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A New Route to 1-Chlorosilatrane

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Abstract—A method for the synthesis of 1-chlorosilatrane by the reaction of organyltrichlorosilanes $RSiCl_3$ (R = Vin, Ph) and tetrachlorosilane with triethanolamine or its hydrochloride was developed. This simple and economical method allows obtaining 1-chlorosilatrane in 60% yield.

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1-Chlorosilatrane ClSi(OCH₂CH₂)₃N (ClSa) is used as a precursor in the synthesis of many 1-substituted silatranes, as well as in theoretical studies of molecular and stereoelectronic structure of chelate silicon compounds [1–4]. For the synthesis of ClSa and its analog, 1-chloro(3,7,10-trimethyl)silatrane, the following methods have been used.

(1) The reaction of 1-hydrosilatrane with elemental chlorine in the presence of an acceptor of hydrogen chloride [5]:

 $Cl_2 + HSi (OCH_2 CH_2)_3N \rightarrow ClSi (OCH_2 CH_2)_3N + HCl.$

By the same way 1-chloro-3,7,10-trimethylsilatrane was obtained, in the absence of the HCl acceptor [5].

(2) 3,7,10-Trimethylsilatrane reaction with *N*-chloro-succinimides [5]:

 $(CH_2CO)_2NCl + HSi(OCHMeCH_2)_3N \rightarrow ClSi (OCHMeCH_2)_3N + (CH_2CO)_2NH.$

(3) The reaction of 1-ethoxysilatrane with phosphorus or sulfur chlorides [6]:

$$\begin{split} R(O)Cl_2 + 2C_2H_5OSi(OCH_2CH_2)_3N &\rightarrow 2ClSi(OCH_2CH_2)_3N \\ &+ R(O)(OC_2H_5)_2, \\ R = ClP, CH_3P, S. \end{split}$$

(4) 1-Hydrosilatrane chlorination by organic or organosilicon chlorides [7–9]:

$$RCl + HSi(OCH_2CH_2)_3N \rightarrow ClSi(OCH_2CH_2)_3N + RH,$$

R = PhCO, Ph₃C, Me₃Si.

(5) Homolytic reaction of haloalkanes with 1-allylsilatrane [7, 10]:

 $\begin{aligned} \text{RCl} + \text{CH}_2 = \text{CHCH}_2\text{Si}(\text{OCH}_2 \text{ CH}_2)_3\text{N} &\rightarrow \text{ClSi}(\text{OCH}_2\text{CH}_2)_3\text{N} \\ &+ \text{CH}_2 = \text{CHCH}_2\text{R}, \\ \text{R} = \text{CCl}_3, \text{CF}_3, \text{C}_3\text{F}_7. \end{aligned}$

(6) Reaction of tetrachlorsilane with tris(2-trimethylsiloxyethyl)amine [11]:

 $\begin{array}{l} SiCl_4 + (Me_3SiOCH_2CH_2)_3N \\ \rightarrow ClSi(OCH_2CH_2)_3N + 3Me_3SiCl. \end{array}$

(7) The reaction of C-substituted tris(2-hydroxyalkyl)amines or related hydrochlorides with organyltrichlorosilanes [12]:

$$\begin{aligned} \text{RSiCl}_3 + (\text{HOCHMeCH}_2)_n(\text{HOCH}_2\text{CH}_2)_{3-n}\text{N}\cdot(\text{HCl})_m \\ \rightarrow \text{ClSi} (\text{OCHMeCH}_2)_n(\text{OCH}_2\text{CH}_2)_{3-n}\text{N} + \text{RH} \\ + (2+m)\text{HCl}, \end{aligned}$$

 $R = CH_2 = CH, C_6H_5, ClCH_2CH_2, Cl_3P; n = 1 - 3; m = 0, 1.$

We have shown that ClSa is formed easily in the reaction of triethanolamine or its hydrochloride (chloroprotatrane) with tetrachlorosilane according to the equation:

SiCl₄ + (HOCH₂CH₂)₃N·*n*HCl

$$\rightarrow$$
 ClSi(OCH₂CH₂)₃N + (3 + *n*) HCl,
 $n = 0, 1.$

Of particular interest is the unusual formation ClSa in the reaction of chloroprotatrane with the organyltrichlorosilanes containing a π -electron system connected to the silicon atom (CH₂=CH, C₆ H₅). This process proceeds with the cleavage of the C(*sp*²)–Si bond by the liberated HCl along the equation:

$$\begin{split} \text{RSiCl}_3 + (\text{HOCH}_2\text{CH}_2)_3\text{N}\cdot\text{HCl} &\to \text{ClSi}(\text{OCH}_2\text{ CH}_2)_3\text{N} \\ &\quad + \text{RH} + 3\text{HCl}, \\ \text{R} = \text{CH}_2 = \text{CH}, \text{ C}_6\text{ H}_5. \end{split}$$

Noteworthy that in the reaction of triethanolamine with $C_6H_5SiCl_3$ phenylsilatrane is formed [13], whereas the product of the reaction of triethanolamine hydrochloride with phenyltrichlorosilane is 1-chlorosilatrane. Reactions of vinyltrichlorosilane and tetra-chlorosilane with triethanolamine were carried out in an argon atmosphere in chloroform at a temperature from -5 to 0°C. Reactions of vinyl- and phenyl-trichlorosilanes, and tetrachlorosilane with triethanolamine with triethanolamine hydrochloride were carried out in the absence of a solvent with a gradual increase in temperature to 130–150°C. The yield of 1-chloro-silatrane in all cases was ~60%.

EXPERIMENTAL

The IR spectra were recorded on a Specord IR-75 instrument from the tablets with KBr. The ¹H and ¹³C NMR spectra were recorded on a Bruker-400 spectrometer at the operating frequencies 400 and 100 MHz, respectively. As an internal reference was used HMDS.

Reaction of viniltrichlorosilane with triethanolamine. To a solution of 0.8 g of vinyltrichlorosilane in 20 ml of CHCl₃ cooled to $-5-0^{\circ}$ C at stirring in an argon atmosphere was added dropwise a solution of 0.75 g of triethanolamine in 20 ml of CHCl₃. Then chloroform was distilled off from the reaction mixture, the resulting solid residue was heated in a vacuum (2– 3 mm Hg) at 110–120°C for 2 h to decompose the complex of ClSa with HCl, and extracted with methylene chloride. From the extract 0.63 g (61%) of 1-chlorosilatrane was isolated with the decomposition point above 200°C. Found, %: C 34.68, H 6.11, Cl 17.34, N 6.31, Si 13.29, C₆H₁₂ClNO₃Si, Calculated, %: C 34.36, H 5.77, Cl 16.90, N 6.68, Si 13.39. ¹H NMR spectrum, δ, ppm (CH₂Cl₂): 3.91 m (OCH₂), 2.97 m $(CH_2N).$

The precipitate insoluble in CH_2Cl_2 was recrystallized from hot ethanol, and 0.35 g of triethanolamine-HCl with mp 180–181°C was isolated. Found, %: C 37.33, H 8.57, Cl 18.51, N 7.97. C₆H₁₆ClNO₃. Calculated, %: C36.82, H 8.69, Cl 19.10, N 7.54.

Reaction of tetrachlorosilane with triethanolamine. Similarly from 0.85 g of SiCl₄ and 0.75 g of triethanolamine 0.5 g (48%) of 1-chlorosilatrane was obtained. Found, %: C 34.38, H 5.90, Cl 17.22, N 6.53, Si 13.56. C₆H₁₂CINO₃Si. Calculated, %: C 34.36, H 5.77, Cl 16.90, N 6.68, Si 13.39. **Reaction of phenyltrichlorosilane with triethanolamine hydrochloride**. A mixture of 1.06 g of phenyltrichlorosilane with 0.93 g of triethanolamine hydrochloride was heated in argon at atmospheric pressure at $150-160^{\circ}$ C for 2 h, then 2 h in a vacuum (5–8 mm Hg) at the same temperature. The solid reaction product was extracted with methylene chloride. From the extract 0.58 g (56%) of 1-chlorosilatrane was isolated with the decomposition temperature above 200°C. Found, %: C 34.26, H 5.53, Cl 17.02, N 7.00, Si 12.95. C₆H₁₂ClNO₃Si. Calculated, %: C 34.36, H 5.77, Cl 16.90, N 6.68, Si 13.39.

Reaction of viniltrichlorosilane with triethanolamine hydrochloride. Similarly from 0.41 g of viniltrichlorosilane and and 0.47 g triethanolamine hydrochloride 0.32 g (60%) of 1-chlorosilatrane was obtained. Found, %: C 34.55, H 5.80, Cl 16.83, N 6.84, Si 13.20. C₆ H₁₂ClNO₃Si. Calculated, %: C 34.36, H 5.77, Cl 16.90, N 6.68, Si 13.39.

Reaction of tetrachlorosilane with triethanolamine hydrochloride. Similarly from 0.85 g of tetrachlorosilane and 0.93 g of triethanolamine hydrochloride 0.45 g (43%) of 1-chlorosilatrane was obtained.

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