

PREPARATION, CHEMISTRY AND SPECTRA OF (SILYLMETHYL)-PYRROLES

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Pyrrolylsilicon compounds have been prepared by the reaction of pyrrolyl Grignard reagent, pyrrolyllithium or pyrrolylpotassium with chlorosilanes, and by an exchange reaction between pyrrole and hexamethyldisilazane¹⁻⁴. All of these preparations gave compounds containing the silicon-nitrogen bond. One exception exists, *viz.*, [3-(2,5-dimethyl-1-pyrrolyl)propyl]triethoxysilane⁵, a product of the reaction of (3-aminopropyl)triethoxysilane and 2,5-hexanedione. 2-(Trimethylsilyl)pyrrole³ was erroneously reported as shown by Fessenden and Crowe⁴. These workers found the hydrolytic stability of 1-(trimethylsilyl)pyrrole superior to that of other silazanes and noted its failure to rearrange to 2- or 3-(trimethylsilyl)pyrrole on heating.

In these regards it was of interest to compare the solvolytic stability of 1-(trimethylsilylmethyl)pyrrole with benzyltrimethylsilane in alcoholic base and to determine the susceptibility of 1-(trimethylsilylmethyl)pyrrole to thermal rearrangement. The results of an ancillary interest in the preparation of new functional 1-(silylmethyl)pyrroles and the first 2- and 2,5-silylpyrroles are also reported here.

Recent studies⁶ set 650° as the optimum temperature for the rearrangement of 1-methylpyrrole to 2-methylpyrrole. In view of this finding and the fact that Fessenden and Crowe used relatively mild conditions (247°) in their study of 1-(trimethylsilyl)pyrrole, a reexamination of its thermal stability under more rigorous conditions was indicated. At 650° in a heated flow system under argon the remarkable thermal stability of this silylpyrrole was again demonstrated, there being no detectable change in the material when examined by gas chromatography and infrared techniques. This was not the case with 1-(trimethylsilylmethyl)pyrrole. Under the above conditions this compound produced an effluent whose gas chromatogram was extremely complex. A reactor temperature of 550°, however, produced a chromatogram showing only one major product. The empirical formula and NH absorption in the infrared (Table 2) suggested a simple rearrangement.

N-methylation of the rearranged product gave a material identical with that obtained by reaction of the monolithium derivative of 1-methylpyrrole with (chloromethyl)trimethylsilane. It was established earlier by Shirley *et al.*⁷ that metalating 1-methylpyrrole with butyllithium gave 2-lithio-1-methylpyrrole (and 2,5-dilithio-1-methylpyrrole in the case of dilithiation). The evidence was obtained by carbonating the lithium derivatives with solid carbon dioxide and comparing the melting points of the metalation acids or esters and hydrazides with the values of the known compounds in the literature. Thus, the identity of the rearrangement product was verified as 2-(trimethylsilylmethyl)pyrrole.

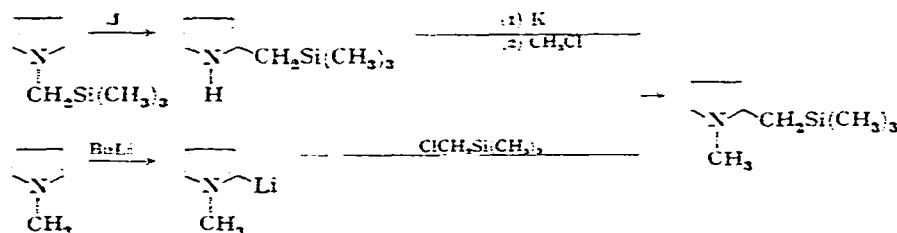
TABLE I

INFRARED SPECTRA OF 1-SUBSTITUTED PYRROLES ($\begin{array}{c} \text{---} \\ | \\ \text{N-X} \\ | \\ \text{---} \end{array}$)

Band positions in cm^{-1} . Intensities: s = strong, m = medium, w = weak, sh = shoulder. $\text{X}^1 = -\text{Si}(\text{CH}_3)_3$, $\text{X}^2 = -\text{CH}_2\text{Si}(\text{CH}_3)_3$, $\text{X}^3 = -\text{CH}_2\text{Si}(\text{CH}_3)_2(\text{OC}_2\text{H}_5)$, $\text{X}^4 = -\text{CH}_2\text{Si}(\text{CH}_3)(\text{OC}_2\text{H}_5)_2$, $\text{X}^5 = -\text{CH}_2\text{Si}(\text{OC}_2\text{H}_5)_3$.

X^1	X^2	X^3	X^4	X^5	Assignment
3110 w	3110 w	3110 w	3110 w	3110 w	C-H stretching on pyrrole ring
2967 m	2960 m	2970 m	2975 m	2994 m	C-H stretching
	2902 w	2890 m	2928 w	2933 w	C-H stretching
			2886 m	2907 m	C-H stretching
1563 w	1532 w	1529 w	1547 w	1546 w	
1475 m	1500 m	1498 m	1498 m	1502 m	1-substituted pyrrole ring ^b
		1437 sh	1443 w	1443 w	Si-OC ₂ H ₅
1412 w	1414 m	1406 sh	1415 sh		C-H bending (antisym.) of Si-CH ₃
		1391 m	1393 m	1395 m	Si-OC ₂ H ₅
		1302 sh	1306 sh	1308 w	Si-OC ₂ H ₅
1332 w					
1296 w		1292 sh	1294 w	1297 sh	
1274 sh	1276 m	1276 m	1276 m	1282 m	1-substituted pyrrole ring ^b
1259 s	1254 s	1255 s	1262 m		C-H bending (sym.) of Si-CH ₃
1224 w					
1193 s					Si-N stretching(?) ^c
		1163 m	1165 m	1167 m	Si-OC ₂ H ₅
		1105 s	1104 s	1103 s	Si-OC ₂ H ₅
1086 s	1090 s	1087 s	— ^d	— ^d	1-substituted pyrrole ring ^b
		1078 s	1080 s	1085 s	Si-OC ₂ H ₅
1070 w					
1048 s	1062 s	1062 sh	1064 sh	1066 sh	1-substituted pyrrole ring ^b
947 m	967 m	966 m	— ^d	— ^d	1-substituted pyrrole ring ^b
		949 m	958 s	966 s	Si-OC ₂ H ₅
				945 sh	
843 s	850 s				-Si(CH ₃) ₃
		840 s	832 m	818 m	
		799 m	793 s	800 m	-Si(CH ₃) ₃
760 m	762 m				
		750 sh	766 w	774 m	
731 s	717 s	720 s	718 s	721 s	C-H out-of-plane bending on pyrrole ring ^b
695 sh	696 w	692 sh		683 w	

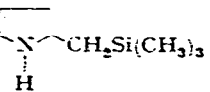
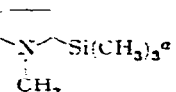
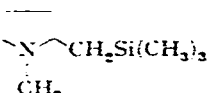
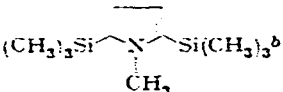
^a Matches previously-published spectrum¹. ^b This set of bands, which also appears in the infrared spectra of 1-methylpyrrole and 1-*n*-butylpyrrole, seems to be characteristic of the 1-substituted pyrrole ring. ^c A discussion of the difficulty in assigning the Si-N stretching has been published¹¹. ^d Band obscured by strong Si-OC₂H₅ absorption.



The rearrangement conditions were optimized to give as nearly as possible a single product in order to simplify the task of separation. Jacobson *et al.*⁸ observed 3-methylpyrrole in addition to 2-methylpyrrole from the thermal rearrangement of

TABLE 2

INFRARED ABSORPTION MAXIMA (cm⁻¹) OF 2-SUBSTITUTED SILYLPYRROLES

	3484 sh (N-H stretching), 3380 s (N-H stretching), 3100 w (C-H stretching on pyrrole ring), 2956 m (C-H stretching), 2892 w (C-H stretching), 1566 m, 1537 sh, 1470 m, 1453 sh, 1428 w, 1413 w (antisym. C-H bending of Si-CH ₃), 1389 sh, 1276 sh, 1262 sh, 1247 s (sym. C-H bending of Si-CH ₃), 1163 m, 1121 w, 1095 m, 1078 m, 1023 s, 955 m, 883 w, 845 s [-Si(CH ₃) ₃], 782 m, 759 m [-Si(CH ₃) ₃], 705 s (C-H out-of-plane bending on pyrrole ring).
	3100 w (C-H stretching on pyrrole ring), 2957 s (C-H stretching), 2900 w (C-H stretching), 1517 m, 1448 m, 1406 m, 1345 w, 1292 s, 1250 s (sym. C-H bending of Si-CH ₃), 1205 m, 1120 m, 1087 m, 1053 w, 998 w, 884 m, 837 s [-Si(CH ₃) ₃], 753 s, 718 s (C-H out-of-plane bending on pyrrole ring), 688 w, 677 w
	3100 w (C-H stretching on pyrrole ring), 2955 s (C-H stretching), 2920 sh, 2984 m, 1542 m, 1492 s, 1470 sh, 1442 m, 1413 m, 1300 m, 1247 s (sym. C-H bending of Si-CH ₃), 1194 m, 1154 m, 1093 m, 1076 sh, 1050 w, 997 m, 891 m, 842 s [-Si(CH ₃) ₃], 774 m, 753 m, 693 s (C-H out-of-plane bending on pyrrole ring). The spectra of both preparations were essentially identical.
	3118 w, 3100 w (C-H stretching on pyrrole ring), 2964 s (C-H stretching), 2900 w (C-H stretching), 1495 w, 1477 m, 1433 w, 1422 w, 1407 (antisym. C-H bending of Si-CH ₃), 1351 w, 1332 m, 1285 w, 1270 w, 1252 sh, 1243 s (sym. C-H bending of Si-CH ₃), 1175 s, 1160 sh, 1076 sh, 1027 w, 919 s, 835 s [-Si(CH ₃) ₃], 762 w, 752 s (C-H out-of-plane bending on pyrrole ring), 688 m

^a The infrared spectrum of the original sample showed a sharp band of medium intensity at 2015 cm⁻¹. In the spectrum of another sample, trapped from the gas chromatograph, the 2015 cm⁻¹ band was weaker - evidence that this band is due to an impurity. The impurity is thought to be something containing a cumulative double bond (N=Y=Z). The N=Y=Z grouping has a very strong band at this frequency. ^b This compound was examined in the solid state as a split mull and then as a solid film crystallized from the melt on a KBr plate. Both preparations gave the same infrared pattern.

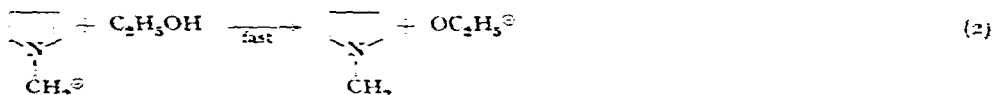
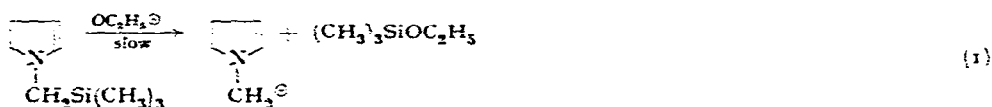
1-methylpyrrole. It is not unlikely that 3-(trimethylsilylmethyl)pyrrole could be isolated from a run at higher temperatures and might indeed be the impurity observed with the 2-(trimethylsilylmethyl)pyrrole (see EXPERIMENTAL).

There is no compelling reason to believe that the mechanism involved in this rearrangement is any different from that postulated for a similar system by Patterson *et al.*⁹, namely, a homolytic carbon-nitrogen bond cleavage followed by recombination at the 2-position. Whereas, Patterson's rearrangement⁹ was inherently intramolecular no similarly positive statement can be made about the rearrangement of 1-(trimethylsilylmethyl)pyrrole. In fact, it has not been shown whether the fundamental rearrangement, that of 1-methylpyrrole, is inter- or intramolecular.

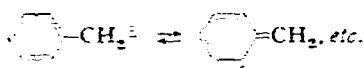
The base-catalyzed alcoholysis to which both 1-(trimethylsilylmethyl)pyrrole and benzyltrimethylsilane were subjected showed a greater extent of reaction with the benzyl compound, *i.e.*, the pyrrole compound was the more stable. This was determined by calibrated gas chromatographic analysis. The mode of cleavage at the Si-C bond was the same in both cases giving 1-methylpyrrole plus ethoxytrimethyl-

silane, and toluene plus ethoxytrimethylsilane, respectively. 1-(Trimethylsilylmethyl)pyrrole was also more stable than 1-(trimethylsilyl)pyrrole which was quantitatively cleaved by alcoholic base in one minute at room temperature⁴. Only 4.4% of the 1-(trimethylsilylmethyl)pyrrole was cleaved after 12 hours at reflux.

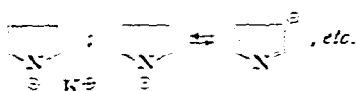
These results are consistent with the mechanism discussed for benzylsilicon compounds by Eaborn¹⁰:



The 1-pyrrolylmethyl anion would not have as great a resonance stabilization as the benzyll anion,



Hence, step (1) above would be slower for the pyrrole compound than in the cleavage of benzyltrimethylsilane. Using the same reasoning, the pyrrole anion must have great resonance stabilization. This is seen in the easy formation of the potassium salt:



Hence, step (1) above corresponding to the base-catalyzed cleavage of 1-(trimethylsilyl)pyrrole would produce the highly stabilized pyrrole anion which would explain why this cleavage occurs so readily.

The structures of 1-methyl-2-(trimethylsilyl)pyrrole and 1-methyl-2,5-bis(trimethylsilyl)pyrrole, a nicely crystalline compound, are based on the conclusions noted above by Shirley and coworkers. The preparation of the related 2,5-bis(chlorodimethylsilyl)-1-methylpyrrole deserves special note*. Its reactive functionality required a reverse procedure, the addition of the 2,5-dilithio-1-methylpyrrole to an excess of dichlorodimethylsilane. The remaining compounds, the (ethoxysilylmethyl)pyrroles, were prepared by reaction of potassium pyrrole and the appropriate (chloromethyl)ethoxysilane.

EXPERIMENTAL

The elemental analyses were the work of Galbraith Laboratories, Inc., Knoxville, Tennessee. Gas chromatographic analyses and trappings were performed with a

* The extreme reactivity of the lithium derivative was evidenced during the first preparation by sparking in the argon-filled flask containing the chlorosilane. It was during the second preparation that, perhaps due to insufficient removal of air by the argon, the sparking was followed by an explosion.

Model 500 instrument, F and M Scientific Co., using a $\frac{1}{4}$ in \times 4 ft column packed with 20 % General Electric Co. SE-30 silicone gum on 80-100 mesh Diaport S (F and M Scientific Co.) and helium as the carrier gas. Boiling points are uncorrected. The infrared spectra were recorded on either a Perkin-Elmer Model 21 spectrometer, equipped with a sodium chloride prism, or a Model 521 spectrometer, equipped with a grating. Liquid compounds were examined as a thin film of neat liquid between sodium chloride or potassium bromide plates.

Special attention is drawn to the hazard noted with the use of 2,5-dilithio-1-methylpyrrole.

1-(Trimethylsilylmethyl)pyrrole

Pyrrolylpotassium was prepared from 34.4 g (0.88 g-atom) of diced potassium metal and 79 g (1.18 mole) of pyrrole (Aldrich Chemical Co., Inc.) in 350 ml of dry toluene under a blanket of dry nitrogen. Then 108 g (0.88 mole) of (chloromethyl)-trimethylsilane which had been prepared from chloro(chloromethyl)dimethylsilane by the method of Nozakura¹² was added. The mixture was refluxed for 72 h at which time a small sample failed to show the presence of (chloromethyl)trimethylsilane when examined chromatographically. The reaction mixture was filtered under nitrogen through a fritted glass disc and the filtrate was fractionally distilled. There was obtained 80.0 g (59% yield) of product, b.p. 84° (30 mm), n_D^{25} 1.4744, d_4^{25} 0.872. (Found: C, 62.90; H, 10.01; N, 9.05; Si, 18.39. $C_8H_{15}NSi$ calcd.: C, 62.67; H, 9.86; N, 9.14; Si, 18.32%.)

1-(Ethoxydimethylsilylmethyl)pyrrole

This compound was prepared by the same procedure on a 0.5 mole scale using (chloromethyl)ethoxydimethylsilane¹³. Fractional distillation gave 16.5 g (18% yield) of product, b.p. 120° (50 mm), n_D^{25} 1.4664, d_4^{25} 0.930. (Found: C, 58.96; H, 9.35; N, 7.64; Si, 15.32. $C_9H_{17}NOSi$ calcd.: C, 59.06; H, 9.16; N, 7.91; Si, 15.07%.)

1-(Diethoxymethylsilylmethyl)pyrrole

This preparation was conducted on a 0.5 mole scale by the above procedure using (chloromethyl)diethoxymethylsilane¹⁴. Distillation gave 57.5 g (54% yield) of product, b.p. 123° (30 mm), n_D^{25} 1.4574, d_4^{25} 0.968. (Found: C, 56.41; H, 9.02; N, 6.80; Si, 13.39. $C_{10}H_{19}NO_2Si$ calcd.: C, 56.28; H, 9.00; N, 6.56; Si, 13.17%.)

1-(Triethoxysilylmethyl)pyrrole

Pyrrolylpotassium was prepared on a 0.5 mole scale in 150 ml of dry benzene. Then 106.5 g (0.5 mole) of (chloromethyl)triethoxysilane¹⁵ was added and the mixture was refluxed for 24 h at which time (chloromethyl)triethoxysilane was no longer detected (gas chromatography). Distillation of the filtrate from the reaction mixture afforded 50.2 g (41% yield) of product, b.p. $136-137^\circ$ (29 mm), n_D^{25} 1.4488, d_4^{25} 0.995. (Found: C, 54.33; H, 8.56; N, 5.66; Si, 11.64. $C_{12}H_{21}NO_3Si$ calcd.: C, 54.28; H, 8.69; N, 5.76; Si, 11.58%.)

1-Methyl-2-(trimethylsilyl)pyrrole

The lithium derivative of 1-methylpyrrole was prepared by refluxing 0.5 mole of *n*-butyllithium in hexane (Foote Mineral Co.) and 40.5 g (0.5 mole) of 1-methyl-

pyrrole (Aldrich Chemical Co., Inc., redistilled from calcium hydride) under an argon atmosphere until butane was no longer evolved (ca. 20 h). After cooling the mixture to 0°, 54.3 g (0.5 mole) of chlorotrimethylsilane was added dropwise. No reaction was evident. On warming to room temperature an exothermic reaction occurred which caused the mixture to reflux. The reaction mixture was cooled, 250 ml of water was added and the hexane layer was separated and dried with sodium sulfate. Fractional distillation gave a 6 g fraction, b.p. 95–97° (40 mm), n_D^{25} 1.4850, d_4^{25} 0.888. (Found: C, 62.72; H, 9.60; N, 9.00; Si, 18.46. $C_4H_{13}NSi$ calcd.: C, 62.67; H, 9.86; N, 9.14; Si, 18.32 %.)

1-Methyl-2,5-bis(trimethylsilyl)pyrrole

A second fraction was isolated from the distillation of 1-methyl-2-(trimethylsilyl)pyrrole amounting to 14 g, b.p. 137.5–140° (40 mm). This product crystallized and was further purified by sublimation, m.p. 76.2–77.5°. (Found: C, 58.63; H, 10.17; N, 6.24; Si, 24.97. $C_{11}H_{23}NSi_2$ calcd.: C, 58.59; H, 10.28; N, 6.21; Si, 24.92 %.)

2,5-Bis(chlorodimethylsilyl)-1-methylpyrrole

The dilithium derivative of 1-methylpyrrole was prepared by refluxing a mixture of 625 ml of a hexane solution containing 64 g (1.0 mole) of *n*-butyllithium and 40.5 g (0.5 mole) of 1-methylpyrrole (Aldrich Chemical Co., redistilled from calcium hydride) under an argon atmosphere until the evolution of butane ceased. This preparation was added under argon at 0° to 371 g of dichlorodimethylsilane. Toward the end of the addition, solids which had formed on the wall of the reaction flask below the addition funnel were seen to glow momentarily. The mixture darkened on warming to room temperature and was then filtered under argon pressure through a fritted disc. Distillation of the filtrate gave a product fraction, 7.0 g, b.p. 161–162° (28 mm), n_D^{25} 1.5130, d_4^{25} 1.096. (Found: C, 40.41; H, 6.61; Cl, 26.31; N, 5.28; Si, 20.82. $C_9H_{17}Cl_2NSi_2$ calcd.: C, 40.59; H, 6.43; Cl, 26.62; N, 5.26; Si, 21.09 %.)

During a second preparation when the dilithiopyrrole reagent was being added to the dichlorodimethylsilane, the mixture exploded violently resulting in a fire.

Comparison of the stability of benzyltrimethylsilane and 1-(trimethylsilylmethyl)pyrrole in alcoholic base

Benzyltrimethylsilane¹⁶ (1.00 g) was refluxed for 12 h with a solution prepared from 1 g of potassium hydroxide and 19 g of absolute ethyl alcohol. A calibrated gas chromatographic analysis of the mixture for the toluene to benzyltrimethylsilane ratio indicated a 35.0 ± 0.7 % conversion of the benzyltrimethylsilane to toluene. The other product was identified by gas chromatographic analysis as ethoxytrimethylsilane by a comparison with the retention time of an authentic sample.

1-(Trimethylsilylmethyl)pyrrole (1.00 g) was refluxed for 12 h with a solution prepared from 1 g of potassium hydroxide and 19 g of absolute ethyl alcohol. A calibrated gas chromatographic analysis for the ratio of 1-methylpyrrole to 1-(trimethylsilylmethyl)pyrrole indicated a 4.41 ± 0.02 % conversion of 1-(trimethylsilylmethyl)pyrrole to 1-methylpyrrole. Ethoxytrimethylsilane was again identified as the other product.

Rearrangement of 1-(trimethylsilylmethyl)pyrrole

The reactor was a vertical Pyrex tube (300 × 25 mm) with a fritted disc sealed across the tube at mid-length, a thermocouple in a Pyrex well which extended almost to the fritted disc, and with provisions for feeding argon at the same time the reactant was being added from a dropping funnel at the top of the tube. Crushed Berl saddles were placed on the fritted disc to a depth of 75 mm. The outlet was provided with a water-cooled condenser and receiver. The entire tube was heated electrically with a tube furnace. An initial trial at $650 \pm 3^\circ$ showed (gas chromatography) that 1-(trimethylsilylmethyl)pyrrole was converted to at least twenty compounds in one pass. However, one pass at $550 \pm 3^\circ$ gave only one product plus the starting material. A second pass at 550° gave an increased conversion plus a small amount of a second product. In this manner 102 g of reactant was processed in two passes at 35 minutes per pass to give 97.5 g of effluent. Its gas chromatogram showed 54% starting material, 39% 2-(trimethylsilylmethyl)pyrrole and 7% of the second product (peak area basis). Distillation of the effluent on a spinning band column gave 26.7 g, b.p. $94\text{--}95.5^\circ$ (10 mm) of 2-(trimethylsilylmethyl)pyrrole free of starting material but containing 9% of the second product. Final purification was effected by gas chromatographic trapping technique. Chromatographically pure material had n_D^{25} 1.4873, d_4^{25} 0.897. (Found: C, 62.60; H, 9.89; N, 9.07; Si, 18.53. $C_8H_{15}NSi$ calcd.: C, 62.67; H, 9.86; N, 9.14; Si, 18.32%.)

1-Methyl-2-(trimethylsilylmethyl)pyrrole by methylation of 2-(trimethylsilylmethyl)pyrrole

Impure 2-(trimethylsilylmethyl)pyrrole, 14 g (91% pure), isolated in the previous experiment, was added under argon to a well-stirred mixture of 3.2 g of diced potassium metal and 100 ml of dry toluene. The flask contents were refluxed for 4 h at which time the potassium was no longer visible. The mixture was cooled to room temperature and methyl chloride was bubbled in slowly with external cooling until the exothermic reaction had ceased. The mixture was refluxed for 0.5 h, cooled and filtered under argon pressure through a fritted glass disc. Simple distillation of the filtrate afforded 11.1 g of material, b.p. $85\text{--}101^\circ$ (20 mm), which consisted of three compounds in the ratio 0.15, 0.16, 1.00 (gas chromatography, peak area basis). The desired product, the major component, was isolated by gas chromatographic trapping technique, n_D^{25} 1.4840, d_4^{25} 0.882. (Found: C, 64.96; H, 9.80; N, 8.60; Si, 16.91. $C_9H_{17}NSi$ calcd.: C, 64.63; H, 10.24; N, 8.38; Si, 16.75%.)

1-Methyl-2-(trimethylsilylmethyl)pyrrole by reaction of 2-lithio-1-methylpyrrole and (chloromethyl)trimethylsilane

1-Methylpyrrole, 60 g (0.74 mole), was added to a solution (470 ml) of 0.75 mole of butyllithium in hexane. The mixture was refluxed under argon overnight after which time butane evolution had ceased. Then 90.6 g (0.74 mole) of (chloromethyl)-trimethylsilane was added and the mixture was refluxed for 24 h. To the cooled reaction mixture 100 ml of water was added, the hexane layer was separated, dried (Na_2SO_4), and fractionally distilled to give 9.0 g of product, b.p. $117\text{--}118^\circ$ (30 mm). Additional purification by gas chromatography gave the product, n_D^{25} 1.4839, d_4^{25} 0.882. (Found: C, 64.48; H, 10.29; N, 8.36; Si, 16.83. $C_9H_{17}NSi$ calcd.: C, 64.63; H, 10.24; N, 8.38; Si, 16.75%.)

ACKNOWLEDGEMENT

The author expresses his appreciation for the painstaking effort expended by Mr. PHILIP J. LAUNER in recording and assembling the infrared data.

SUMMARY

The compounds, $\text{RCH}_2\text{Si}(\text{CH}_3)_x[\text{O}(\text{C}_2\text{H}_5)]_{3-x}$, where $x = 0, 1, 2, 3$ and $\text{R} = 1\text{-pyrrolyl}$, were prepared. $\text{RCH}_2\text{Si}(\text{CH}_3)_3$ was cleaved in alcoholic base by the same mode as $\text{C}_6\text{H}_5\text{CH}_2\text{Si}(\text{CH}_3)_3$ but to a lesser degree. The failure of $\text{RSi}(\text{CH}_3)_3$ to rearrange thermally (650°) was confirmed; $\text{RCH}_2\text{Si}(\text{CH}_3)_3$ rearranged (550°) to the 2-pyrrolyl isomer whose structure was determined by N-methylation and comparison with 1-methyl-2-(trimethylsilylmethyl)pyrrole prepared by an alternate path. Lithiation of 1-methylpyrrole followed by reaction with (1) chlorotrimethylsilane gave 1-methyl-2-(trimethylsilyl)pyrrole and 1-methyl-2,5-bis(trimethylsilyl)pyrrole, and (2) with dichlorodimethylsilane gave 2,5-bis(chlorodimethylsilyl)-1-methylpyrrole.

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