1958) 47; *Chem. Abstr.*, **52**, 11734f (1958).

(4) C. A. Kraus and W. K. Nelson, *J. Am. Chem. Soc.*, **56**, 195 (1934).



By treatment of trimethylchlorosilane with potassium pyrrole there was obtained a 38% yield of *N*-trimethylsilylpyrrole (I).



Since a similar reaction using pyrrol Grignard reagent and lithium pyrrole has been reported to give 2-trimethylsilylpyrrole,¹⁰ the *N*-silylpyrrole was also prepared by an exchange reaction of pyrrole with hexamethyldisilazane,¹¹ of the type reported by Speier *et al.*¹² This reaction would not be expected to yield the 2-isomer unless a rearrangement takes place after the initial reaction. Evidence presented later indicates that this does not readily occur. To our knowledge, this is the first reported amine-disilazane exchange reaction utilizing a secondary amine.

The infrared spectrum of compound I is void of bands at 2.9 μ and at 9.8 μ . Pyrrole exhibits bands at both of these wave lengths. Frisch and Kary¹⁰ assigned the structure of their compound,¹³ which has a boiling range of 148–151° (compound I boils at 153°), on the presence of a strong band at 2.99 μ , which would indicate the presence of an NH group. Their published spectrum also contains a band at 9.8 μ . When the spectrum of compound I contained bands at these two wave lengths, the gas chromatogram also showed a large peak corresponding to pyrrole. However, when compound I was purified by use of separation on the gas chromatography unit, both of these bands in the infrared disappeared. This suggests that Frisch and Kary used the spectrum of a mixture of pyrrole and *N*-trimethylsilylpyrrole (I) for their structure assignment. The possibility that the small band at 3.2 μ in the spectrum of I is the NH band is eliminated by comparison with the spectrum of tetrapyrrolylsilane (II), prepared *via* the method of Reynolds.¹⁴ In the spectrum of this compound a band appears at 3.2 μ , indicating that this band is due to the CH on the pyrrole ring rather than an NH group. Of further interest is a strong band at 9.55 μ which appears in the spectra of both I and II. A number of silazanes prepared in this laboratory show a band in the region between 9.5 μ and 9.9 μ . However, since pyrrole also

shows a band in this region, no conclusive assignment of this band to the Si—N function can be made. A correlation study of the infrared spectra of the Si—N and the Si—N—Si functions is being undertaken in this laboratory and will be published in detail later.

Further substantiation for our structure assignment is found in the gas phase analysis using a Carbowax substrate column. The Carbowax column is selective for polar compounds and increases the expected retention time of compounds exhibiting a polarity within the molecule. The retention times for pyrrole, *N*-methylpyrrole¹⁵ and 2-methylpyrrole¹⁶ and the *N*-trimethylsilylpyrrole (I) are summarized in Table I, where it may be seen that the *N*-silylpyrrole (I) exhibited behavior similar to that of the *N*-methylpyrrole rather than that of the 2-methylpyrrole.

TABLE I
RETENTION TIMES USING A CARBOWAX SUBSTRATE COLUMN
AND BOILING POINTS FOR PYRROLE DERIVATIVES^a

Compound	Retention Time, Min.	Boiling Point
Pyrrole	6.10	130
<i>N</i> -Methylpyrrole	1.80	114
2-Methylpyrrole	7.30	149 ^b
<i>N</i> -Trimethylsilylpyrrole	2.10	153

^a Column temperature was 160°. Column length was 10'. The flow rate was 60 ml./min. See Experimental for other details. ^b H. Fischer and H. Orth, *Die Chemie des Pyrroles*, Akademische Verlagsgesellschaft, M.B.H., Leipzig, 1934, p. 40.

Since no higher boiling components could be detected using the Carbowax or the Silicone column at high temperatures, it is indicated that no 2-silylpyrrole was present in the distillation fraction boiling 150–153°.

N-Trimethylsilylpyrrole (I) was also obtained by treatment of the Grignard reagent of pyrrole with trimethylchlorosilane; however, the yield of I was very small. Polymerization of pyrrole prevented complete recovery of the *N*-silylpyrrole which had been detected in the gas chromatogram. Again, no peak in the gas chromatogram corresponding to 2-trimethylsilylpyrrole could be detected.

N-Trimethylsilylpyrrole is a colorless liquid boiling at 153°. Its ultraviolet spectrum (cyclohexane) is similar to that of pyrrole except that the extinction coefficient is smaller. No λ_{max} could be detected between 2250 Å and 2500 Å.

For the investigation of the cleavage of the *N*-trimethylsilylpyrrole, gas chromatography (5' Sil-

(10) K. C. Frisch and R. M. Kary, *J. Org. Chem.*, **21**, 931 (1956).

(11) It should be noted here that the exchange reaction would not occur in the absence of ammonium sulfate.

(12) J. L. Speier, R. Zimmerman, and J. Webster, *J. Am. Chem. Soc.*, **78**, 2278 (1956).

(13) 2-Trimethylsilylpyrrole.

(14) Ref. 9(a).

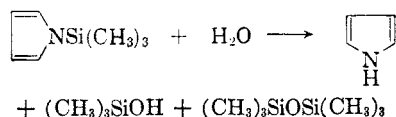
(15) Obtained through the courtesy of the Ansul Corporation.

(16) Prepared by A. J. Castro and M. Hugo of this laboratory.

cone column) was utilized for analysis of the product ratios. The extent of cleavage was judged by the increase in the area under the pyrrole peak and the corresponding decrease in that under the *N*-silylpyrrole peak. The other products detected in the gas chromatograms were trimethylsilanol, trimethylethoxysilane or hexamethyldisiloxane, depending upon the reaction conditions which were employed.

Upon reflux of the *N*-silylpyrrole with water for twelve hours and extraction and distillation of the ether-soluble fraction, complete cleavage was observed. Pyrrole was isolated and identified by gas phase chromatographic comparison with an authentic sample and by its infrared spectrum. Other products observed in the gas chromatogram of the ether-soluble material were hexamethyldisiloxane and, presumably, trimethylsilanol. The disiloxane was identified by gas chromatographic comparison with an authentic sample of this material, and the presence of the trimethylsilanol is suggested by the strong band below 3.0μ in the infrared spectrum of the lower-boiling fraction. Gas chromatography indicates that this infrared band is not due to water.

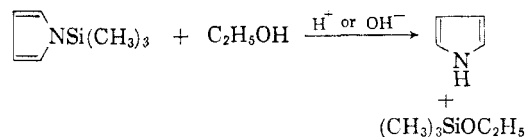
Besides showing the susceptibility of this silazane to cleavage in boiling water, the experiment indicates that the pyrrole moiety had not undergone cleavage or rearrangement during the preceding reactions. This observation lends further support to the assigned structure of I. Such mild conditions would not be expected to cleave a Si—C bond, as would be the case if the compound were 2-trimethylsilylpyrrole.



The stability of the *N*-silylpyrrole to cleavage in a homogeneous medium was next investigated. In ethanol, the *N*-silylpyrrole was found to be stable up to three days at room temperature. When the solution was heated under reflux for one hour, only about 0.1% cleavage could be detected. When an aqueous-ethanol (33% water by volume) solution was used, the cleavage was detected proceeding at a reasonable rate. When the solution had been heated under reflux for thirty minutes about 20% cleavage could be detected and, after one hour of reflux, about 30% could be detected by gas phase analysis.

The cleavage of the *N*-silylpyrrole was found to be catalyzed by either acid or base. When a drop of hydrochloric acid was added to an ethanolic solution of the *N*-silylpyrrole at room temperature, quantitative cleavage took place in less than one minute. Pyrrole and trimethylethoxysilane were detected as the cleavage products. No trace

of the *N*-silylpyrrole could be detected in the gas chromatogram.



Similar results were observed when a small amount of potassium hydroxide was added to an ethanol solution of the *N*-silylpyrrole at room temperature. Again the cleavage was quantitative in less than one minute. The major products of the cleavage were pyrrole and trimethylethoxysilane. Again no trace of the *N*-silylpyrrole could be detected in the gas chromatogram.

The cleavage of I by boiling water, acids, and bases is not surprising in light of the known chemistry of the silazanes and the disilazanes.¹⁷ However, the stability of I in ethanolic solution is unusual. Nonsterically-hindered silazanes¹⁸ generally undergo cleavage very rapidly in homogeneous media. *N*-Trimethylsilylpyrrolidine¹⁹ cleaves when exposed to moist air, and great care is necessary to keep the molecule intact. Miner²⁰ reports that the di-*t*-alkoxydiaminosilanes form tetraalkoxysilanes when warmed with a primary alcohol. This suggests that there is some stabilization of the silazane bond in *N*-trimethylsilylpyrrole, probably due to *d*-orbital participation of the silicon atom in the aromatic system of the pyrrole ring, a type of participation suggested by Rochow, Hurd, and Lewis²¹ in trisilylamine [(H₃Si)₃N]. Such *d*-orbital participation is also found to a small extent in other silyl aromatic compounds.²²

No evidence of thermal rearrangement of the silyl group to the 2- or the 3-position of pyrrole could be obtained.²³ When the *N*-silylpyrrole was heated seventeen hours in a sealed tube at 225°, extensive charring resulted. Gas phase analysis of the liquid remaining after the pyrolysis showed only the starting *N*-silylpyrrole. No other isomers could be detected. When *N*-trimethylsilylpyrrole was heated under reflux with diphenyl ether (b.p. 247°)

(17) R. O. Sauer and R. H. Hasek, *J. Am. Chem. Soc.*, **68**, 241 (1946).

(18) Hexaphenyldisilazane [H. H. Reynolds, L. A. Bigelow, and C. A. Kraus, *J. Am. Chem. Soc.*, **51**, 3067 (1929)] and *N*-triphenylsilylhydrazobenzene [D. Wittenberg, M. V. George, T. C. Wu, D. H. Miles, and H. Gilman, *J. Am. Chem. Soc.*, **80**, 4532 (1958)] are purified by crystallization from alcoholic solutions.

(19) Unpublished observations from this laboratory.

(20) See Ref. 7.

(21) E. G. Rochow, D. T. Hurd and R. N. Lewis, *The Chemistry of Organometallic Compounds*, John Wiley and Sons, Inc., New York, 1957, p. 32.

(22) (a) H. Soffer with T. DeVries, *J. Am. Chem. Soc.*, **73**, 5817 (1951); (b) R. A. Benkeser and H. R. Krysiak, *J. Am. Chem. Soc.*, **75**, 2421 (1953).

(23) *N*-Alkylpyrroles are reported to form 2-alkylpyrroles when heated to 200–250° [R. H. Wiley, *Organic Chemistry, An Advanced Treatise*, Vol. IV, H. Gilman, ed., John Wiley and Sons, Inc., New York, 1953, p. 749].

for twelve hours, no decomposition was observed and, again, no other isomers could be detected in the gas chromatogram.

EXPERIMENTAL²⁴

Technique of gas phase analysis. For the gas phase analyses, an Aerograph gas phase chromatography unit was employed. Two columns, both obtained from the Wilkens Instrument Co., were used: a 5' column, Silicone on firebrick, for non-polar separation, and a 10' column, Carbowax 20M on firebrick, for separation of polar compounds. The temperature was held constant for a given analysis, and the helium flow was held constant at 100 ml. per minute.

Two injection techniques were used for analysis: (a) injection into the instrument of an undiluted sample and (b) dilution of 50–100 mg. of the sample with 1 ml. of ether or benzene and injection of an aliquot of this solution. In each case, the volume of sample injected was 0.005 ml.

Peak assignments were made by comparison of retention times and, in some cases, by the addition of known material to the unknown mixture. The retention times were measured from the air peak rather than from the actual time of injection and are accurate to 0.05 min. (3 sec.).

The areas under the peaks are reported as percentages of the total area under all the observed peaks, not including that of the solvent. These are not the correct percentages of the components in the mixture, but are reasonable approximations.

N-Trimethylsilylpyrrole (I). A. From potassium pyrrole. In a 500-ml. round bottom flask, fitted with reflux condenser, mechanical stirrer, and dropping funnel, were placed 50 ml. of sodium-dried ether, 25 ml. of sodium-dried benzene and 13.4 g. (0.20 mole) of pyrrole (obtained Ansul Chemical Company). To this solution was added 7.4 g. (0.19 mole) of diced metallic potassium. The mixture was heated under reflux for 1.5 hr. and then cooled to room temperature, and 16.2 g. (0.15 mole) of trimethylchlorosilane was added over a 5-min. period. After the addition the mixture was allowed to stand at room temperature for 48 hr.

The reaction mixture was then filtered to remove the potassium chloride which had formed, and the filtrate was distilled at atmospheric pressure. The *N*-silylpyrrole was collected in seven fractions, 8.0 g., b.p. 150–152°, n_D^{20} 1.4654–1.4621. A redistilled sample was used for analysis.

Anal. Calcd. for $C_7H_{13}NSi$: C, 60.5; H, 9.4; N, 10.1; Si, 20.3. Found: C, 60.9; H, 9.4; N, 9.2; Si, 19.9, 20.4.²⁵

Gas phase analysis data, using the Carbowax column is tabulated in Table I.

B. From pyrrylmagnesium iodide. To 200 ml. of an ether solution of methylmagnesium iodide, freshly prepared from

(24) All melting points and boiling points are uncorrected. Fractional distillations were accomplished using a 2-meter modified Podbeilniak column (*cf.* J. Cason and H. Rapoport, *Laboratory Text in Organic Chemistry*, Prentice-Hall, Inc., New York, 1950, p. 237). Infrared spectra were recorded using thin films or carbon tetrachloride solutions on a Beckman IR-4 instrument. The ultraviolet spectrum was obtained using a Beckman Model DU Spectrophotometer. Carbon, hydrogen, and nitrogen analyses were performed by the Berkeley Microanalytical Laboratory. Silicon analyses were performed in this laboratory.

(25) The silicon analysis was accomplished by slow oxidation with fuming sulfuric acid and ignition to constant weight. When nitric acid was used with sulfuric acid, the analysis was *ca.* 10% low, presumably due to the formation of stable compounds which were lost during the ignition. Fuming sulfuric acid was necessary because I decomposed extremely slowly in concentrated sulfuric acid, even at 150°. In view of the rapid acid-catalyzed cleavage of I to pyrrole, this stability in hot concentrated sulfuric acid is not understood.

42.5 g. (0.25 mole) of methyl iodide and 7.3 g. (0.3 mole) of magnesium, was added 16.7 g. (0.25 mole) of pyrrole. The solution was heated under reflux for 15 min., then cooled to room temperature. To this mixture was then added, dropwise, 27.0 g. (0.25 mole) of trimethylchlorosilane. A moderately exothermic reaction took place. After the addition had been completed, the mixture was heated under reflux for 2 hr., then allowed to stand overnight. The reaction mixture was filtered and the bulk of the ether removed by slow distillation at atmospheric pressure. An attempt to distill fractionally this material resulted in the formation of a solid black cake, which was removed from the flask and extracted with ether overnight using a Soxhlet extractor. The ether soluble material was then distilled and 2.0 g. (6%) of *N*-trimethylsilylpyrrole was obtained, b.p. 150–152°. A considerable amount of semisolid pot residue remained and was investigated using the gas phase chromatography instrument for the possible presence of other trimethylsilylpyrrole isomers. In the gas chromatogram, only one high-boiling component could be detected, its retention time the same as that of an authentic sample of *N*-trimethylsilylpyrrole.

C. From hexamethyldisilazane. Hexamethyldisilazane was prepared in 45% yield using the procedure of Sauer²⁶ from 1.0 mole of trimethylchlorosilane and excess ammonia gas. The disilazane was isolated by distillation, b.p. 122–124°, n_D^{20} 1.4075 (*lit.*,²⁷ b.p. 124–126°, n_D^{20} 1.4080).

In a 100-ml. round bottom flask were placed 15.2 g. (0.094 mole) of hexamethyldisilazane, 11.5 g. (0.17 mole) of pyrrole and a few crystals of ammonium sulfate. The mixture was heated for 6 hr. at 110° then fractionally distilled without further work-up. There was obtained 13.5 g. (51%) of the *N*-silylpyrrole, b.p. 150–151°. Gas phase analysis of product using both Carbowax and Silicone columns showed that it was identical with the compound obtained from potassium pyrrole and trimethylchlorosilane. Only starting material and the *N*-silylpyrrole were detected in the gas chromatogram.

Attempts without ammonium sulfate were unsuccessful. No reaction product was obtained when pyrrole and the disilazane were heated 10 hr. in ether solution or when they were heated 12 hr. without solvent. In both these reactions, the starting materials were recovered upon distillation and no *N*-silylpyrrole could be detected in the gas chromatograms of the pot residues.

Cleavage of N-trimethylsilylpyrrole with water. In a 50-ml. round bottom flask were placed 13.9 g. (0.10 mole) of *N*-trimethylsilylpyrrole and 20 ml. of water. The mixture was heated under reflux for 12 hr. During the reflux period, no color change was observed. The mixture was then continuously extracted with ether for 3 hr. A second continuous extraction for 12 hr. yielded no additional material. After drying with sodium sulfate, the ether from the first extraction was removed by slow distillation and the resulting material was fractionally distilled. Two main fractions were observed in this distillation: Fraction 1, 5.6 g., b.p. 98–102°, a mixture of trimethylsilanol and hexamethyldisiloxane; Fraction 2, 5.9 g., b.p. 128–130°, pyrrole. The total weight recovered (including the intermediate fractions) was 15.9 g.

Gas phase analysis (Silicone column, $T = 148^\circ$) of the first main fraction yielded two peaks: peak 1, retention time, 0.32 min. and peak 2, retention time, 0.65 min. The area under peak 1 was *ca.* 60%, and that of peak 2, *ca.* 40%. The retention time of peak 2 was the same as that of an authentic sample of hexamethyldisiloxane. It is believed that peak 1 corresponds to trimethylsilanol, although it was not compared to an authentic sample of that compound. A large band at 2.80μ (—OH) in the infrared spectrum of this lower-boiling fraction was observed.

(26) R. O. Sauer, *J. Am. Chem. Soc.*, **66**, 1707 (1944).

(27) Ref. 26.

The infrared spectrum of the last fraction and that of pyrrole were identical. Gas phase chromatography at 148° and at 130° using a Silicone column showed peaks which had the same retention times as those of an authentic sample of pyrrole.

Attempted reaction of N-trimethylsilylpyrrole with ethanol. In a 10-ml. Erlenmeyer flask were placed 116 mg. of *N*-trimethylsilylpyrrole and 2.0 ml. of ethanol (containing less than 1% water), and the mixture was swirled for 1 min. A 0.005-ml. aliquot was removed and injected into the gas phase instrument (Silicone column, T = 110°). Only one peak, which had the same retention time as that of *N*-trimethylsilylpyrrole was observed. The ethanol mixture was then heated under reflux for 1 hr., after which time another 0.005-ml. aliquot was injected into the gas phase instrument. This time two peaks were detected, the major one having the same retention time as the *N*-trimethylsilylpyrrole and the second (shorter retention time) the same as that of pyrrole; however, the area of the pyrrole peak was only 0.12% of the total area of the two peaks. The mixture was allowed to stand 3 days at which time the area under the pyrrole peak was 0.14% of the total area. No other compounds, besides ethanol, were detected in any of the gas chromatograms.

Reaction with aqueous ethanol. In a 10-ml. Erlenmeyer flask were placed 56 mg. of *N*-trimethylsilylpyrrole, 1.0 ml. of ethanol, and 0.5 ml. of water. After 15 min. a 0.005-ml. aliquot was removed and injected into the gas phase instrument (Silicone column, T = 110°). The major peak was that of *N*-trimethylsilylpyrrole. A small deflection in the baseline having the same retention time as pyrrole was detected; however, the area was too small for an area comparison. After the solution had been heated under reflux for 30 min., the pyrrole peak had increased to 19.5% of the total, and after 1 hr., 29%.

Acid-catalyzed reaction. In a 10-ml. Erlenmeyer flask were placed 110 mg. of *N*-trimethylsilylpyrrole, 2.0 ml. of ethanol and 1 drop of concentrated hydrochloric acid. The solution was swirled and, in less than 1 min. after the initial mixing, a 0.005-ml. aliquot was injected into the gas phase instrument (Silicone column, T = 105°). Three peaks were observed: peak 1, retention time, 0.80 min., area, 22%; peak 2, retention time, 12.0 min., area, 30%; and peak 3, retention time, 1.60 min., area, 48%. Under the same conditions, pyrrole had a retention time of 1.60 min. and *N*-trimethylsilylpyrrole, 5.20 min. No trace of the *N*-trimethylsilylpyrrole could be detected. Peak 2 had the same retention

time as a sample of trimethylethoxysilane prepared from trimethylchlorosilane and ethanol.

Base-catalyzed reaction. In a 10-ml. Erlenmeyer flask were placed 71 mg. of *N*-trimethylsilylpyrrole and 1.0 ml. of ethanol. To this solution was added 4 mg. of potassium hydroxide (in ethanol) and the mixture was swirled for 1 min., then a 0.005 ml. aliquot was injected into the gas phase instrument (Silicone column, T = 105°). Two major peaks were observed and the trace of a third was detected; peak 1, retention time, 0.04 min., trace; peak 2, retention time, 0.74 min., 51%; peak 3, retention time, 1.56 min., 48%. Under the same conditions, the retention time for pyrrole was 1.57 min. and the time for *N*-trimethylsilylpyrrole was 5.15 min. No deflection in the base line could be detected at 5.15 min., indicating the absence of the *N*-silylpyrrole. Peak 2 had the same retention time as a sample of trimethylethoxysilane prepared from trimethylchlorosilane and ethanol.

Attempted thermal rearrangement of N-trimethylsilylpyrrole. One gram of *N*-trimethylsilylpyrrole was sealed in a glass tube and heated at 225° for 17 hr. By the end of the heating period the material had undergone extensive charring. An aliquot of the liquid remaining was analyzed using gas phase chromatography (Silicone column, T = 110°), and only one peak (*N*-silylpyrrole) could be detected.

Another attempt was made, using diphenyl ether as solvent. A mixture of 10 ml. of diphenyl ether (b.p. 259°) and 1.0 g. of *N*-trimethylsilylpyrrole was heated under reflux for 12 hr. No charring was observed. Gas phase analysis of the reaction mixture indicated that the *N*-silylpyrrole had not undergone rearrangement. Only peaks corresponding to the *N*-silylpyrrole and the diphenyl ether were detected. *N*-Trimethylsilylpyrrole was isolated from the reaction mixture using the gas phase instrument; its infrared spectrum was identical with that of the starting *N*-silylpyrrole.

Tetrapyrrolylsilane (II). To 0.2 mole of potassium pyrrole in 150 ml. of ether and 75 ml. of benzene was added 0.05 mole of silicon tetrachloride over a 30-min. period, and the mixture was heated under reflux for 45 min. The potassium chloride was filtered from the mixture and the solution was allowed to stand overnight. The white, needle-like crystals which formed were filtered and recrystallized from benzene to yield 0.7 g. (4.5%) of tetrapyrrolylsilane (II), m.p. 167.5–168.5° (lit.,²⁸ m.p. 173°).

SAN JOSE, CALIF.

(28) Ref. 9(a).

[CONTRIBUTION NO. 11 FROM THE EXPLORATORY RESEARCH LABORATORY OF DOW CHEMICAL OF CANADA, LIMITED]

Organophosphorus Compounds. VII.^{1a} Alkyl- and Arylphosphorodihalidothioates Containing Fluorine

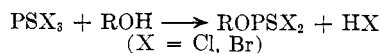
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O-Alkyl- and *O*-arylphosphorodifluoridothioates were prepared from phosphorus thiohalides with alcohols and phenols. *O*-Arylphosphorochlorofluoridothioates were prepared from phosphorus thiodichlorofluoride and phenols.

The synthesis of *O*-alkylphosphorodihalidothioates were first reported by Pistschimuka^{2,3} and in-

volved the reaction of phosphorus thiochloride or bromide with an alcohol:^{4,5,6}



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