REACTION OF ALKANETHIOLS WITH 1-TRIALKYLSILYL, 1-TRIALKYLGERMYL, AND 1-TRIALKYLSTANNYL DERIVATIVES OF 2-SUBSTITUTED ACETYLENES

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Previously [1] while studying the photochemical reaction of alkanethiols with trialkylethynylgermanes and trialkylethynylstannanes we had established that two molecules of C_4H_9SH add even with a deficiency of the alkanethiol to the triethylethynylgermane to give triethyl[1,2-bis(butylthio)ethyl]germane. At the same time, triethylethynylstannane with n-butyl mercaptan gives a mixture of 1,2-bis(butylthio)ethylene and the 1,2- and 1,1-bis(triethylstannyl)ethylenes.

In the present paper we studied the photochemical addition of alkanethiols to the 1-triethylsilyl, 1-triethylgermyl, and 1-triethylstannyl derivatives of 2-substituted acetylenes of type $R_3MC \equiv CR^1$ (M = Si, Ge, Sn; R^1 = Alk, Ar, R_3M). When M = Si, Ge (R = Ar) the sole reaction products are compounds (I) and (II).

$$R_3MC{\equiv}CR^1 + HSR^2 \xrightarrow{h\nu} \underset{\text{(I), (II)}}{R_3MC(SR^2){=}CHR^1} \qquad (1)$$

$$M = Si;\ R = CH_3;\ R^1 = C_6H_5;\ R^2 = n\text{-}C_4H_9\ \text{(I)};$$

$$M = Ge;\ R = C_2H_5;\ R^1 = C_6H_5;\ R^2 = n\text{-}C_4H_9\ \text{(II)}$$

In contrast to $R_3MC \equiv CH$ (I), the alkanethiols add much more slowly in this case and the yield of adducts (I) and (II) after irradiation at 60°C for 30 h is respectively 39.3 and 66.3%.

Two parallel reactions proceed when M = Sn: addition to the triple bond (2) and cleavage of the Sn–C bond (3), in which connection the latter predominates.

$$R_3SnC{\equiv}CR^1 + HSR^2 \begin{cases} \longrightarrow R_3SnC(SR^2){=}CHR^1 & (2) \\ \longrightarrow R_3SnSR^2 + HC{\equiv}CR^1 & (3) \end{cases}$$

The adducts, formed according to scheme (2) could be obtained when $R^1 = C_6H_5$ (III) and $n\text{-}C_4H_9S$ (IV). Only the cleavage products of the Sn–C bond according to scheme (3) are formed when $R = n\text{-}C_4H_9$.

Bis(triethylstannyl)acetylene reacts with an equimolar amount of the alkanethiols both under UV irradiation and in the absence of an initiator, even at ~20°, with the predominant cleavage of one Sn–C bond.

$$(C_2H_5)_3SnC{\equiv}CSn(C_2H_5)_3 + HSR \rightarrow (C_2H_5)_3SnC{\equiv}CH + (C_2H_5)_3SnSR \qquad (4)$$

Since the yield of triethylethynylstannane reaches 65%, this reaction can serve as a convenient method for the preparation of triorganylethynylstannanes. The addition of inhibitors of radical processes (hydroquinone, elemental sulfur) to the reaction mixture is practically without effect on the reaction. This can indicate that the cleavage of bis(triethylstannyl)acetylene has an ionic character.

The bis(trialkylsilyl)acetylenes [2] and bis(triethylgermyl)acetylene do not react with alkanethiols even in the presence of initiators of free radical reactions. The structure of the obtained compounds (I)-(IV), summarized in Table 1, was confirmed by the IR and NMR spectral data (Table 2).

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TABLE 1. Properties of Synthesized Compounds

Compound	Yield, %	Bp, °C (p, mm of Hg)	n_D^{20}	d_4^{20}	Found					Empirical formula	Calculated, %				
					C, %	H, %	S, %	M, %	*MR*		C, %	H, %	S, %	M, %	*MR*
(I)	39,3	135—137(4)	1,5508	0,9574	68,35	9,04	11,99	10,54	85,20	$C_{15}H_{24}SSi$	68,11	9,14	12,12	10,61	88;11
(II)	66,3	158—161(3)	1,5598	1,0822	61,86	8,45	9,05	20,63	101,34	$C_{18}H_{30}SGe$	61,57	8,61	9,13	20,70	104,89
(III)	23,0	142—145(1,5)	1,5785	1,2255	53,13	7,49	7,92	30,75	102,8	$C_{17}H_{28}SSn$	53,15	7,61	8,34	30,90	104,1
(IV)	20,6	150—154(2)	1,5403	—	45,70	8,21	16,09	30,13	—	$C_{15}H_{32}S_2Sn$	45,58	8,16	16,23	30,04	—

TABLE 2. Parameters of NMR Spectra of Synthesized Compounds

Compound	Formula	Isomer*	τ_{CH_3CM} (τ_{CH_3M})	τ_{CH_2M}	τ_{CH_3} (в C_4H_9S)	$\tau_{CH_2CH_2}$	τ_{CH_2S}	$\tau_{(CH_3)_2C}$	τ_{CHS}	$\tau_{C_6H_5}$	$\tau_{C=CH}$	Ratio of cis:trans
(I)	$(CH_3)_3SiC(SC_4H_9)=CHC_6H_5$	cis	10,1	—	9,18	8,56	7,93	—	—	2,16—3,33	3,30	2 : 5
		trans	9,90	—	9,36	8,81	7,69	—	—	2,16—3,36	3,22	
(II)	$(C_2H_5)_3GeC(SC_4H_9)=CHC_6H_5$	cis	9,05	9,28	9,05	8,66	7,51	—	—	2,25—3,10	3,28	3 : 2
		trans	9,05	9,28	9,05	8,40	7,20	—	—	2,25—3,10	3,16	
(III)	$(C_2H_5)_3SnC(SC_3H_7\text{-}i)=CHC_6H_5$	cis	8,96	9,27	—	—	—	8,6	7,14	2,20—3,28	3,39	1 : 4
		trans	8,96	9,27	—	—	—	8,67	6,60	2,20—3,28	3,28—3,28	
(IV)	$(C_2H_5)_3SnC(SC_3H_7\text{-}i)=CHSC_4H_9$	cis	8,78	9,13	9,05	8,50	7,46	8,75	6,86	—	4,01	1 : 2
		trans	8,78	9,13	8,95	8,50	7,43	8,75	6,86	—	3,64	

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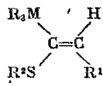
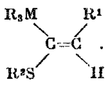
*cis-isomer , trans-isomer .

EXPERIMENTAL METHOD

1-(n-Butylthio)-1-(trimethylsily)-2-phenylethylene (I). Into a Pyrex glass ampul were charged 9.7 g of 1-trimethylsilyl-2-phenylacetylene and 4.0 g of n-butyl mercaptan. The mixture was irradiated with the UV light of a PRK-2 lamp for 30 h at 60°. Fractional distillation gave 4.6 g (39.3%) of adduct (I) with bp 135-137° (4 mm); n_D^{20} 1.5508 (see Table 1). Compound (II) was also obtained under similar conditions.

1-(Isopropylthio)-1-(triethylstannyl)-2-phenylethylene (III). Into a quartz test tube, equipped with a cooling finger, was charged a mixture of 13.1 g of 1-triethylstannyl-2-phenylacetylene and 3.2 g of isopropyl mercaptan. The mixture was irradiated with UV light at 15° for 10 h. Besides the cleavage products of the Sn–C bond, namely phenylacetylene and triethyl(isopropylthio)stannane, distillation of the reaction mixture gave 3.7 g (23%) of adduct (III), bp 142-145° 1.5 (mm); n_D^{20} 1.5785. Compound (IV) was obtained under the same conditions. The yield of adduct (III) is 12% when the reaction is run under the conditions of obtaining compound (I).

Reaction of 1-Triethylstannyl-1-hexyne with n-Butyl Mercaptan. A mixture of 11.7 g of 1-triethylstannyl-1-hexyne and 3.7 g of n-butyl mercaptan was irradiated with UV light at 60° for 30 h. It was established by GLC that the reaction mixture contains only the cleavage products of the Sn–C bond.

Reaction of bis(Triethylsilyl)-, bis(Triethylgermyl)-, and bis(Triethylstannyl)acetylenes with n-Butyl Mercaptan. a) A mixture of 4.8 g of bis(triethylsilyl)acetylene and 1.6 g of n-butyl mercaptan was irradiated at 60° for 50 h. All of the starting compounds were recovered unchanged after fractional distillation. A similar result was obtained when a mixture of bis(triethylgermyl)acetylene and n-butyl mercaptan was irradiated.

b) A mixture of 6.7 g of bis(triethylstannyl)acetylene and 1.6 g of n-butyl mercaptan was kept in a sealed ampul for 50 h at ~20°. After fractional distillation we obtained 2.3 g (65%) of triethylethynylstannane with bp 48-50° (8 mm); n_D^{20} 1.4770 [3]. The IR spectrum has bands (ν, cm^{-1}) at 2008 ($C \equiv C$) and 3280 ($H-C\equiv$). In addition, we isolated 4.0 g (87%) of triethyl(butylthio)stannane [4] with bp 114-117° (8 mm); n_D^{20} 1.5130.

c) An equimolar mixture of bis(triethylstannyl)acetylene and n-butyl mercaptan was irradiated with UV light for 30 h at 60°. It was shown by GLC that the reaction mixture contains only the cleavage products of the Sn–C bond.

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CONCLUSIONS

1. A study was made of the photochemical reaction of alkanethiols with the 1-trialkylsilyl, 1-trialkylgermyl, and 1-trialkylstannyl derivatives of 2-substituted acetylenes $R_3MC \equiv CR^1$. Due to the lower stability of the $Sn-C \equiv C$ bond the compounds where M = Sn react with alkanethiols to give predominantly its cleavage products. When M = Si or Ge the addition products of the alkanethiols to the triple bond, $R_3MC(SR^2) = CHR^1$, are formed in satisfactory yields.

2. The alkanethiols do not react with the bis(trialkylsilyl)- and bis(trialkylgermyl)acetylenes under the same conditions, while with bis(triethylstannyl)acetylene they react to give the cleavage products of one $Sn-C \equiv C$ bond.

LITERATURE CITED

1. M. G. Voronkov, R. G. Mirskov, and V. I. Rakhlin, Zh. Obshch. Khim., 44, 954 (1974).
2. N. V. Komarov, O. G. Yarosh, L. P. Vakhrushev, and N. F. Chernov, Zh. Obshch. Khim., 40, 1171 (1970).
3. M. F. Shostakovskii, N. V. Komarov, I. S. Guseeva, and V. K. Misyunas, Dokl. Akad. Nauk SSSR, 158, 918 (1964).
4. S. Sasin, J. Org. Chem., 18, 1142 (1953).