NEW METHOD FOR THE SYNTHESIS OF TRIALKYL(TRIORGANYLSILYLALKYLTHIO)SILANES AND TRIALKYL(TRIORGANYLSILYLALKYLTHIO)GERMANES

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Trimethyl(triorganylsilylalkylthio)silanes $(CH_3)_3SiS(CH_2)nSiR_3$ were obtained by the hydrosilylation of the corresponding trimethyl(thioalkenyl)silanes [1] but such compounds with n = 1 could not be prepared by this method. Trialkyl(triorganylsilylalkylthio)germanes have not yet been reported.

We have developed a one-step method for the synthesis of trialkyl(triorganyllalkylthio) silanes and the corresponding germanes with the general formula $R_3MS(CH_2)nSiR_3'$, where M = Si and Ge, R = Et, R' = alkyl and alkoxyl, and n = 1-3. The yields were 80-94%. This synthesis is based on the reaction of triorganylsilylalkanethiols with bis(triethylsilyl)mercury (I) or with bis(triethylgermyl)mercury (II) by the general scheme:

$$(R_3M)_2Hg + HS(CH_2)_n\ SiR_3' \rightarrow [R_3M\text{—}Hg\text{—}S(CH_2)_nSiR_3'] \rightarrow$$

$$\xrightarrow[-Hg]{} R_3MS(CH_2)_nSiR_3' + RMH + Hg$$

$$\text{(III)} - \text{(VII)} \qquad \text{(VIII)} - \text{(IX)}$$

$$R = Et,\ R' = OMe,\ M = Si,\ n = 1\ \text{(III)};\ R = Et,\ R' = OMe,\ Me = Ge,\ n = 1\ \text{(IV)};\ R = Et,\ R' = OMe,\ M = Si,\ n = 2\ \text{(V)};\ R = Et,\ R' = OMe,\ M = Ge,\ n = 2\ \text{(VI)};\ R = Et,\ R' = CH_3,\ M = Si,\ n = 3\ \text{(VII)};\ R = Et,\ M = Si\ \text{(VIII)};\ R = Et,\ M = Ge\ \text{(IX)}$$

This reaction apparently proceeds through the formation of an intermediate containing an SHg—M (M = Si or Ge) group, which is unstable [2].

The reaction of (I) and (II) with thiols has not been reported and the above reaction is the first reported example.

Silanes (III)-(VII) are colorless, high-boiling liquids with a weak odor. Their yields, physical constants, and elemental analysis data are given in Table 1. Triethylsilane (VIII) and triethylgermane (IX) were identified by gas—liquid chromatography. The assigned structures were confirmed by ^1H and ^{29}Si NMR spectroscopy. The $(MeO)_3Si$ group proton signals are at 3.5-3.6 ppm, while the ^{29}Si signals for the $(MeO)_3Si$ group are in the range from —45 to —49 ppm.

TABLE 1. $(C_2H_5)\ MS(CH_2)nSiR_3'$

Compound	R'	n	Yield, %	Bp, °C (p, mm Hg)	d_4^{20}	n_D^{20}	MR		$\frac{\text{Found}}{\text{Calculated}}$, %				
							found	calculated	C	H	S	Si	Ge
(III)	OCH_3	1	80	138 (10)	0,9970	1,4640	78,20	78,12	42,87 42,51	9,33 9,28	10,89 11,34	19,83 19,88	
(IV)	OCH_3	1	85,9	130–131 (5)	1,1636	1,4780	79,56	80,83	36,72 36,73	7,98 8,01	9,82 9,80	8,30 8,58	21,43 22,02
(V)	OCH_3	2	87,3	78–79 (0,3)	0,9868	1,4610	82,24	82,77	45,28 44,54	9,51 9,51	10,25 10,81	18,90 18,94	
(VI)	OCH_3	2	94,0	91–92 (0,7)	1,1345	1,4765	84,85	85,48	38,26 38,74	8,08 8,27	8,72 9,40	8,46 8,23	21,84 21,26
(VII)	CH_3	3	89,5	136–137 (10)	0,8711	1,4740	84,72	84,81	55,12 54,88	11,31 11,51	11,40 12,21	20,90 21,39	

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EXPERIMENTAL

The NMR spectra were taken on an FX-900 spectrometer with tetramethylsilane as the internal standard.

The reactions were carried out in sealed evacuated ampuls by our previous procedure [3]. Typical examples of this synthesis are given below.

Triethyl(trimethoxysilylmethylthio)silane (III). A sample of 4.67 g bis(triethylsilyl) mercury was added to 1.82 g (mercaptomethyl)trimethoxysilane in 5 ml dry benzene and was heated for 15 min at 50°C. A total of 2.16 g mercury was removed. The yield of mercury was 100%. The fraction with bp 80-108° was distilled off the mixture. Gas—liquid chromatography showed that this fraction contained triethylsilane. Distillation of the residue in vacuum gave 2.44 g (80%) (III). Products (IV)-(VII) were obtained by analogy. PMR spectrum (δ, ppm, $CDCl_3$)(III): 3.60 s (CH_3O), 1.58 s (CH_2), 0.67-1.08 m [$(CH_3CH_2)_3Si$]. ^{29}Si NMR spectrum: —49.7 ([$(CH_3O)_3Si$], 24.2 [$(CH_3CH_2)_3Si$]; (V)) 3.54 s (CH_3O), 2.54 m (CH_2S), 0.68-1.07 m [$(CH_3CH_2)_3Si$]. ^{29}Si NMR spectrum: —45.6 [$(CH_3O)_3Si$], 22.2 [$(CH_3CH_2)_3Si$]; (VI)) 3.54 s (CH_3O), 2.55 m (CH_2S), 1.06 m [$(CH_3CH_2)_3Ge$)]. ^{29}Si NMR spectrum: —45.5 [$(CH_3O)_3Si$].

CONCLUSIONS

A new method was developed for the synthesis of trialkyl(triorganylsilylalkylthio)silanes and trialkyl(triorganylsilylalkylthio)germanes with the general formula $R_3MS(CH_2)_nSiR_3'$ (M = Si or Ge) by the reaction of the corresponding triorganylsilylalkenethiols with bis(trialkylsilyl)mercury or bis(trialkylgermyl)mercury.

LITERATURE CITED

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