SYNTHESIS OF NEW trans-1,2-DISILYLETHYLENE DERIVATIVES BY HYDROSILYLATION OF ETHYNYLSILANES

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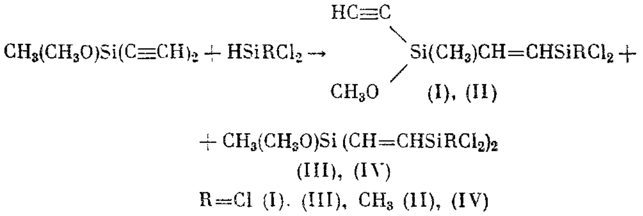
As an expansion of our research on ethynylalkoxysilanes [1-3], in the present paper we studied the hydrosilylation of ethynylsilanes with chlorohydrosilanes in the presence of H_2PtCl_6 and the alcoholysis of the thus-obtained adducts with methanol.

The hydrosilylation of $(CH\equiv C)_2Si(OCH_3)CH_3$ with Cl_3SiH and $Cl_2(CH_3)SiH$, the same as in the case of $(CH\equiv C)_2Si(CH_3)_2$ [4], proceeds in steps, and by varying the reactant ratio it can be easily directed toward the formation of the mono- and diadducts (I)-(IV).



(I), (II)

(III), (IV)

R=Cl (I), (III), CH_3 (II), (IV)

The hydrosilylation of ethynyl-substituted trimethyl-, dimethylmethoxy-, and methyldimethoxysilanes with methyl(phenyl)chlorosilane leads to the formation of trans-1,2-disilylethylenes (V)-(VII), while the alcoholysis of the latter with CH_3OH in the presence of urea leads to methoxysilanes (VIII)-(X). The alcoholysis of (I)-(IV) under analogous conditions smoothly yields $(CH_3)(CH\equiv C)(CH_3O)SiCH=CHSi(CH_3)_{3-n}(OCH_3)_n$ [n = 2(XI) and 3(XII)] and $CH_3(CH_3O)Si[CH=CHSi(CH_3)_{3-n}(OCH_3)_n]_2$ [n = 2(XIII) and 3(XIV)].

$$(CH_3)_{3-n}(CH_3O)_nSiC\equiv CH + HSi(CH_3)(C_6H_5)Cl \rightarrow \underset{(V)-(VII)}{(CH_3)_{3-n}(CH_3O)_nSiCH{=}CHSi(CH_3)(C_6H_5)Cl} \rightarrow$$

$$\xrightarrow{CH_3OH} \underset{(VIII)-(X)}{(CH_3)_{3-n}(CH_3O)_nSiCH{=}CHSi(CH_3)(C_6H_6)OCH_3}$$

$$n=0\,(V),\,(VIII);\quad n=1\,(VI),\,(IX);\quad n=2\,(VII),\,(X)$$

The addition of $Cl_2(CH_3)SiH$ to $CH\equiv CSi(OCH_3)_3$ gave 1-trimethoxysilyl-2-methyldichlorosilylethylene (XV), while the alcoholysis of the latter with CH_3OH gave methylpentamethoxy-1,2-disilylethylene [3].

$$(CH_3O)_3SiC\equiv CH + HSi(CH_3)Cl_2 \rightarrow \underset{(XV)}{(CH_3O)_3SiCH{=}CHSi(CH_3)Cl_2} \xrightarrow{CH_3OH}$$

$$\rightarrow \underset{(XVI)}{(CH_3O)_3SiCH{=}CHSi(OCH_3)_2CH_3}$$

The yield, properties, and analysis data of the synthesized compounds are given in Table 1. Their structure was confirmed by the NMR spectra (Tables 2 and 3).

EXPERIMENTAL

The NMR spectra were obtained on a Tesla BS-487B spectrometer for 10-30% CCl_4 solutions (internal standard = cyclohexane).

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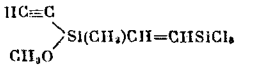
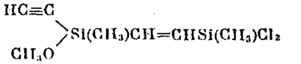
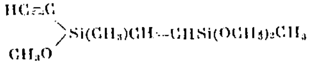
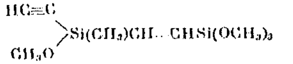
TABLE 1. Properties of Synthesized Compounds

Compound	Formula	Yield, %	bp, °C (p, mm of Hg)	n_D^{20}	d_4^{20}	Found/Calculated, % C	Found/Calculated, % H	Found/Calculated, % Si	Empirical formula
(I)	 $(HC{\equiv}C)(CH_3O)Si(CH_3)CH{=}CHSiCl_3$	65,6	61(5)	1,4655	1,1934	—	—	—	$C_6H_9Si_2Cl_3O$
(II)	 $(HC{\equiv}C)(CH_3O)Si(CH_3)CH{=}CHSi(CH_3)Cl_2$	66,8	88(8)	1,4595	1,0987	—	—	—	$C_7H_{12}Si_2Cl_2O$
(III)	$CH_3O(CH_3)Si(CH{=}CHSiCl_3)_2$	70,8	120(6)	1,4865	1,3335	—	—	—	$C_6H_{10}Si_3Cl_6O$
(IV)	$CH_3O(CH_3)Si[CH{=}CHSi(CH_3)Cl_2]_2$	69,5	117(5)	1,4810	1,1734	—	—	—	$C_8H_{16}Si_3Cl_4O$
(V)	$(CH_3)_3SiCH{=}CHSi(CH_3)(C_6H_5)Cl$	78,5	121(11)	1,5150	1,0003	—	—	—	$C_{12}H_{19}Si_2Cl$
(VI)	$(CH_3)_2(CH_3O)SiCH{=}CHSi(CH_3)(C_6H_5)Cl$	68,5	125(4)	1,5119	1,0414	—	—	—	$C_{12}H_{19}Si_2ClO$
(VII)	$CH_3(CH_3O)_2SiCH{=}CHSi(CH_3)(C_6H_5)Cl$	67	126(3)	1,5075	1,0837	—	—	—	$C_{12}H_{19}Si_2ClO_2$
(VIII)	$(CH_3)_3SiCH{=}CHSi(CH_3)(C_6H_5)OCH_3$	69,5	125(11)	1,4965	0,9425	62,46 62,33	8,93 8,85	22,28 22,42	$C_{13}H_{22}Si_2O$
(IX)	$CH_3O(CH_3)_2SiCH{=}CHSi(CH_3)(C_6H_5)OCH_3$	67,2	113(3)	1,4945	0,9754	58,60 58,58	8,24 8,85	21,25 21,08	$C_{13}H_{22}Si_2O_2$
(X)	$CH_3(CH_3O)_2SiCH{=}CHSi(CH_3)(C_6H_5)OCH_3$	66,4	129(6)	1,4865	1,0082	55,56 55,27	7,74 7,14	19,90 19,85	$C_{13}H_{22}Si_2O_3$
(XI)	 $(HC{\equiv}C)(CH_3O)Si(CH_3)CH{=}CHSi(OCH_3)_2CH_3$	46	90(5)	1,4340	0,9577	45,22 46,91	8,21 8,88	24,26 24,12	$C_9H_{18}Si_2O_3$
(XII)	 $(HC{\equiv}C)(CH_3O)Si(CH_3)CH{=}CHSi(OCH_3)_3$	54	98(5)	1,4325	1,0067	43,85 44,31	7,44 7,35	22,79 22,80	$C_9H_{18}Si_2O_4$
(XIII)	$CH_3O(CH_3)Si[CH{=}CHSi(OCH_3)_2CH_3]_2$	48	143—144(5)	1,4440	1,0364	42,81 42,86	8,38 8,57	23,30 25,04	$C_{12}H_{28}Si_3O_5$
(XIV)	$CH_3O(CH_3)Si[CH{=}CHSi(OCH_3)_3]_2$	52	154(5)	1,4395	1,0706	38,83 39,09	7,43 7,65	23,30 22,83	$C_{12}H_{28}Si_3O_7$
(XV)	$(CH_3O)_3SiCH{=}CHSi(CH_3)Cl_2$	68,1	83(5)	1,4405	1,1539	—	—	—	$C_6H_{14}Si_2Cl_2O_3$
(XVI)	$CH_3O)_3SiCH{=}CHSi(OCH_3)_2CH^{*}_3$	55,6	90(5)	1,4195	1,0268	—	—	—	$C_8H_{20}Si_2O_5$

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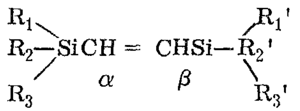
* Cf. [3].

TABLE 2. Parameters of NMR Spectra of Compounds*

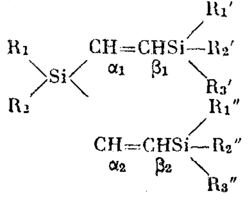


$$(R_1)(R_2)(R_3)\overset{\alpha}{SiCH}=\overset{\beta}{CHSi}(R_1')(R_2')(R_3')$$

Compound	R_1	R_2	R_2	R'_1	R'_2	R'_3	Chemical shift (τ, ppm)								SSCC ($^3J_{\alpha\beta}$, Hz)
							CH α	CH β	R_1	R_2	R_3	R'_1	R'_2	R'_3	
(V)	CH_3	CH_3	CH_3	CH_3	Cl	C_6H_5	3,14	3,35	9,90	9,90	9,90	9,31	—	2,84—2,19	22,2
(VIII)	CH_3	CH_3	CH_3	CH_3	OCH_3	C_6H_5	3,49	3,34	9,88	9,88	9,88	9,59	6,58	2,84—2,29	22,7
(IX)	CH_3	CH_3	OCH_3	CH_3	OCH_3	C_6H_5	3,25	3,25	9,82	9,82	6,62	9,58	6,56	2,94—2,27	—
(XII)	CH_3	$HC{\equiv}C$	OCH_3	OCH_3	OCH_3	OCH_3	3,31	3,50	9,71	7,50	6,54	6,49	6,49	6,49	22,7

* The resonance of the olefinic protons is depicted by multiplets of the AB type.

TABLE 3. Parameters of NMR Spectra of Compounds



$$(R_1)(R_2)Si(\overset{\alpha_1}{CH}=\overset{\beta_1}{CHSi}(R_1')(R_2')(R_3'))(\overset{\alpha_2}{CH}=\overset{\beta_2}{CHSi}(R_1'')(R_2'')(R_3''))$$

Compound	R_1	R_2	R_1'	R_2'	R_3'	R_1''	R_2''	R_3''	Chemical shift (τ, ppm)												SSCC, Hz	
									CH α_1	CH β_1	CH α_2	CH β_2	R_1	R_2	R_1'	R_2'	R_3'	R_1''	R_2''	R_3''	trans $^3J_{\alpha_1\beta_1}$	trans $^3J_{\alpha_2\beta_2}$
(XIII)	CH_3	OCH_3	CH_3	OCH_3	OCH_3	CH_3	OCH_3	OCH_3	3,28	3,50	3,28	3,50	9,76	6,58	9,87	6,54	6,54	9,87	6,54	6,54	23,0	23,0

1-Methyl(ethynyl)methoxysilyl-2-trichlorosilylethylene (I). To a mixture of 12.4 g of $(CH \equiv C)_2Si(OCH_3)CH_3$ (XVII) and 0.02 ml of an 0.2 N solution of H_2PtCl_6 in isopropanol at 40-50°C were added 6.8 g of $HSiCl_3$ in drops. The mixture was heated at 80-90° for 0.5 h. Distillation gave 6 g of unreacted (XVII), 8.66 g (65.6%) of (I), and 2.2 g of bis[β-(trichlorosilyl)vinyl]methyl(methoxy)silane (III). Compounds (II), (V)-(VII), and (XV) were obtained in a similar manner (see Table 1).

Bis[β-(trichlorosilyl)vinyl]methyl(methoxy)silane (III). This was obtained from 3.1 g of (XVII) and 6.8 g of $HSiCl_5$, in 70.8% yield (7.1 g). In addition, we isolated 1.75 g of (I). Compound (IV) was obtained in a similar manner (see Table 1).

1-Trimethylsilyl-2-methyl(phenyl)methoxysilylethylene (VIII). With stirring, to a mixture of 2.4 g of urea, 50 ml of MeOH, and 50 ml of petroleum ether (bp 90-92°) was added 10.16 g of (V) in drops. The mixture was heated at 60° for 0.5 h, cooled, the lower layer was separated, extracted with 10 ml of petroleum ether, the extract was combined with the upper layer, and the petroleum ether was distilled off under reduced pressure. Vacuum-distillation of the residue gave 6.95 g (69.5%) of (VIII). Compounds (IX)-(XIV) and (XVI) were obtained in a similar manner (see Table 1).

CONCLUSIONS

Eight new trans-1,2-disilylethylenes were synthesized by the hydrosilylation of $(CH \equiv C)_2Si(OCH_3)CH_3$ with $HSiCl_3$ and $HSi(CH_3)Cl_2$, and also of $(CH_3)_3SiC \equiv CH$, $CH_3O(CH_3)_2SiC \equiv CH$, and $CH_3(CH_3O)_2SiC \equiv CH$ with $HSi(CH_3)(C_6H_5)Cl$, and of $(CH_3O)_3SiC \equiv CH$ with $HSi(CH_3)Cl_2$. The alcoholysis of these compounds with MeOH gave the corresponding methoxy derivatives.

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1-ETHYNYL-3-CHLOROMETHYLTETRAMETHYLDISILOXANE AND SOME OF ITS REACTIONS

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As an expansion of our research on ethynylalkoxysilanes [1-3], in the present paper we studied the cohydrolysis of $CH \equiv CSi(CH_3)_2(OC_2H_5)$ with $ClCH_2Si(CH_3)_2Cl$ and the reaction of the organomagnesium derivatives of the thus-formed hydrolysis product, 1-ethynyl-3-chloromethyltetramethyldisiloxane (I), with CH_2O, CH_3COCH_3, $(CH_3)_3SiCl$, and Br_2, the hydrosilylation of (I) with $HSi(CH_3)Cl_2$, its condensation with hexachlorocyclopentadiene, morpholine, and piperidine, and also exchange of the Cl atom in it by I under the influence of NaI.

The indicated cohydrolysis leads to the formation of 1-ethynyl-3-chloromethyltetramethyldisiloxane (I). The 1,3-diethynyl- and 1,3-di(chloromethyl)tetramethyldisiloxanes are obtained as by-products here.

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