

LETTERS  
TO THE EDITOR

Synthesis and Thermal Stability  
of *N*-(Chlorodimethylgermylmethyl)-*N*-methyl-*O*-(trimethylsilyl)salicylamide

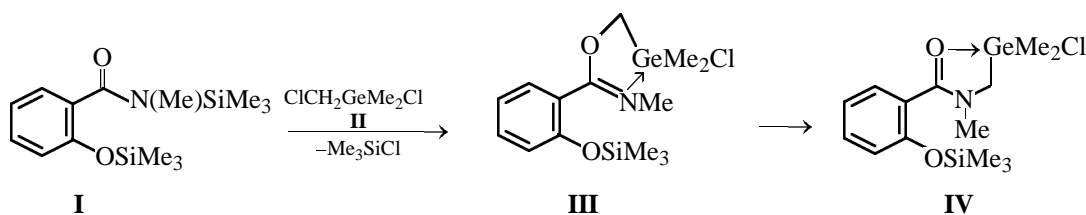
S. Yu. Bylikin, E. P. Kramarova, A. G. Shipov, Vad. V. Negrebetskii, and Yu. I. Baukov

Russian State Medical University, Moscow, Russia

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*N,O*-Bis(trimethylsilyl)-*N*-methylsalicylamide (**I**) reacts with chloro(chloromethyl)dimethylsilane under mild conditions with liberation of chlorotrimethylsilane and intermediate formation of a five-coordinate silicon compound, *N*-(chlorodimethylsilylmethyl)-*N*-methyl-*O*-(trimethylsilyl)salicylamide. On fractionation or standing at room temperature the latter undergoes intramolecular cyclization to 2,2,4-trimethyl-1-oxa-4-aza-2-silabenzocycloheptan-5-one with liberation of chlorotrimethylsilane [1, 2]. By contrast, chloro(chloromethyl)dimethylgermane (**II**) reacts with compound **I** at room temperature within 1.5–2 h in pentane to give, first, intermediate *O*-alkylation product **III** whose spectral characteristics are close to those of the products of syntheses on the basis of amides and lactams [3]. Thus, the IR spectrum of compound **III** shows a strong imidate absorption at  $1678\text{ cm}^{-1}$ , and the  $^1\text{H}$  NMR spectrum contains signals of the  $\text{Me}_2\text{Ge}$  (0.97 ppm),  $\text{MeN}$  (2.96 ppm),

and  $\text{OCH}_2\text{Ge}$  (4.08 ppm) groups. After standing for some days at room temperature compound **III** isomerized to *N*-germylmethylation product **IV**. This conversion is accompanied by disappearance in the IR spectrum of the absorption band at  $1678\text{ cm}^{-1}$  and appearance of absorption bands at 1597 and  $1500\text{ cm}^{-1}$  due to the five-membered  $\text{O} \rightarrow \text{Ge}$  chelate fragment [3]. The half-conversion period of compound **III** to **IV** in the reaction mixture was ca. 3 days at room temperature. No further conversion of compound **IV** into a germanium-containing heterocycle with chlorotrimethylsilane liberation occurred even on vacuum fractionation at a temperature above  $200^\circ\text{C}$ . This points to a strongly reduced reactivity of five-coordinate germanium chlorides compared with their silicon analogs toward trimethylsilyl phenol ethers [4], apparently, on account of a weaker  $\text{O} \rightarrow \text{M}$  coordination interaction in germanium analogs [5].



*N*-(Chlorodimethylgermylmethyl)-*N*-methyl-*O*-(trimethylsilyl)salicylamide (**IV**). *a*. A solution of 0.94 g of  $\text{ClCH}_2\text{GeMe}_2\text{Cl}$  in 2 ml of pentane was added to a solution of 1.37 g of compound **I** in 3 ml of pentane. The reaction mixture was stirred for 1.5 h at room temperature. In the IR spectrum of the reaction mixture we observed gradual disappearance of

the absorption band of the starting compound at  $1636\text{ cm}^{-1}$  and appearance of a strong absorption band at  $1678\text{ cm}^{-1}$  due to *O*-germylation product **III**. Further on the band at  $1678\text{ cm}^{-1}$  disappeared and bands at 1598 and  $1520\text{ cm}^{-1}$  appeared, belonging to *N*-germylation product **IV**.

*b.* A distillation flask was charged with 2.6 ml of  $\text{ClCH}_2\text{GeMe}_2\text{Cl}$  and 5.50 g of compound **I**. At 90–155°C,  $\text{Me}_3\text{SiCl}$  (1.09 g) was distilled off. The residue was fractionated to obtain 4.16 g (85%) of compound **IV**, bp 215–217°C (10 mm). IR spectrum ( $\text{CHCl}_3$ ),  $\nu$ ,  $\text{cm}^{-1}$ : 1598 s, 1520 w.  $^1\text{H}$  NMR spectrum ( $\text{CDCl}_3$ ),  $\delta$ , ppm: 0.08 s (9H,  $\text{SiMe}_3$ ), 0.77 s (6H,  $\text{GeMe}_2$ ), 2.88 s + s (5H,  $\text{NCH}_2\text{C} + \text{NCH}_2\text{Ge}$ ), 6.6–7.3 m (4H,  $\text{C}_6\text{H}_4$ ). Found, %: C 45.35; H 6.12.  $\text{C}_{14}\text{H}_{24}\text{ClGeNO}_2\text{Si}$ . Calculated, %: C 44.88; H 6.45.

The IR spectra of  $\text{CHCl}_3$  solutions were taken on a Specord IR-75 instrument in KBr. The  $^1\text{H}$  NMR spectra were obtained on a Varian XL-400 spectrometer (400.1 MHz) in the pulse mode with subsequent Fourier transform and  $^2\text{H}$  stabilization of resonance conditions. The chemical shifts were measured relative to internal TMS.

### ACKNOWLEDGMENTS

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