POSSIBILITY OF THE REARRANGEMENT OF bis-SILICON-CONTAINING MERCAPTALS TO ETHERS OF DITHIOETHYLENE GLYCOL

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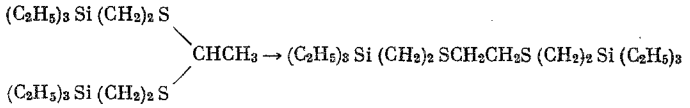
In studying the process for the thiylation of triethylsilylethyl thiovinyl ether $(C_2H_5)_3Si(CH_2)_2SCH=CH_2$ with triethylsilylethyl mercaptan $(C_2H_5)_3Si(CH_2)_2SH$ under electrophilic and homolytic conditions we discovered a phenomenon [1] that was identified as being the rearrangement of symmetrical bis-silicon-containing mercaptals to the isomeric ethers of dithioethylene glycol

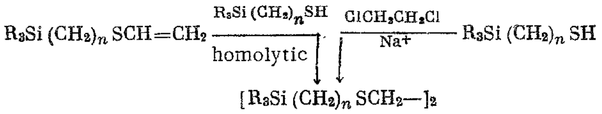


$$[(C_2H_5)_3Si(CH_2)_2S]_2CHCH_3 \rightarrow (C_2H_5)_3Si(CH_2)_2SCH_2CH_2S(CH_2)_2Si(C_2H_5)_3$$

In subsequent studies we decided to expand the gamut of the studied symmetrical mercaptals in order to ascertain the effect of the structure of the studied compounds on their tendency to rearrange. In all cases the mercaptals were obtained by two methods: by the thiylation of trialkylsilylalkyl thiovinyl ethers under electrophilic conditions and by the reaction of $R_3Si(CH_2)_nSH$ with acetaldehyde

$$R_3Si(CH_2)_nSCH=CH_2 \xrightarrow[H^+]{R_3Si(CH_2)_nSH} [R_3Si(CH_2)_nS]_2CHCH_3 \xleftarrow[H^+]{CH_3CHO} R_3Si(CH_2)_nSH$$

The isomeric bis-silicon-containing ethers of dithioethylene glycol were also synthesized by two routes according to the scheme



$$\begin{tikzcd} R_3Si(CH_2)_nSCH{=}CH_2 \arrow[dr, "R_3Si(CH_2)_nSH", "\text{homolytic}"'] & & R_3Si(CH_2)_nSH \arrow[dl, "ClCH_2CH_2Cl"', "Na^+"] \\ & {[R_3Si(CH_2)_nSCH_2-]_2} & \end{tikzcd}$$

$$R = CH_3, C_2H_5, C_3H_7,\ n = 1, 2, 3$$

TABLE 1. Physicochemical Constants of Synthesized Compounds

Compound	Bp, °C (p, mm of Hg)	n_D^{20}	d_4^{20}	MR		Found, %				Calcd., %			
				found	calcd.	C	H	S	Si	C	H	S	Si
$[(CH_3)_3Si(CH_2)_2S-]_2CHCH_3$	170 (4)	1,4880	0,9087	93,15	92,85	49,40	10,66	20,72	19,50	48,95	10,27	21,78	19,08
$[(CH_3)_3Si(CH_2)_2SCH_2-]_2$	185 (5)	1,4920	0,9154	93,39		49,10	10,40	21,30	19,30				
$](C_2H_5)_2CH_3SiCH_2-S-]_2CHCH_3$	160 (4)	1,4970	0,9230	102,31	102,11	52,44	10,92	19,40	17,25	52,10	10,62	19,87	17,40
$[(C_2H_5)_2CH_3SiCH_2SCH_2-]S$	165 (5)	1,4995	0,9306	102,06		52,40	10,76	20,12	17,44				
$[(CH_3)_3Si(CH_2)_3S-]_2CHCH_3$	149 (2,5)	1,4850	0,9041	102,30	102,11	51,90	10,70	19,70	17,80	52,10	10,62	19,87	17,40
$[(CH_3)_3Si(CH_2)_3SCH_2-]_2$	150 (3)	1,4880	0,9087	102,32		51,88	10,59	19,54	17,91				
$[(C_3H_7)_3Si(CH_2)_2S-]_2CHCH_3$	222 (3)	1,4930	0,9037	148,89	148,41	62,40	11,50	14,20	11,90	62,25	11,75	13,85	12,13
$[(C_3H_7)_3Si(CH_2)_2SCH_2-]_2$	220 (2)	1,4950	0,9055	148,95		62,30	11,70	13,90	12,00				

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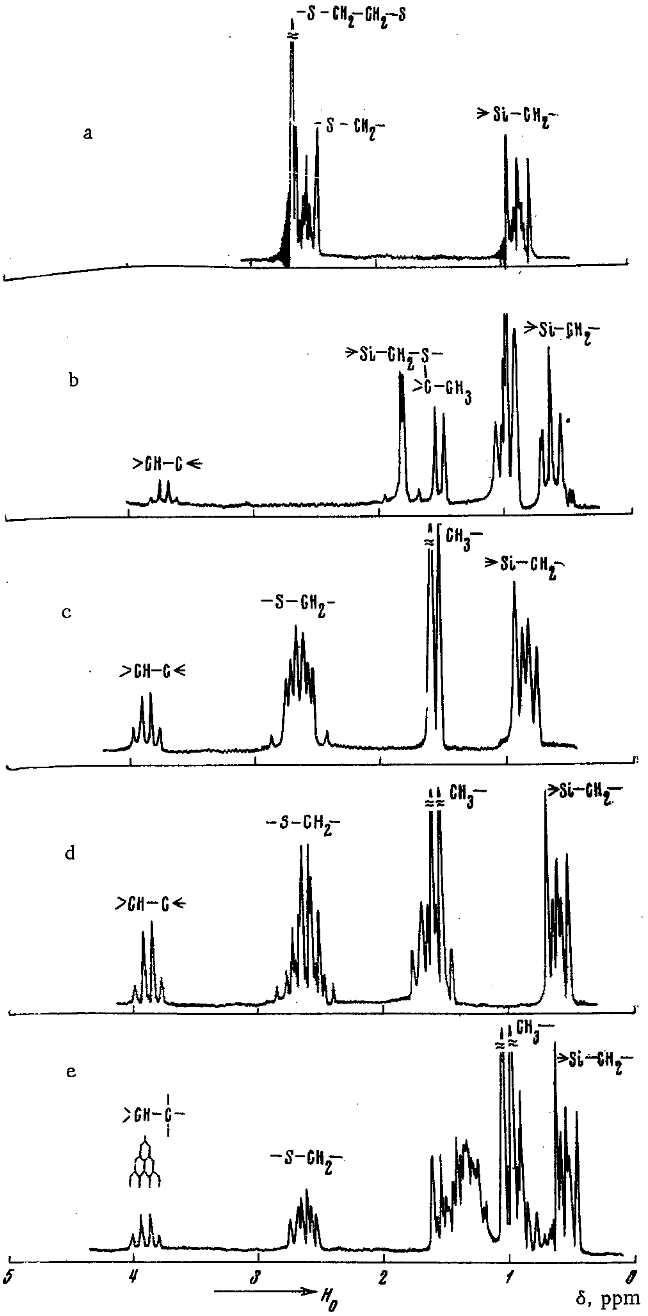

Fig. 1. PMR spectra*: a) $(CH_3)_3Si(CH_2)_2-S(CH_2)_2-S(CH_2)_2Si(CH_3)_3$; b) $\begin{matrix}CH_3(C_2H_5)_2SiCH_2S\\CH_3(C_2H_5)_2SiCH_2S\end{matrix}\!>\!CH-CH_3$; c) $\begin{matrix}(CH_3)_3Si(CH_2)_2S\\(CH_3)_3Si(CH_2)_2S\end{matrix}\!>\!CH-CH_3$; d) $\begin{matrix}(CH_3)_3Si(CH_2)_3S\\(CH_3)_3Si(CH_2)_3S\end{matrix}\!>\!CH-CH_3$; e) $\begin{matrix}(C_3H_7)_3Si(CH_2)_2S\\(C_3H_7)_3Si(CH_2)_2S\end{matrix}\!>\!CH-CH_3$.

In order to obtain the starting thiovinyl ethers, besides the known method [2-4], we used for the first time a method that is based on the reaction of silicon-containing thioacetates with acetylene in the presence of KOH [5]

$$R_3Si\,(CH_2)_n\,SCOCH_3 \xrightarrow[NaOH]{CH\equiv CH} R_3Si\,(CH_2)_n\,SCH{=}CH_2$$

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* The signal of the protons of the $CH_3-Si\leqslant$group was used as the internal standard of monotonic stabilization and is not shown in the spectra.

The given method is very convenient, since it makes it possible to combine the preliminary cleavage of the thioacetate to the mercaptan in one step with the vinylation.

A study of the process for the formation of symmetrical mercaptals and the bis-silicon-containing ethers of dithioethylene glycol, isomeric with them, disclosed that these compounds differ slightly in their physicochemical constants (Table 1). In view of this the need arose of finding a method for rigidly proving the structure of the investigated compounds, and in the case of observed isomerization – the need of using the given method to establish the mechanism of this process. As such a method we selected the method of proton magnetic resonance spectroscopy. The following was established in the course of studying the PMR spectra of the investigated compounds: the reaction of $R_3Si(CH_2)_nSH$ with dichloroethane, and also the homolytic addition of $R_3Si(CH_2)_nSH$ to $R_3Si(CH_2)_nSCH=CH_2$; both yield reaction products whose spectra are identical. For the case where $R_3Si=(CH_3)_3Si$, and $n = 2$, the PMR spectrum is shown in Fig. 1a. The presence in it of a singlet with the chemical shift $\delta \approx 2.69$ ppm, and two multiplets, with $\delta \approx 2.57$ and 0.86 ppm, corroborates the linear structure of the product.

In all cases, the reaction products of the trialkylsilylalkyl mercaptans with acetaldehyde were identified as being the pure symmetrical bis-silicon-containing mercaptals $[R_3Si(CH_2)_nS-]_2CHCH_3$, where $R = CH_3-$, C_2H_5-, C_3H_7-, and $n = 1, 2, 3$. The PMR spectra of $[R_3Si(CH_2)_nS-]_2CHCH_3$ in the case where $R_3Si- = CH_3(C_2H_5)_2\cdot Si-$, $n = 1$; $R_3Si = (CH_3)_3Si-$, $n = 2$; $R_3Si = (CH_3)_3Si-$, $n = 3$; and $R_3Si- = (C_3H_7)_3Si-$, $n = 2$, are respectively shown in Fig. 1. The presence in the PMR spectra of a quadruplet in the region $\delta = 3.71$-3.90 ppm, belonging to the proton of the fragment $>CH-C\overset{\diagup}{\underset{\diagdown}{-}}$, and a doublet in the region $\delta = 1.50$-1.58 ppm, belonging to the protons of a methyl group, corroborates the isostructure of the compounds. The character of the multiplicity of the signals of the protons of the fragment $\overset{\diagdown}{\underset{\diagup}{-}}Si(CH_2)_n-S-$ in the PMR spectra testifies to the hindered rotation of the protons relative to the Si–C and C–S bonds.

The attempted isomerization of the investigated mercaptals, in the presence of tert-butyl peroxide as catalyst and also without it, at a temperature of 120°, disclosed that the isomeric ether of dithioethylene glycol, as follows from the PMR spectra, is not formed. Changes in the spectrum, testifying to a partial decomposition of the compound, were observed in the experiment using tert-butyl peroxide. In order to determine if the PMR spectra could be used to detect the mercaptal as impurity in the dithioethylene glycol ether, or the reverse, we prepared some standard mixtures of the appropriate isomers. On the basis of the PMR spectra of these mixtures it was established that 3-5% of the mercaptal in the dithioethylene glycol ether, or the same amount of the dithioethylene glycol ether in the mercaptal, can be distinctly detected.

A study of the properties of the thiylation products of organosilicon vinyl sulfides on the example of asymmetrical bis-silicon-containing mercaptals is being continued.

EXPERIMENTAL METHOD

Trimethylsilylethyl Thiovinyl Ether. Into a 1-liter autoclave were charged 7.7 g of trimethylsilylethyl thioacetate, 3 g of KOH, 15 ml of CH_3OH and 50 ml of dioxane. The operating pressure of the acetylene in the autoclave was 20 atm, the reaction temperature was 90-100°, and the time of heating was 4-5 h. We obtained 4.5 g of substance (60-70%) with bp 60-61° (5.5 mm), n_D^{20} 1.4760; d_4^{20} 0.8671. Found: C 52.23; H 10.03; S 20.14; Si 17.03%; MR 52.21. $C_7H_{16}SSi$. Calculated: C 52.46; H 10.05; S 19.89; Si 17.52%, MR 51.65.

Trimethylsilylethyl thiovinyl ether was also obtained by the previously described method [2] in 70-80% yield, bp 55-54° (5 mm); n_D^{20} 1.4760; d_4^{20} 0.8662.

Symmetrical Organosilicon Mercaptals and Dithioethylene Glycol Ethers. The constants of the synthesized compounds, obtained by the previously described methods [1, 4], are given in Table 1.

The PMR spectra of the organosilicon mercaptals and dithioethylene glycol ethers were taken on a JNM-4H-100 "JEOL" spectrometer, with an operating frequency of 100 MHz, using CCl_4 as the solvent, and adding $CHCl_3$ as the internal standard in the case of RCH_3.

CONCLUSIONS

A study was made of the PMR spectra of some symmetrical organosilicon mercaptals and dithioethylene glycol ethers; their isomerization was not observed.

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