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Pyrrylsilanes

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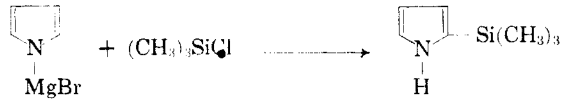
Pyrrylsilanes, a new class of heterocyclic silanes, were prepared by two different methods. In the first, pyrrylmagnesium bromide was reacted with methylchlorosilanes. The second method involved metalation of pyrrole by means of butyllithium, followed by the reaction of the resulting pyrryllithium with methylchlorosilanes. 2-Pyrryltrimethylsilane, made by the above two routes, was found to be identical by determination of analytical, physical, and infrared absorption data. Strong absorption at 2.99μ, indicating the presence of the unsubstituted N—H group, served as further evidence for the location of the trimethylsilyl group in the 2-position of the pyrrole nucleus. In addition to 2-pyrryltrimethylsilane, 2-pyrrylmethyldichlorosilane was prepared, which on hydrolysis yielded a white polymeric siloxane.

The chemistry of heterocyclic silane derivatives has been little explored. Benkeser and Currie[1] prepared 2-thienyl- and 2-furyl-trimethylsilane by reaction of thiophene or furan with butyllithium and trimethylchlorosilane. Other thienylsilanes and thienyl-substituted polysiloxanes were also studied by Gilman and Plunkett,[2] Gilman, Benkeser, and Dunn,[3] and by George.[4]

Pyridylchlorosilanes were reported by Bluestein[5] using the direct method. Other pyridylsilane derivatives and piperidinosilanes were made by Allen and Burness[6] and Breederveld and Waterman.[7]

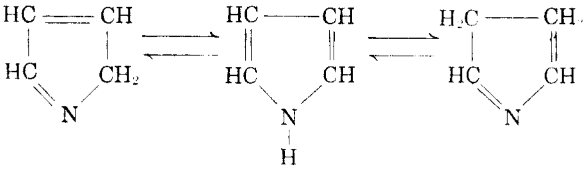
Gilman and Nobis[8] prepared 4-trimethyl- and 4-triphenyl-silyldibenzothiophene by reaction of dibenzothiophene with *n*-butyllithium and the corresponding chlorosilane derivative. However, no pyrrylsilanes have been reported in literature so far.

The pyrrylsilanes reported in this paper were prepared by two different methods. The first method consisted of the reaction of pyrrylmagnesium bromide (I) with methylchlorosilanes. Thus 2-pyrryltrimethylsilane (II) was prepared from pyrrylmagnesium bromide and trimethylchlorosilane:



I II

Some controversy exists in the literature concerning the structure of the pyrrylmagnesium halides[9,10] and the mechanism of reactions with alkyl or acyl halides, but it is reasonably well established that the pyrrole Grignard compounds are N-magnesium derivatives. Subsequent reactions with alkyl or acyl halides leads, in the majority of cases, to C-substitution in the 2-position. The fact that pyrrylmagnesium halides behave in most reactions as if the $-$MgX group is in the 2-position has led to the assumption that pyrrole is tautomeric with the α- and β-pyrrolenines[11] as shown below, although infrared and Raman spectra data indicate the absence of the tautomeric pyrrolenine structures.[12,13]



Alternately, pyrrole can be regarded as a resonance hybrid, since resonance occurs with structures such as those shown below:

The latter assumption leads to a structure which is in accord with the properties exhibited by pyrrole. Experimental evidence, particularly with regard to the kinetics of iodination furnished by Doak and Corwin[14] and Brunings and Corwin[15] indicates that

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(1) Benkeser and Currie, *J. Am. Chem. Soc.*, **70**, 1780 (1948).

(2) Gilman and Plunkett, *J. Am. Chem. Soc.*, **71**, 1117 (1949).

(3) Gilman, Benkeser, and Dunn, *J. Am. Chem. Soc.*, **72**, 1690 (1950).

(4) George, U.S. Patent 2,640,818 (1953); [*Chem. Abstr.*, **47**, 9055 (1953)].

(5) Bluestein, U.S. Patent 2,584,665 (1952); [*Chem. Abstr.*, **46**, 4279 (1952)].

(6) Allen and Burness, U. S. Patent 2,500,110 (1950); [*Chem. Abstr.*, **44**, 5744 (1950)].

(7) Breederveld and Waterman, *Research* (*London*), **5**, 537 (1952); [*Chem. Abstr.*, **47**, 3169 (1953)].

(8) Gilman and Nobis, *J. Am. Chem. Soc.* **72**, 2629 (1950).

(9) Nenitzescu, *Bull. soc. chim. Romania*, **11**, 130 (1930); [*Chem. Abstr.*, **24**, 2458 (1930)].

(10) Gilman and Heck, *J. Am. Chem. Soc.* **52**, 4949 (1930).

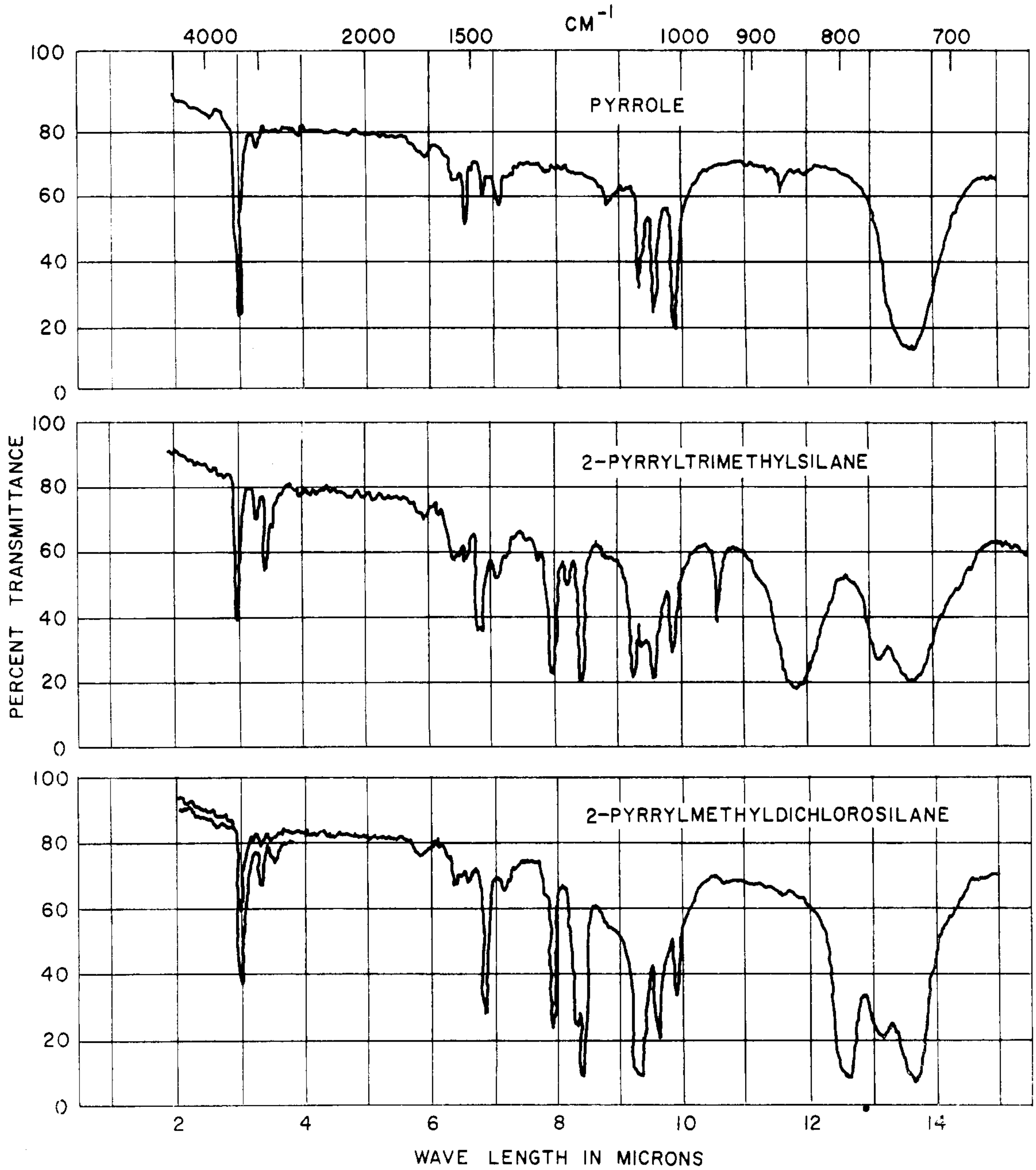
(11) Fischer and Orth, *Die Chemie des Pyrrols*, Vol. I, p. 7, Leipzig, 1934.

(12) Zumwalt and Badger, *J. Chem. Phys.*, **7**, 629 (1939).

(13) Lord and Miller, *J. Chem. Phys.*, **10**, 328 (1942).

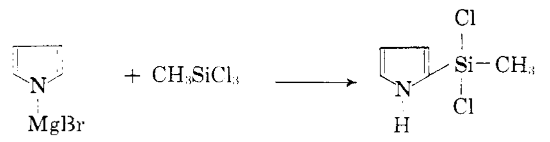
(14) Doak and Corwin, *J. Am. Chem. Soc.*, **71**, 159 (1949).

(15) Brunings and Corwin, *J. Am. Chem. Soc.*, **64**, 594 (1942).



resonance rather than tautomerism is involved in substitution reactions of pyrrole. Infrared data on compound II showed strong absorption at 2.99 μ indicating the presence of the unsubstituted NH grouping as further evidence for the substitution of the trimethylsilyl group in the 2-position.

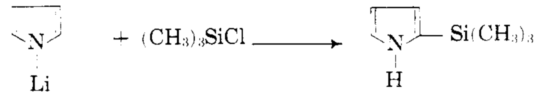
Likewise, pyrrylmagnesium bromide reacted with methyltrichlorosilane to yield 2-pyrrylmethyldichlorosilane (III):



I III

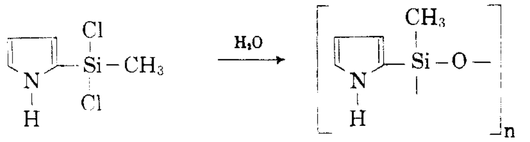
The second method used in the preparation of the pyrrylsilane derivatives was the reaction of pyrryllithium (IV) with methylchlorosilanes. Pyrryllithium was prepared by metalation of pyrrole with butyllithium, similar to the method used by Benkeser and Currie[1] in the case of the corresponding 2-thienyl and 2-furyl derivatives.

2-Pyrryltrimethylsilane, (II), prepared from pyrryllithium (IV) and trimethylchlorosilane was found to be identical to the product prepared *via* the Grignard reaction.



IV II

2-Pyrrylmethyldichlorosilane (III) on hydrolysis with water yields a white polymer (V).



III V

The white polymer (V) on standing darkens fairly rapidly and assumes a brown color.

EXPERIMENTAL

Pyrrylmagnesium bromide was prepared by a modification of the original method of Oddo.[16] Ethylmagnesium bromide was prepared from 218 g. of ethyl bromide, 48.6 g. of magnesium filings, and 500 cc. of ether. A solution of 132 g. of pyrrole (practical grade, Brothers Chem. Co., Orange, N. J.) in 150 cc. of ether was added gradually with cooling. After the addition was completed, it was allowed to come to room temperature and was finally refluxed for 2 hours. The pyrrylmagnesium bromide solution assumed a dark green color.

2-Pyrryltrimethylsilane (II). *Method "A."* A solution of 108.5 g. of trimethylchlorosilane in 150 cc. of ether was added slowly to half of the above prepared pyrrylmagnesium bromide. The addition was regulated at such a rate that moderate refluxing was maintained. Afterwards, the mixture was refluxed for 2 hours. The inorganic precipitate was filtered off and washed with ether. The solvent and other low-boiling materials were removed from the filtrate by distillation. The residual liquid was fractionated. The redistilled product distilled at 149–151° as a colorless liquid.

n_D^{24} 1.4670; d_4^{24} 0.875;; M_R (Calc'd): 44.7; M_R (Found): 44.1. The yield was about 72.5 g. (52% yield based on the chlorosilane used).

Anal. Calc'd for $C_7H_{13}NSi$: N, 10.1; Si, 20.1. Found: N, 10.7; Si, 19.7.

2-Pyrryltrimethylsilane in acetone solution produces a bright red color on acidification with hydrochloric acid.

2-Pyrrylmethyldichlorosilane (III). To a solution of 149.5 g. of methyltrichlorosilane in 250 cc. of ether was added gradually half of the above prepared pyrrylmagnesium bromide solution. The reaction was exothermic and the addition of the Grignard solution was regulated to maintain gentle refluxing. Afterwards, the mixture was refluxed for one hour. The inorganic precipitate was filtered off and washed with ether. After removal of the solvent and other low-boiling materials, the product distilled at 67° at 4.8 mm. (82° at 5.9 mm.). On redistillation, 2-pyrrylmethyldichlorosilane distilled at 37° at 0.25 mm. as a colorless liquid which fumed strongly on exposure to air. The yield was 75 g. (42% based on the chlorosilane used).

Anal. Calc'd for $C_5H_7Cl_2NSi$: C, 33.3; H, 3.9; N, 7.8; Si, 15.55. Found: C, 32.5; H, 3.8; N, 7.8; Si, 14.7.

Pyrrylmethyldichlorosilane on addition of acetone forms a deep red solution. On prolonged exposure to the air, a strongly exothermic reaction takes place resulting in some resinification. This is probably caused by the action of traces of hydrochloric acid which is formed by partial hydrolysis of III.

Pyrryllithium. *n*-Butyllithium was made using the procedure reported by Gilman and co-workers.[17] A yield of about 80% of *n*-butyllithium was obtained. The *n*-butyllithium solution, prepared from 8.6 g. of lithium metal (in wire form), 68.5 g. of butyl bromide and 300 g. of ether, was charged gradually into a 1000-cc. 3-necked flask, containing 29.5 g. of pyrrole and 50 cc. of ether. A mildly exothermic reaction took place and the product changed from clear orange solution to a gray-green slurry. After the addition had been completed, stirring was continued for one hour.

2-Pyrryltrimethylsilane (II). *Method "B".* To the above prepared pyrryllithium slurry was added gradually a solution of 43 g. of trimethylchlorosilane in 100 cc. of ether. After the addition was completed, which took place with slight heat evolution, the mixture was refluxed for one hour. The inorganic precipitate was filtered off and the filtrate was freed from solvent. The residual liquid was fractionated. The product distilled at 149–152° as a colorless liquid, n_D^{24} 1.4653; d_4^{24} 0.875; M_R (Calc'd): 44.7; M_R (Found): 43.9. The yield was 22 g. (40% of theoretical yield, based on the amount of trimethylchlorosilane used).

Anal. Calc'd. for $C_7H_{13}NSi$: N, 10.1; Si, 20.1. Found: N, 9.8; Si, 19.8.

The infrared data were obtained on a Perkin-Elmer double beam recording infrared spectrophotometer, Model 21. In all cases, liquid film preparations in capillary thickness were used. Pyrrole was used as a standard reference fluid.

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(16) Oddo, *Gazz. chim. ital.*, **39**, I, 649 (1909).

(17) Gilman, Beel, Brannen, Bullock, Dunn, and Miller, *J. Am. Chem. Soc.*, **71**, 1499 (1949).