PHOTOCHEMICAL THIYLATION OF Si-METHOXY-SUBSTITUTED 1,2-DISILYLETHYLENES

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Previously it was shown [1,2] that Si-hexaalkyl-trans-1,2-disilylethylenes photochemically add butyl mercaptan and thioacetic acid. In order to synthesize some new types of monomers we studied the thiylation of a number of Si-substituted 1,2-disilylethylenes, which contained reactive methoxy groups on either one or both of the Si atoms. Here it proved that the reaction of the 1,2-bis(alkylmethoxysilyl)ethylenes is much slower than that of the Si-hexaalkyldisilethylenes [1,2]. Despite prolonged UV irradiation, the yields of the thiylation products do not exceed 45%, and only in the case of adding methyl mercaptan do they reach 80%.

$$R_{3-n}(CH_3O)_nSiCH{=}CHSi(OCH_3)_nR_{3-n} + R'SH \xrightarrow{h\nu}$$
$$\rightarrow R_{3-n}(CH_3O)_nSi\underset{\displaystyle SR}{\underset{|}{C}}HCHSi(OCH_3)_nR_{3-n}$$

(I)—(XIV)

$R = CH_3$, $R' = C_4H_9$, $n = 1$ (I); $R = CH_3$, $R' = C_4H_9$, $n = 2$ (II); $R' = C_4H_9$, $n = 3$ (III); $R = CH_3$, $R' = COCH_3$, $n = 1$ (IV); $R = CH_3$, $R' = COCH_3$, $n = 2$ (V); $R' = COCH_3$, $n = 3$ (VI); $R^2 = CH_3$ and C_2H_5, $R' = C_4H_9$, $n = 1$ (VII); $R^2 = CH_3$ and C_2H_5, $R' = COCH_3$, $n = 1$ (VIII); $R = C_2H_5$, $R' = COCH_3$, $n = 1$ (IX); $R = CH_3$, $R' = C_6H_5$, $n = 1$ (X); $R = CH_3$, $R' = CH_3$, $n = 1$ (XI); $R = CH_3$, $R' = CH_3$, $n = 2$ (XII); $R' = CH_3$, $n = 3$ (XIII); $R^2 = CH_3$ and C_2H_5, $R' = CH_3$, $n = 1$ (XIV).

TABLE 1. NMR Spectral Data for Adducts

$$(CH_3)_3Si\underset{\displaystyle SR}{\underset{|}{C}}HCH_2Si(OCH_3)_n(CH_3)_{3-n} + (CH_3)_3SiCH_2\underset{\displaystyle SR}{\underset{|}{C}}HSi(OCH_3)_n(CH_3)_{3-n}$$

(τ, ppm)

Compound	R	n	τ_{CH}	τ_{CH_2}	$\tau_{(CH_3)_3}$	$\tau_{(CH_3)_{3-n}}$	τ_R	τ_{OCH_3}
(XV)	C_4H_9	1	8,24 8,23	8,8—9,3	9,94	9,86 9,84	7,47 (α) 8,50 (β — γ) 9,0 (δ)	6,61 6,57
(XVI)	C_4H_9	2	8,25 8,22	8,8—9,3	9,92	9,83 9,82	7,47 (α) 8,50 (β — γ) 9,0 (δ)	6,44 6,40
(XVII)	C_4H_9	3	8,21 8,16	8,8—9,3	9,90 9,91	—	7,47 (α) 8,50 (β — γ) 9,0 (δ)	6,41 6,37
(XVIII)	$COCH_3$	1	7,15 7,09	8,9—9,5	9,96 9,95	9,90 9,87	7,71	6,64 6,59
(XIX)	$COCH_3$	2	7,16 7,07	8,9—9,5	9,98 9,95	9,92 9,91	7,71	6,52
(XX)	$COCH_3$	3	7,14 7,01	8,9—9,5	9,94 9,93	—	7,71	6,49 6,46
(XXI)	CH_3	1	8,34 8,32	8,8—9,3	9,91	9,86 9,82	7,93 7,92	6,60 6,56
(XXII)	CH_3	2	8,30 8,27	8,8—9,3	9,92	9,83 9,82	7,94 7,91	6,51 6,48
(XXIII)	CH_3	3	8,26 8,23	8,8—9,3	9,96 9,95	—	7,95 7,91	6,47 6,44

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TABLE 2. Constants of Adducts $R_{3-n}(CH_3O)_nSi\underset{|\atop SR}{C}HCH_2Si(OCH_3)_nR_{3-n}$

Compound	R	R′	n	Yield, %	bp, °C (p, mm of Hg	n_D^{20}	d_4^{20}	MR found	MR calculated	Found, % C	H	S	Si	Empirical formula	Calculated, % C	H	S	Si	Irradiation time, h
(I)	CH_3	C_4H_9	1	35,0	132(8)	1,4630	0,9368	85,65	86,49	49,00	10,41	10,53	19,14	$C_{12}H_{30}O_2SSi_2$	48,97	10,20	10,88	19,01	24
(II)	CH_3	C_4H_9	2	36,5	136(7)	1,4525	1,0101	87,31	88,12	43,94	9,41	9,85	17,35	$C_{12}H_{30}O_4SSi_2$	44,13	9,25	9,81	17,25	54
(III)	—	C_4H_9	3	31,6	147(5)	1,4430	1,0686	88,95	89,76	40,96	8,72	8,50	14,62	$C_{12}H_{30}O_6SSi_2$	40,19	8,42	8,94	15,66	45
(IV)	CH_3	$COCH_3$	1	32,4	130(10)	1,4640	1,0092	76,70	77,14	42,95	8,56	11,68	20,60	$C_{10}H_{24}O_3SSi_2$	42,81	8,62	11,43	20,00	58
(V)	CH_3	$COCH_3$	2	45,2	135(9)	1,4555	1,0891	78,18	78,79	38,40	8,08	10,08	18,25	$C_{10}H_{24}O_5SSi_2$	38,31	7,71	10,22	17,91	40
(VI)	—	$COCH_3$	3	30,0	140(5)	1,4490	1,1727	78,96	80,43	33,87	7,13	9,29	17,76	$C_{10}H_{24}O_7SSi_2$	34,86	7,01	9,30	16,30	40
(VII)	$CH_3 + C_2H_5$	C_4H_9	1	45,6	142(5)	1,4635	0,9470	93,93	95,78	51,52	10,45	9,56	16,98	$C_{14}H_{34}O_2SSi_2$	52,14	10,62	9,93	17,44	42
(VIII)	$CH_3 + C_2H_5$	$COCH_3$	1	31,0	133(9)	1,4710	1,0013	86,16	86,45	44,54	8,69	10,53	18,67	$C_{12}H_{28}O_3SSi_2$	46,77	9,17	10,39	18,22	39
(IX)	C_2H_5	$COCH_3$	1	30,8	155(5)	1,4720	0,9906	95,80	95,75	49,10	9,39	9,00	17,51	$C_{14}H_{32}O_3SSi_2$	49,99	9,58	9,52	16,68	58
(X)	CH_3	C_6H_5	1	40,0	175(6)	1,5130	1,0223	92,49	92,02	53,35	8,37	10,47	17,48	$C_{14}H_{26}O_2SSi_2$	53,45	8,33	10,19	17,86	30
(XI)	CH_3	CH_3	1	80,0	101(5)	1,4600	0,9547	72,44	72,53	42,84	9,58	12,99	22,09	$C_9H_{24}O_2SSi_2$	42,80	9,58	12,69	22,24	28
(XII)	CH_3	CH_3	2	78,2	129(11)	1,4540	1,0311	74,72	74,18	38,15	8,70	11,39	19,86	$C_9H_{24}O_4SSi_2$	37,99	8,50	11,27	19,75	28
(XIII)	—	CH_3	3	72,8	130(11)	1,4360	1,1166	74,41	74,30	34,10	7,74	8,48	17,90	$C_9H_{24}O_6SSi_2$	34,15	7,64	10,12	17,74	28
(XIV)	$CH_3 + C_2H_5$	CH_3	1	73,3	116(5)	1,4640	0,9479	81,67	81,78	46,85	9,83	11,53	19,88	$C_{11}H_{28}O_2SSi_2$	47,08	9,91	11,42	20,02	28

TABLE 3. Constants of Adducts $(CH_3)_3Si\underset{|\atop SR}{C}HCH_2Si(OCH_3)_n(CH_3)_{3-n} + (CH_3)_3SiCH_2\underset{|\atop SR}{C}HSi(OCH_3)_n(CH_3)_{3-n}$

Compound	R	n	Yield, %	bp, °C (p, mm of Hg	n_D^{20}	d_4^{20}	MR found	MR calculated	Found, % C	H	S	Si	Empirical formula	Calculated, % C	H	S	Si
(XV)	C_4H_9	1	83,1	111(6)	1,4646	0,8963	85,87	85,66	51,97	10,96	11,47	20,43	$C_{12}H_{30}OSSi_2$	51,73	10,85	11,57	20,17
(XVI)	C_4H_9	2	77,2	118(4)	1,4595	0,9288	86,79	86,48	49,09	10,59	10,72	19,35	$C_{12}H_{30}O_2SSi_2$	48,92	10,27	10,88	19,07
(XVII)	C_4H_9	3	76,9	122(6)	1,4555	0,9621	87,68	87,30	46,24	9,82	10,28	17,48	$C_{12}H_{30}O_3SSi_2$	46,40	9,74	10,32	18,09
(XVIII)	$COCH_3$	1	92,0	109(6)	1,4680	0,9512	77,31	76,34	45,46	9,24	12,29	21,36	$C_{10}H_{24}O_2SSi_2$	45,41	9,15	12,12	21,24
(XIX)	$COCH_3$	2	80,2	112(6)	1,4656	0,9975	77,84	77,16	42,79	8,80	11,67	20,62	$C_{10}H_{24}O_3SSi_2$	42,81	8,61	11,43	20,03
(XX)	$COCH_3$	3	74,6	104(2)	1,4592	1,0267	79,00	77,98	40,44	8,24	10,82	18,89	$C_{10}H_{24}O_4SSi_2$	40,51	8,16	10,82	18,95
(XXI)	CH_3	1	68,7	100(13)	1,4660	0,9147	71,61	71,71	45,55	10,33	13,28	23,73	$C_9H_{24}OSSi_2$	45,70	10,22	13,55	23,75
(XXII)	CH_3	2	71,4	98(9)	1,4570	0,9612	71,55	72,53	42,76	9,60	12,30	22,47	$C_9H_{24}O_2SSi_2$	42,87	9,59	12,69	22,24
(XXIII)	CH_3	3	72,8	105(7)	1,4504	0,9848	73,36	73,60	41,48	9,11	10,60	20,47	$C_9H_{24}O_3SSi_2$	40,25	9,08	11,19	20,91

When the reaction of thiols with the unsymmetrical 1-(trimethylsilyl)-2-(methylmethoxysilyl)ethylenes was studied it proved necessary to determine both the structure and the composition of the obtained adducts. In this case the thiols add with much greater vigor, and the yields of the thiylation products are 75-90% (irradiation for 8 h). The structure of all of the synthesized compounds was confirmed by the NMR spectral data (Table 1).

$$(CH_3)_3SiCH{=}CHSi(OCH_3)_n(CH_3)_{3-n} + RSH \rightarrow (CH_3)_3Si\underset{\underset{SR}{|}}{C}HCH_2Si(OCH_3)_n(CH_3)_{3-n}$$

$$+ (CH_3)_3SiCH_2\underset{\underset{SR}{|}}{C}HSi(OCH_3)_n(CH_3)_{3-n}$$

$$(XV)-(XXIII)$$

$R = C_4H_9$, $n = 1$ (XV); $R = C_4H_9$, $n = 2$ (XVI); $R = C_4H_9$, $n = 3$ (XVII); $R = COCH_3$, $n = 1$ (XVIII); $R = COCH_3$, $n = 2$ (XIX); $R = COCH_3$, $n = 3$ (XX); $R = CH_3$, $n = 1$ (XXI); $R = CH_3$, $n = 2$ (XXII); $R = CH_3$, $n = 3$ (XXIII)

An analysis of the NMR spectra of the reaction products of the thiols with unsymmetrical Si-substituted 1,2-disilylethylenes disclosed that both of the isomeric adducts (XV)-(XXIII) are formed in all cases. The presence of an asymmetric C atom in the $SiCH_2CH(SR)Si$ fragment leads to a nonequivalence of the protons of the methylene group, and the spectrum of this fragment belongs to the ABX type. The chirality of the C atom is also reflected on the signals of the substituents on the Si atom attached to it (in the case where the substituents are different). Thus, in the compounds with n = 2 (the substituent is $Si(OCH_3)_2CH_3$) the methoxy groups form three signals with intensities of 1:1:2, of which the highest signal belongs to the isomer $(CH_3)_3SiCH(SR)CH_2Si(OCH_3)_2CH_3$, while the other two are formed by the nonequivalent methoxy groups of the other isomer. In a similar manner, the methyl groups in the compounds with n = 1 (the substituent is $Si(CH_3)_2OCH_3$) give three signals. An increase in the temperature fails to lead to an averaging of these signals, which testifies that the corresponding protons (or groups) have a structural, and not a conformational nonequivalence. In all cases the ratio of the isomers is equal to 1:1 (except when R = alkyl and n = 3, where the ratio $(CH_3)_3SiCH(SR)CH_2Si(OCH_3)_3$: $(CH_3)_3SiCH_2CH(SR)Si(OCH_3)_3$ = 2:1).

EXPERIMENTAL METHOD

The NMR spectra of 10% solutions of the compounds in CCl_4 were obtained on a Tesla BS-487B spectrometer (80 MHz), using cyclohexane as the internal standard.

<u>1,2-Bis(dimethylmethoxysilyl)-butylthioethane (I)</u>. A mixture of 4.16 g of 1,2-bis(dimethylmethoxysilyl)ethylene and 1.8 g of butyl mercaptan in a sealed Pyrex glass ampul was irradiated with UV light (PRK-4 lamp) for 24 h and then distilled. We obtained 2.82 g of (I) (Table 2).

Compounds (II)-(X) and (XV)-(XX) were obtained in a similar manner (Tables 2 and 3).

<u>1-(Trimethylsilyl)-2-dimethylylmethoxysilyl)-1-methylthioethane and 1-(Trimethylsilyl)-2-(dimethylmethoxysilyl)-2-(dimethylthioethane (XXI)</u>. A mixture of 1.88 g of 1-(trimethylsilyl)-2-(dimethylmethoxysilyl)-ethylene and 1.5 g of methyl mercaptan was irradiated in a Pyrex glass ampul for 8 h. Then the ampul was cooled in solid CO_2, opened, the excess MeSH was evaporated, and the compound was distilled. We obtained 1.62 g of (XXI) (see Table 3).

Compounds (XI)-(XIV), (XXII), and (XXIII) were synthesized in a similar manner (see Tables 2 and 3).

CONCLUSIONS

1. A number of new sulfur-containing organosilicon monomers was synthesized by the reaction of 1,2-bis(alkylmethoxysilyl)- and 1-(trimethylsilyl)-2-(methylmethoxysilyl)ethylenes with mercaptans and thioacetic acid.

2. Based on the NMR spectral data, the 1-(trimethylsilyl)-2-(methylmethoxysilyl)ethylenes form two isomeric adducts in a 1:1 ratio.

LITERATURE CITED

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