



## USE OF CHLORO(CHLOROMETHYL)DIMETHYLSILANE IN THE SYNTHESIS OF SILICON DERIVATIVES OF PYRROLE

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### Abstract

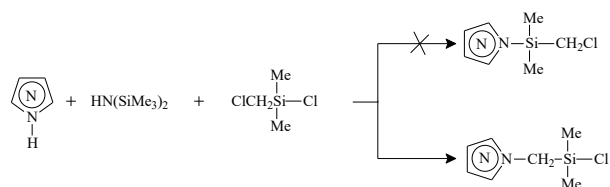
The reaction of pyrrole with hexamethyldisilazane/chloro(chloromethyl)dimethylsilane is shown to lead to the formation of only the transsilylation product—previously unknown 1-[(chloromethyl)dimethylsilyl]-1H-pyrrole. This product was also obtained by the counter synthesis through the interaction of 1-(trimethylsilyl)-1H-pyrrole with chloro(chloromethyl)dimethylsilane. Unlike diazoles, in this case no rearrangement of the Cl–CH<sub>2</sub>–Si–N bond system into the Cl–Si–CH<sub>2</sub>–N system and isomerization of the transsilylation product into the silicon methylation product are realized.

**Key words:** nitrogen-containing heterocyclic compounds, pyrrole, silicon derivatives of pyrrole, chloro(chloromethyl)dimethylsilane.

### Introduction

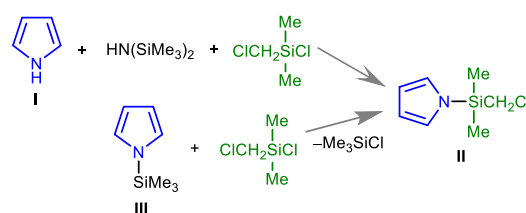
The synthesis and investigation of the properties of nitrogen-containing heterocyclic compounds comprise one of the most promising research areas in organic chemistry for a long time [1]. Of particular interest are five-membered aromatic heterocycles containing one or two nitrogen atoms, such as pyrrole and diazoles. Along with the great practical significance, these compounds have theoretical and synthetic potential, including the investigations on relationships between the chemical properties and reaction directions in their structures.

Earlier Kirilin *et al.* [2], using the examples of five-membered aromatic heterocycles containing two nitrogen atoms, showed that diazoles react with a hexamethyldisilazane/chloro(chloromethyl)dimethylsilane system (Scheme 1) to form exclusively silicon methylation products.



**Scheme 1.** Reaction of diazoles with a hexamethyldisilazane/chloro(chloromethyl)dimethylsilane system.

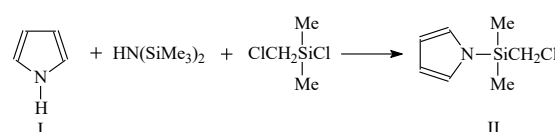
According to the suggested scheme, this interaction, including the reaction of 3,5-dimethylpyrazole (Scheme 2), proceeds through the formation of a transsilylation product, the further isomerization of which leads to a silicon methylation product.



**Scheme 2.** Reaction of 3,5-dimethylpyrazole with a hexamethyldisilazane/chloro(chloromethyl)dimethylsilane system.

### Results and discussion

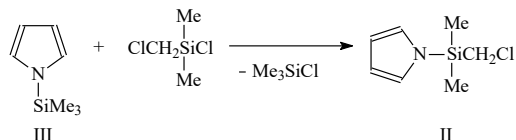
We found that, on passing to an aromatic heterocycle containing one nitrogen atom in its composition, namely, pyrrole, the process regularities change. Thus, the interaction of pyrrole (I) with a hexamethyldisilazane/chloro(chloromethyl)dimethylsilane system (Scheme 3) leads only to a transsilylation product—previously unknown 1-[(chloromethyl)dimethylsilyl]-1H-pyrrole (II) (method A).



**Scheme 3.** Reaction of pyrrole with a hexamethyldisilazane/chloro(chloromethyl)dimethylsilane system.

The reaction was accomplished upon heating at 95 °C under vigorous stirring for 3.5 h. The yield of product **II** was 86%.

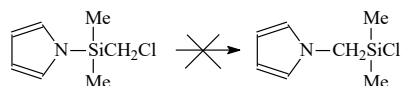
1-[(chloromethyl)dimethylsilyl]-1H-pyrrole was also obtained by the counter synthesis (Scheme 4) through the interaction of 1-(trimethylsilyl)-1H-pyrrole (**III**) with chloro(chloromethyl)dimethylsilane (method **B**).



**Scheme 4.** Reaction of 1-(trimethylsilyl)-1H-pyrrole (**III**) with chloro(chloromethyl)dimethylsilane.

The process was performed by heating the reaction mixture until the release of chlorotrimethylsilane ceased. The yield of product **II** composed 89%.

Unlike diazoles, in this case no rearrangement of the Cl–CH<sub>2</sub>–Si–N bond system into the Cl–Si–CH<sub>2</sub>–N system and isomerization of a transsilylation product into a silicon methylation product were realized (Scheme 5). As a result, 1-[(chloromethyl)dimethylsilyl]-1H-pyrrole (**II**), *i.e.* the transsilylation product, was isolated as the target product.



**Scheme 5.** Possible rearrangement of the Cl–CH<sub>2</sub>–Si–N bond system into the Cl–Si–CH<sub>2</sub>–N system.

The results obtained and the existing literature data allow us to conclude that the formation of a silicon methylation product in reactions of nitrogen-containing heterocyclic compounds bearing a conjugated bond system with the silylating agents hexamethyldisilazane/chloro(chloromethyl)dimethylsilane or their trimethylsilyl derivatives with chloro(chloromethyl)dimethylsilane requires the presence of a second nucleophilic center in the starting compound.

## Experimental section

The IR spectra were recorded on a Specord IR-75 spectrometer in thin layer for liquids. The <sup>1</sup>H NMR spectra were registered on a Bruker WP-300 spectrometer operating at 400 MHz using CDCl<sub>3</sub> as a solvent and an internal standard.

All manipulations were carried out under a dry nitrogen atmosphere.

**Synthesis of 1-[(chloromethyl)dimethylsilyl]-1H-pyrrole (**II**) (method **A**).** Chloro(chloromethyl)dimethylsilane (10.66 g, 74 mmol) was added dropwise to a mixture of pyrrole (5.00 g, 74 mmol) and hexamethyldisilazane (6.57 g, 41 mmol). The

stirred reaction mixture was heated at 95 °C for 3.5 h. The fractionation under reduced pressure gave 11.14 g of compound **II**. Yield: 86%. Bp: 114–116°C/5 mmHg, n<sub>D</sub><sup>20</sup> = 1.4850. IR (ν/cm<sup>-1</sup>): 3080 (CH–CH). <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 0.61 (s, 6H, SiMe), 2.79 (s, 2H, SiCH<sub>2</sub>), 6.29 (s, 2H, CH), 6.83 (s, 2H, CH) ppm. Anal. Calcd for C<sub>7</sub>H<sub>12</sub>NSiCl: C, 48.39; H, 6.91; N, 8.06. Found: C, 48.22; H, 6.97; N 8.18%.

**Synthesis of 1-[(chloromethyl)dimethylsilyl]-1H-pyrrole (**II**) (method **B**).** A mixture of 1-(trimethylsilyl)-1H-pyrrole (3.99 g, 29 mmol) and chloro(chloromethyl)dimethylsilane (4.09 g, 29 mol) was heated with a complete condensation head until the evolution of chlorotrimethylsilane ceased. This afforded 4.43 g of the target product. Yield: 89%. Bp = 115–117°C/5 mmHg, n<sub>D</sub><sup>20</sup> = 1.4885. IR (ν/cm<sup>-1</sup>): 3100 (CH–CH). <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 0.62 (s, 6H, SiMe), 2.99 (s, 2H, SiCH<sub>2</sub>), 6.40 (s, 2H, CH), 6.87 (s, 2H, CH) ppm. Anal. Calcd for C<sub>7</sub>H<sub>12</sub>NSiCl: C, 48.39; H, 6.91; N, 8.06. Found: C, 48.22; H, 7.03; N, 8.04%.

## Conclusions

The synthesis and properties of the previously unknown compound, namely, 1-[(chloromethyl)dimethylsilyl]-1H-pyrrole were described. The analysis of the results obtained showed that the reaction of pyrrole with a hexamethyldisilazane/chloro(chloromethyl)dimethylsilane system leads to the formation of only the transsilylation product. This product was also obtained by the counter synthesis through the interaction of 1-(trimethylsilyl)-1H-pyrrole with chloro(chloromethyl)dimethylsilane. In contrast to diazoles, in this case no rearrangement of the Cl–CH<sub>2</sub>–Si–N bond system into the Cl–Si–CH<sub>2</sub>–N system and isomerization of the transsilylation product into the silicon methylation product were realized. The reason for this is likely to be the absence of a second nucleophilic center in the starting nitrogen-containing heterocyclic compound.

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## References

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