METHYL-SUBSTITUTED trans-1,2-DISILYLETHYLENE DERIVATIVES

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As a continuation of studying the hydrosilylation of ethynylsilanes in the presence of the Speier catalyst [1-3] we synthesized a number of previously unknown methyl-substituted 1,2-disilylethylene derivatives, which contain ethynyl, phenyl, and methoxy groups on the silicon atom.

The reaction of methyltriethynylsilane with an equimolar amount of either methyldichlorosilane or trichlorosilane gave both the mono- and the diaddition products

$$CH_3Si(C{\equiv}CH)_3 + HSiRCl_2 \rightarrow \underset{\text{(I), (II)}}{CH_3(HC{\equiv}C)_2SiCH{=}CHSiRCl_2}$$

$$\underset{\text{(III), (IV)}}{CH_3(HC{\equiv}C)Si(CH{=}CHSiRCl_2)_2}$$

$$R = CH_3\ \text{(I), (III)};\ Cl\ \text{(II), (IV)}$$

The reaction of (I) with ethynylmagnesium bromide gave 1,2-bis(methyldiethynylsilyl)ethylene (V)

$$\text{(I)} + 2HC{\equiv}CMgBr \rightarrow CH_3(HC{\equiv}C)_2SiCH{=}CHSi(C{\equiv}CH)_2CH_3\ \text{(V)}$$

A number of other ethynyl-substituted 1,2-disilylethylenes was obtained in a similar manner

$$(CH_3)_{3-n}(HC{\equiv}C)_nSiCH{=}CHSi(CH_3)_{3-m}Cl_m + mHC{\equiv}CMgBr \rightarrow$$
$$\rightarrow \underset{\text{(VI)}-\text{(IX)}}{(CH_3)_{3-n}(HC{\equiv}C)_nSiCH{=}CHSi(CH_3)_{3-m}(C{\equiv}CH)_m}$$

$$n = 0,\ m = 2\ \text{(VI)};\ n = 0,\ m = 3\ \text{(VII)};\ n = 1,\ m = 2\ \text{(VIII)};\ n = 1,\ m = 3\ \text{(IX)}$$

The reaction of the chloro derivatives with methanol in the presence of urea leads smoothly to the corresponding methoxy derivatives

$$(CH_3)_{3-n}(HC{\equiv}C)_nSiCH{=}CHSi(CH_3)_{3-m}Cl_m + mCH_3OH \xrightarrow{mOC(NH_2)_2}$$
$$\rightarrow \underset{\text{(X)}-\text{(XV)}}{(CH_3)_{3-n}(HC{\equiv}C)_nSiCH{=}CHSi(CH_3)_{3-m}(OCH_3)_m}$$

$$n = 0,\ m = 2\ \text{(X)};\ n = 0,\ m = 3\ \text{(XI)};\ n = 1,\ m = 2\ \text{(XII)};\ n = 1,\ m = 3\ \text{(XIII)};\ n = 2,\ m = 2\ \text{(XIV)};\ n = 2,\ m = 3\ \text{(XV)}$$

The reaction of compound (III) with CH_3MgI gave bis-[β-(trimethylsilyl)vinyl]methyl(ethynyl)silane (XVI)

$$\text{(III)} + 4CH_3MgI \rightarrow CH_3(CH{\equiv}C)Si[CH{=}CHSi(CH_3)_3]_2\ \text{(XVI)}$$

1-(Trichlorosilyl)-2-(trimethoxysilyl)ethylene (XVII)

$$(CH_3O)_3SiC{\equiv}CH + HSiCl_3 \rightarrow (CH_3O)_3SiCH{=}CHSiCl_3\ \text{(XVII)}$$

was synthesized by the addition of $HSiCl_3$ to ethynyltrimethoxysilane, while 1-(ethyldichlorosilyl)-2-(diethylmethoxysilyl)ethylene (XVIII)

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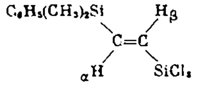
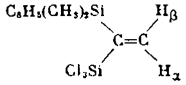
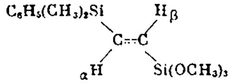
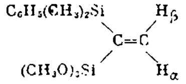
TABLE 1. NMR Spectra of 1,2-Disilylethylene Derivatives

Compound	Formula	Chemical shifts, τ, ppm					
		α-H	β-H	CH_3Si^1	CH_3Si^2	OCH_3	C≡CH
(VI)	$CH_3(HC\equiv C)_2Si\overset{\alpha}{CH}=\overset{\beta}{CH}Si(CH_3)_3$	3,59	3,07	9,63	9,87	—	7,62
(VII)	$(HC\equiv C)_3Si\overset{\alpha}{CH}=\overset{\beta}{CH}Si(CH_3)_3$	3,63	2,88	—	9,85	—	7,50
(VIII)	$CH_3(HC\equiv C)_2Si\overset{\alpha}{CH}=\overset{\beta}{CH}Si(CH_3)_2C\equiv CH$	3,39	3,24	9,58	9,71	—	7,62(1H) 7,54(2H)
(IX)	$(HC\equiv C)_3Si\overset{\alpha}{CH}=\overset{\beta}{CH}Si(CH_3)_2C\equiv CH$	3,43	2,98	—	9,68	—	7,59(1H) 7,42(3H)
(X)	$(CH_3)_3Si\overset{\beta}{CH}=\overset{\alpha}{CH}Si(OCH_3)_2CH_3$	3,65	3,21	9,91	9,91	6,64	—
(XI)	$(CH_3)_3Si\overset{\beta}{CH}=\overset{\alpha}{CH}Si(OCH_3)_3$	3,81	3,12	9,90	--	6,50	—
(XII)	$HC\equiv C(CH_3)_2Si\overset{\alpha}{CH}=\overset{\beta}{CH}Si(OCH_3)_2CH_3$	3,33	3,57	9,81	9,71	6,56	7,68
(XIII)	$HC\equiv C(CH_3)_2Si\overset{\alpha}{CH}=\overset{\beta}{CH}Si(OCH_3)_3$	3,20	3,61	9,72	—	6,50	7,62
(XIV)	$CH_3(HC\equiv C)_2SiCH=CHSi(OCH_3)_2CH_3$	3,31	3,31	9,84	9,58	6,54	7,55
(XV)	$CH_3(HC\equiv C)_2Si\overset{\alpha}{CH}=\overset{\beta}{CH}Si(OCH_3)_3$	3,27	3,45	9,57	--	6,44	7,51
(XIX)	$(CH_3O)_3SiCH=CHSi(OCH_3)_3$	3,53	3,53	—	--	6,45	—
(XXI)	$(CH_3)_3Si\overset{\beta}{CH}=\overset{\alpha}{CH}Si(CH_3)_2OCH_3$	3,52	3,35	9,92	9,87	6,65	—
(XXII)	$CH_3O(CH_3)_2SiCH=CHSi(CH_3)_2OCH_3$	3,42	3,42	9,85	9,85	6,56	—
(XXIV)	$C_6H_5(CH_3)_2SiCH=CHSi(CH_3)_3$	3,33	3,33	9,69	9,90	—	--
(XXV)	$C_6H_5(CH_3)_2Si\overset{\beta}{CH}=\overset{\alpha}{CH}Si(C\equiv CH)_2CH_3$	3,58	3,00	9,61	9,61	—	7,62
(XXVII)	$C_6H_5(CH_3)_2Si\overset{\beta}{CH}=\overset{\alpha}{CH}Si(CH_3)_2C\equiv CH$	3,42	3,12	9,63	9,74	—	7,74
(XXVIIIa)	 75%	2,69	3,44	9,57	--	—	—
(XXVIIIb)	 25%	3,14	3,53	9,57	—	—	—
(XXIXa)	 75%	2,98	3,68	9,67	—	6,45	—
(XXIX)	 25%	3,41	3,66	9.57	--	6,56	--
(XXX)	$(CH_3)_2Si[\overset{\beta}{CH}=\overset{\alpha}{CH}Si(OCH_3)_2]_2$	3,64	3,23	9,88	9,81	6,56	—

$$CH_3O(C_2H_5)_2SiC\equiv CH + HSi(C_2H_5)Cl_2 \rightarrow \underset{(XVIII)}{CH_3O(C_2H_5)_2SiCH=CHSi(C_2H_5)Cl_2}$$

was obtained from diethylethynylmethoxysilane and ethyldichlorosilane

The corresponding methoxy derivatives were synthesized by the reaction of compounds (XVII) and (XVIII) with methanol in the presence of urea

$$\underset{(XIX)}{(CH_3O)_3SiCH=CHSi(OCH_3)_3} \text{ and } \underset{(XX)}{CH_3O(C_2H_5)_2SiCH=CHSi(OCH_3)_2C_2H_5}$$

The reaction of 1-(trimethylsilyl)-2-(methyldimethoxysilyl)ethylene and 1-(dimethylmethoxysilyl)-2-(methyldimethoxysilyl)ethylene with an equimolar amount of CH_3MgI gave 1-(trimethylsilyl)-2-(dimethylmethoxysilyl)ethylene and 1,2-bis(dimethylmethoxysilyl)ethylene

$$(CH_3O)_n(CH_3)_{3-n}\,SiCH=CHSi(OCH_3)_2CH_3 + CH_3MgI \rightarrow$$
$$\rightarrow (CH_3O)_n(CH_3)_{3-n}\,SiCH=CHSi(CH_3)_2OCH_3$$
$$(XXI),\ (XXII)$$
$$n = 0\ (XXI);\ n = 1\ (XXII)$$

The 1,2-disilylethylenes that contain a phenyl radical on one of the silicon atoms were synthesized by the hydrosilylation of dimethyl(phenyl)(ethynyl)silane and subsequent reaction of the reaction product with either CH_3MgI or ethynylmagnesium bromide

$$\begin{tikzcd}
C_6H_5(CH_3)_2SiC\equiv CH + HSi(CH_3)Cl_2 \arrow[r] & \underset{(XXIII)}{C_6H_5(CH_3)_2SiCH{=}CHSi(CH_3)Cl_2} \arrow[dl, "CH_3MgI"'] \arrow[d, "HC\equiv CMgBr"] \\
\underset{(XXIV)}{C_6H_5(CH_3)_2SiCH{=}CHSi(CH_3)_3} & \underset{(XXV)}{C_6H_5(CH_3)_2SiCH{=}CHSi(C\equiv CH)_2CH_3}
\end{tikzcd}$$

and also by the hydrosilylation of dimethyldiethynylsilane with methylphenylchlorosilane and subsequent reaction with CH_3MgI

$$(CH_3)_2Si(C\equiv CH)_2 + HSi(C_6H_5)(CH_3)Cl \rightarrow \underset{(XXVI)}{HC\equiv C(CH_3)_2SiCH{=}CHSi(C_6H_5)(CH_3)Cl} \xrightarrow{CH_3MgI}$$
$$\rightarrow \underset{(XXVII)}{HC\equiv C(CH_3)_2SiCH{=}CHSi(CH_3)_2C_6H_5}$$

The addition of $HSiCl_3$ to dimethyl(phenyl)ethynylsilane gave 1-(dimethylphenylsilyl)-2-(trichlorosilyl)-ethylene, which with methanol gives 1-(dimethylphenylsilyl)-2-(trimethoxysilyl)ethylene

$$C_6H_5(CH_3)_2SiC\equiv CH + HSiCl_3 \rightarrow \underset{(XXVIII)}{C_6H_5(CH_3)_2SiCH{=}CHSiCl_3} \xrightarrow[OC(NH_2)_2]{CH_3OH}$$
$$\rightarrow \underset{(XXIX)}{C_6H_5(CH_3)_2SiCH{=}CHSi(OCH_3)_3}$$

Dimethylbis-[β-(methyldimethoxysilyl)vinyl]silane was synthesized in a similar manner

$$(CH_3)_2Si[CH{=}CHSi(CH_3)Cl_2] \xrightarrow[OC(NH_2)_2]{CH_3OH} \underset{(XXX)}{(CH_3)_2Si[CH{=}CHSi(OCH_3)_2CH_3]_2}$$

To confirm the structure of the synthesized compounds we studied their NMR spectra (Table 1). The spectra were obtained on a Tesla BS-487B spectrometer (80 MHz) for 10-15% CCl_4 solutions, using cyclohexane as the internal standard. Except for the symmetrical compounds and (XXIV), the olefinic protons of the 1,2-disilylethylene derivatives are depicted in the spectrum by quadruplets of the AB type. The vicinal spin–spin coupling constants of the olefinic protons are equal to 21-23 Hz, which proves the trans-structure of the obtained compounds. Compounds (XXVIII) and (XXIX) are an exception, the spectrum of which shows that, together with the trans-adduct (XXVIIIa) and (XXIXa), the gem-isomer (XXVIIIb) and (XXIXb) is formed. An AB quadruplet with a spin–spin coupling constant of 5 Hz corresponds to the latter in the region of the olefinic protons. The ratio of the trans- and gem-isomers is 3 : 1.

EXPERIMENTAL METHOD

1-(Methyldiethynylsilyl)-2-(methyldichlorosilyl)ethylene (I) and bis-[β-(Methyldichlorosilyl)vinyl]-methyl(ethynyl)silane (III). To a mixture of 3.7 g of methyltriethynylsilane and 0.01 ml of 0.2 N H_2PtCl_6 in isopropanol at 40-45° was added 3.3 g of methyldichlorosilane. The mixture was heated at 80-90° for 0.5 h. Distillation gave 3.18 g (45.4%) of (I) with bp 92-93° (12 mm); n_D^{20} 1.4780; d_4^{20} 1.0517. Found: MR 62.78. $C_8H_{10}Si_2Cl_2$. Calculated: MR 62.01. In addition, we isolated 3.08 g (44.0%) of (III) with bp 152-154° (13 mm); n_D^{20} 1.4994; d_4^{20} 1.1877. Found: MR 86.41. $C_9H_{14}Si_3Cl_4$. Calculated: MR 86.26.

Compounds (II), (IV), (XVII), (XVIII), (XXIII), (XXVI), and (XXVIII) were obtained in a similar manner (Table 2).

1,2-bis(Methyldiethynylsilyl)ethylene (V). To a solution of 2.33 g of (I) in 5 ml of ether was added the Iotsich reagent that was prepared from 0.46 g of Mg, 2.18 g of C_2H_5Br, and acetylene in 25 ml of THF. After the usual workup we obtained 1.39 g (65.5%) of (V) with bp 114-116° (17 mm), mp 60-62°. Found: C 66.38; H 5.76; Si 25.64%. $C_{12}H_{12}Si_2$. Calculated: C 67.85; H 5.69; Si 26.45%.

Compounds (VI)-(IX) and (XXV) were obtained in a similar manner (see Table 2).

1-(Methyldiethynylsilyl)-2-(methyldimethoxysilyl)ethylene (XIV). With stirring, to a mixture of 2.4 g of urea and 12 ml of methanol in 15 ml of hexane was added 4.46 g of (I) in drops. The mixture was heated at 60° for 1 h, and the lower layer was separated and extracted with 10 ml of hexane. The extract was combined with the main layer, the hexane was distilled off, and the residue was vacuum-distilled. We obtained 3.6 g (74.0%) of (XIV) with bp 111-112° (18 mm); n_D^{20} 1.4618; d_4^{20} 0.9476. Found: C 53.71; H 7.15; Si 24.91%; MR 65.00. $C_{10}H_{16}Si_2O_2$. Calculated: C 53.62; H 7.14; Si 25.04%; MR 64.53.

Compounds (X)-(XIII), (XV), (XIX), (XX), (XXIX), and (XXX) were obtained in a similar manner (see Table 2).

TABLE 2. 1,2-Disilylethylene Derivatives

Compound	Yield,%	Bp, °C (p, mm of Hg)	n_D^{20}	d_4^{20}	*MR*		Found,%			Empirical formula	Calculated,%		
					found	calculated	C	H	Si		C	H	Si
(II)	43,8	86(12)	1,4836	1,1637	62,09	61,57	—	—	—	$C_7H_7Si_2Cl_3$	—	—	—
(IV)	44,5	126(5)	1,5082	1,3408	86,54	85,40	—	—	—	$C_7H_8Si_3Cl_6$	—	—	—
(VI)	67,2	71—72(14)	1,4665	0,8349	63,91	62,88	62,45	8,70	28,79	$C_{10}H_{16}Si_2$	61,41	8,38	29,19
(VII)	65,4	116(25)	mp. 62°		—	—	65,02	6,97	27,87	$C_{11}H_{14}Si_2$	65,27	6,97	27,16
(VIII)	65,8	90—91(10)	1,4770	0,8680	65,89	65,40	65,91	7,03	27,61	$C_{11}H_{14}Si_2$	65,27	6,97	27,16
(IX)	63,8	116(14)	mp. 48°		—	—	67,94	5,81	26,32	$C_{12}H_{12}Si_2$	67,85	5,69	26,45
(X)	61,7	58(10)	1,4270	0,8755	59,97	59,49	46,69	9,55	27,37	$C_8H_{20}Si_2O_2$	47,00	9,86	27,48
(XI)	62,1	102(42)	1,4237	0,9282	60,56	60,31	43,60	9,08	25,46	$C_8H_{20}Si_2O_3$	43,13	9,14	25,49
(XII)	68,3	95(18)	1,4445	0,9123	62,50	61,91	49,66	9,04	25,98	$C_9H_{18}Si_2O_2$	50,04	8,47	26,20
(XIII)	68,9	75(6)	1,4425	0,9543	63,95	62,86	47,09	7,65	24,61	$C_9H_{18}Si_2O_3$	46,91	7,87	24,38
(XV)	70,3	94—95(6)	1,4520	0,9901	65,51	65,35	50,77	6,85	23,38	$C_{10}H_{16}Si_2O_3$	49,84	6,71	23,39
(XVII)	76,0	86(7)	1,4445	1,2542	59,75	59,99	—	—	—	$C_5H_{11}Si_2Cl_3O_3$	—	—	—
(XVIII)	77,5	131(19)	1,4615	1,0437	71,44	71,74	—	—	—	$C_9H_{20}Si_2Cl_2O$	—	—	—
(XIX) [4]	65,5	119(13)	1,4150	1,0739	62,59	62,77	36,16	7,60	21,01	$C_8H_{20}Si_2O_6$	36,17	7,51	20,92
(XX)	73,0	112(12)	1,4375	0,9341	73,69	73,44	49,92	9,77	21,12	$C_{11}H_{26}Si_2O_3$	50,34	9,98	21,32
(XXII)	58,4	44(2)	1,4275	0,8900	58,98	59,49	47,00	9,87	26,96	$C_8O_{20}Si_2O_2$	47,00	9,86	27,13
(XXIII)	91,8	140—141(10)	1,5232	1,0817	77,78	76,82	—	—	—	$C_{11}H_{16}Si_2Cl_2$	—	—	—
(XXIV)	70,4	125(16)	1,5100	0,8804	79,64	77,70	66,39	9,28	23,52	$C_{13}H_{22}Si_2$	67,06	9,41	23,91
(XXV)	62,7	145(9)	1,5245	0,9355	83,28	82,73	70,84	7,16	21,75	$C_{15}H_{18}Si_2$	70,79	7,13	22,08
(XXVI)	44,6	152—153(16)	1,5228	1,0381	78,60	79,78	—	—	—	$C_{13}H_{17}Si_2Cl$	—	—	—
(XXVII)	63,4	120(8)	1,5088	0,9011	80,98	80,21	68,80	8,70	22,78	$C_{14}H_{20}Si_2$	68,81	8,25	22,96
(XXVIII)	77,8	124(5)	1,5220	1,1747	76,78	76,18	—	—	—	$C_{10}H_{13}Si_2Cl_3$	—	—	—
(XXIX)	60,8	140(7)	1,4870	1,0122	80,26	79,95	55,06	8,46	19,24	$C_{13}H_{22}Si_2O_3$	55,29	7,83	19,80
(XXX)	57,5	158(8)	1,4500	0,9608	89,63	88,79	45,39	8,82	26,39	$C_{12}H_{28}Si_3O_4$	45,00	8,82	26,30

1-(Trimethylsilyl)-2-(dimethylmethoxysilyl)ethylene (XXI). With stirring, to a solution of 10.2 g of 1-(trimethylsilyl)-2-(methyldimethoxysilyl)ethylene in 15 ml of ether was added the Grignard reagent, prepared from 1.21 g of Mg and 7.1 g of CH_3I in 25 ml of ether, in drops. The mixture was heated at reflux for 2 h. The obtained precipitate was filtered, the ether was distilled off, and the residue was vacuum-distilled. We obtained 6.02 g (64.0%) of (XXI) with bp 39° (4 mm); n_D^{20} 1.4300; d_4^{20} 0.8222. Found: C 50.98; H 10.70; Si 29.60%; MR 59.20. $C_8H_{20}Si_2O$. Calculated: C 50.98; H 10.71; Si 29.82%; MR 58.67.

1,2-bis(Dimethylmethoxysilyl)ethylene (XXII) was obtained in a similar manner.

bis-[β-(Trimethylsilyl)vinyl]methyl(ethynyl)silane (XVI). To a solution of 2.8 g of (III) in 10 ml of ether was added the Grignard reagent, prepared from 0.76 g of Mg and 4.52 g of CH_3I in 25 ml of ether, in drops. The mixture was heated at reflux for 1 h, cooled, and decomposed with water and 5% HCl solution. After the usual workup and vacuum-distillation we obtained 1.46 g (68.5%) of (XVI) with bp 103-104° (8 mm); n_D^{20} 1.4606; d_4^{20} 0.8296. Found: C 58.77; H 9.83; Si 31.61%; MR 89.43. $C_{13}H_{26}Si_3$. Calculated: C 58.56; H 9.84; Si 31.60%; MR 88.03.

Compounds (XXIV) and (XXVII) were obtained in a similar manner (see Table 2).

CONCLUSIONS

1. Some new methyl-substituted trans-1,2-disilylethylene derivatives were synthesized by the addition of hydrosilanes to methylethynylsilanes and ethynylmethoxysilanes, and a study was made of their reaction with methanol, and also with the methyl- and ethynylmagnesium halides.

2. It was established by the NMR method that all of the obtained compounds have a trans-structure.

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