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LETTERS TO THE EDITOR

Bis-O-silylurethanes in Heterocyclic Synthesis

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It was shown that bis-O-silylurethanes I can be prepared [1] from diamines via transmination (a) of silyl carbamates.

$$H_2N(CH_2)_nNH_2 + Me_3SiOC(O)NEt_2$$

$$\xrightarrow{a} Me_3SiOC(O)NH(CH_2)_nNHC(O)OSiMe_3.$$
I

In the case of N-siloxycarbonylation (b) and carboxylation (c), the process leads to polyureas.

$$H_2N(CH_2)_nNH_2 + HN(SiMe_3)_2 \xrightarrow{b}$$
 $Me_3SiNH(CH_2)_nNHSiMe_3 \xrightarrow{3}$
 $\longrightarrow +NHC(O)NH(CH_2)_{n \to m}$.

We found that replacement of a diamine by a structurally related compound, 1-methyl-1-[2-(1-methylhydrazino)ethyl]hydrazine (II), allows one to synthe size bis-O-silylurethane IV by any of reactions a-c.

$$\begin{array}{c} \text{Me}_3 \text{SiOC(O)NEt}_2 \\ \\ H_2 \text{NNC}_2 H_4 \text{NNH}_2 \longrightarrow \\ \text{Me} \quad \text{Me} \quad \text{Me} \quad \\ \\ \text{Me} \quad \text{Me} \quad \text{Me} \quad \\ \\ \text{II} \\ \\ \text{Me} \quad \text{Me} \quad \\ \\ \text{Me} \quad \text{Me} \\ \\ \text{Me} \quad \text{Me} \\ \\ \text{Me} \quad \text{Me} \\ \\ \text{III} \\ \\ \\ \text{Me} \quad \text{Me} \\ \\ \text{III} \\ \\ \\ \text{Me} \quad \text{Me} \\ \\ \text{Me} \quad \text{Me} \\ \\ \text{Me} \quad \text{Me} \\ \\ \text{III} \\ \\ \\ \text{Me} \quad \text{Me} \text{Me} \quad \text{Me} \quad \text{Me} \\ \\ \text{Me} \quad \text{Me} \quad \text{Me} \quad \text{Me} \\ \\ \text{Me} \quad \text{Me} \quad \text{Me} \quad \text{Me} \quad \text{Me} \\ \\ \text{Me} \quad \text{Me} \quad \text{Me} \quad \text{Me} \\ \\ \text{Me} \quad \text{Me$$

The different behavior of similar starting nitrogencontaining compounds is probably explained by differences in their structure.

Dihydrazine II, like a diamine, has two NH₂ groups. In addition, dihydrazine II has two nonequivalent nitrogen atoms that are not only differently reactive, but are likely, at least initially, to favor formation of bis-O-silylurethane IV and then fast and irreversible intramolecular condensation of the latter into compound V.

$$IV \longrightarrow \begin{matrix} Me & O \\ CH_2-NNHC & O \\ CH_2-NNHC & O + Me_3SiOSiMe \\ CH_2-NNHC & O \\ Me & V \end{matrix}$$

Hexahydro-4,7-dimethyl-1-oxatetrazonine-2,9**dione** (V). a. A mixture of 6.9 g of 1-methyl-1-[2-(1-methylhydrazino)ethyl]hydrazine (II) and 22.9 g of trimethylsilyl diethylcarbamate was heated to 80°C. The precipitate was filtered off, washed with hexane, and dried in a vacuum at 20°C (10 mm Hg) to obtain 8.66 g (77%) of compound V, mp 101-102°C. IR spectrum, v, cm⁻¹: 3110 (NH), 1680 and 1700 (C=O). ¹H NMR spectrum, δ, ppm: 2.35 s (2H, NH), 2.49 s (6H, NCH₃), 2.64 s (4H, CH₂CH₂). Found, %: C 39.44; H 6.24; N 29.47. M 168.18. C₆H₁₂N₄O₃. Calculated, %: C 38.29; H 6.44; N 29.47. M 188.19.

b. Carbon dioxide was passed at 55°C over the course of 2 h through a mixture of 14.76 g of 1-methyl-1-[2-(1-methylhydrazino)ethyl]hydrazine (II) and 20.2 g of hexamethyldisilazane to obtain 17.01 g (72%) of compound V, mp 100–102°C.

c. Carbon dioxide was passed over the course of 4 h through 16.17 g of 2,2,4,7,9,9-hexamethyl-3,4,7,8-tetraaza-2,9-disiladecane (**III**) to obtain 8.26 g (71%) of compound **V**, mp 101–102°C.

The IR spectra were obtained on a Specord IR-75 instrument in mineral oil (for crystalline substances).

The ¹H NMR spectra were obtained on a Bruker WP-80 instrument (80 MHz), solvent and internal reference trichloromethane-*d*. The molecular weight was measured by cryoscopy in benzene.

REFERENCES

1. Mironov, V.F., Sheludyakov, V.D., and Kirilin, A.D., *Zh. Obshch. Khim.*, 1976, vol. 46, no. 10, p. 2396.