Corresponding Member of the Academy of Sciences of the USSR M. F. SHOSTAKOVSKII, N. V. KOMAROV, I. S. GUSEVA, V. K. MISIONAS, A. M. SKLYANOVA, T. D. BURNASHOVA

1965

SovietRxiv

Abstract

Full Text

CHEMISTRY

Corresponding Member of the Academy of Sciences of the USSR M. F. SHOSTAKOVSKII, N. V. KOMAROV, I. S. GUSEVA, V. K. MISIONAS, A. M. SKLYANOVA, T. D. BURNASHOVA

INTERACTION OF ACETYLENES WITH HEXAALKYLDISTANNOXANES

Earlier we ([1–5]) showed that stannanols and dialkylolovooxy compounds differ sharply in the corresponding reactions from their organic and organosilicon analogs.

In this connection it was of considerable interest to investigate the interaction of hexaalkyldistannoxanes with acetylenic compounds.

The investigation showed that hexaalkyldistannoxanes, in contrast to the corresponding organic and organosilicon analogs, readily enter into reaction with acetylenic compounds containing an active hydrogen atom and form acetylenic stannanes and stannanols.

$$R_3SnOSnR_3 + HC \equiv CR' \rightarrow R_3SnC \equiv CR' + R_3SnOH, \qquad (I)$$

where

$$R\text{—}CH_3,\ C_2H_5,\ C_3H_7,\ C_4H_9 \text{ and others.}$$

$$R'\text{—}H,\ Na,\ CH{=}CH_2,\ C{\equiv}CH,\ (CH_3)_3C,\ (CH_3)_3Si,\ C_6H_5,\ -\overset{|}{\underset{|}{C}}OH,$$

$$-\overset{|}{\underset{|}{C}}OCH(OR)CH_3,\ C(=O)-R,\ CH{=}CHOR,\ CH{=}CHNR_2 \text{ and others.}$$

The reaction proceeds autocatalytically.

It is interesting to note that, under ordinary conditions and with an equimolecular ratio of the reagents, the reaction proceeds mainly according to scheme (I). However, in accordance with the fact established earlier by us ([5–8]), in the presence of an excess of the acetylenic component and under more severe conditions,

further interaction of the stannanols formed with acetylenes takes place. Owing to this ability, the indicated reaction becomes controllable and can be carried out either according to scheme (I) or according to scheme (II).

$$R_3SnOSnR_3 + 2R'C \equiv CH \rightarrow 2R_3SnC \equiv CR' + H_2O. \qquad (II)$$

In the case of the interaction of hexaalkyldistannoxanes with acetylene, together with trialkylethynylstannanes there are obtained, in insignificant amounts, bis-(trialkylstannyl)acetylenes. The most probable reason for the formation of the latter is the interaction of acetylene simultaneously with two molecules of hexaalkyldistannoxane

$$2R_3SnOSnR_3 + HC \equiv CH \rightarrow R_3SnC \equiv CSnR_3 + 2R_3SnOH. \qquad (III)$$

Formation of bis-(trialkylstannyl)acetylenes is also possible on the basis of the disproportionation reaction of trialkylethynylstannanes

$$2R_3SnC \equiv CH \rightarrow R_3SnC \equiv CSnR_3 + HC \equiv CH. \qquad (IV)$$

Disproportionation of the latter was observed by us upon heating them with hexaalkyldistannoxanes or upon distillation of a mixture of these substances. Hexaalkyldistannoxanes exert a catalytic action on the disproportionation reaction of trialkylethynylstannanes. An exceptional feature of trialkylethynylstannanes is their reduced reac-

tional ability, manifested in the fact that they do not enter into the reaction of direct interaction with hexaalkyldistannoxanes and do not form bis-(trialkylstannyl)-acetylenes in this way. Meanwhile, analogously constructed carbon and silicon compounds do enter into this reaction

$$R_3XC \equiv CH + R'_3SnOSnR_3 \rightarrow R_3XC \equiv CSnR'_3 + R'_3SnOH,$$

where R and R′ are CH_3 and C_2H_5; X is C and Si.

According to the reactivity of the hydrogen atoms in monosubstituted acetylenes in this reaction, the latter may be arranged in the following series:

$$R_3SiC \equiv CH > R_3C{-}C \equiv CH > R_3SnC \equiv CH.$$

A similar regularity was also observed by us in other chemical reactions, as well as in the study of the IR spectra of the indicated compounds ([9]).

The low activity of acetylenic hydrogen and the weak strength of the tin–acetylene bond of trialkylethynylstannanes are apparently the main reason why the

interaction of ethynylstannanes with trialkylstannanols proceeds contrary to the previously established direction ([5]), according to the scheme

$$R_3SnC \equiv CH + R'_3SnOH \rightarrow R_3SnOSnR'_3 + HC \equiv CH.$$

Because of this feature of ethynylstannanes, the reaction of hexaalkyldistannoxanes with acetylene is reversible

$$R_3SnOSnR_3 + HC \equiv CH \rightleftarrows R_3SnC \equiv CH + R_3SnOH.$$

The interaction of hexaalkyldistannoxanes with sodium acetylide led to the formation only of bis-(trialkylstannyl)-acetylenes.

$$R_3SnOSnR_3 + HC \equiv CNa \rightarrow R_3SnC \equiv CSnR_3 + NaOH.$$

The formation of acetylenic organotin compounds in the interaction of hexaalkyldistannoxanes with acetylenes, apparently, as in the case of stannanols, is associated with donor–acceptor interaction of the lone electrons of the oxygen atom with the proton and of the π-electrons of the acetylenic bond with vacant $5d$-orbitals of the tin atom

$$R_3SnOSnR_3 + HC \equiv CR' \rightarrow \left[\begin{array}{c} R_3SnO\,SnR_3 \\ \downarrow\uparrow \\ HC \equiv CR' \end{array}\right] \rightarrow R_3SnC \equiv CR' + R_3SnOH.$$

At the basis of the mechanism of the reaction under study, the principal role probably belongs to electrophilic proton attack on the oxygen atom and to interaction with the acetylenic anion

$$[R'C \equiv C:]^{(-)}H^{(+)} + R_3SnOSnR_3 \rightarrow \left[\begin{array}{c} SnR_3 \\ (+)/ \\ H{-}O \\ \backslash \\ SnR_3 \end{array}\right] \xrightarrow{R'C\equiv C^{(-)}} R_3SnC \equiv CR' + R_3SnOH.$$

The features and mechanism of this reaction are being studied. The physicochemical constants of the synthesized compounds are presented in Table 1.

Trimethylethynylstannane. Into a test-tube autoclave are placed 24 g of hexamethyldistannoxane, and it is saturated with acetylene under a pressure of 8–12 atm. The autoclave is discharged, the liquid phase is separated from the

crystalline phase and distilled. This gives 8.6 g (65.5%) of trimethylethynylstannane with b.p. 98°/745 mm, 58°/150 mm; n_D^{20} 1.4626, d_4^{20} 1.3602. MR found 38.2, calculated 39.27.

$C_5H_{11}Sn$.	Found, %:	C 31.51; H 5.8; Sn 62.72
	Calculated, %:	C 31.8; H 5.34; Sn 62.86

In addition, 7.5 g of hexamethyldistannoxane with b.p. 130-131°/150 mm and 8.5 g of trimethylstannanol with m.p. 117° are isolated.

Table 1

Physicochemical constants of the synthesized compounds

No.	Compound formula	b.p., °C	Pressure, mm	n_D^{20}	d_4^{20}	MR_D found	MR_D calc.	C, % found	C, % calc.	H, % found	H, % calc.	Sn, % found	Sn, % calc.	Yield, %
1	$(CH_3)_3SnC\equiv CH$	58	150	1.4626	1.3602	38.20	39.27	31.51	31.8	5.18	5.34	62.72	62.86	65
2	$(C_2H_5)_3SnC\equiv CH$	49 – 50	5	1.4770	1.2458	52.37	53.21	41.79	41.61	7.19	6.99	51.42	51.41	64
3	$(n\text{-}C_3H_7)_3SnC\equiv CH$	94	2	1.4780	1.1545	66.95	67.16	48.53	48.39	8.01	8.12	43.28	43.45	50
4	$(n\text{-}C_4H_9)_3SnC\equiv CH$	98 – 99	2.5	1.4765	1.1038	80.55	81.61	53.53	53.39	8.92	8.95	37.32	37.67	47
5	$(C_2H_5)_3SnC\equiv C-C\equiv CH$	60	1	1.5262	1.2626	61.98	60.95	47.45	47.50	6.31	6.33	47.04	46.56	50
6	$(n\text{-}C_3H_7)_3SnC\equiv C-C\equiv CH$	113	1	1.5110	1.1343	78.42	74.84	51.83	52.57	7.84	7.46	38.81	39.96	30
7	$(CH_3)_3SnC\equiv CSn(CH_3)_3$	102	23	m.p. 58°		–	–	27.44	27.32	5.05	5.16	67.78	67.52	97
8	$(C_2H_5)_3SnC\equiv C-C\equiv CSn(C_2H_5)_3$	156	1.5	1.5483	1.3646	107.05	105.53	42.40	41.79	6.58	6.57	52.1	51.62	46
9	$(C_2H_5)_3SnC\equiv CC(CH_3)_3$	59	1.5	1.4710	1.1162	71.87	71.80	50.43	50.21	8.35	8.43	41.72	41.36	25
10	$(C_2H_5)_3SnC\equiv CSi(CH_3)_3$	107	9	1.4805	1.1450	–	–	43.30	43.70	7.85	7.94	–	–	44
11	$(n\text{-}C_3H_7)_3SnC\equiv CC_6H_5$	140	1	1.5388	1.1811	92.53	93.95	–	–	–	–	–	–	70

No.	Compound formula	b.p., °C	Pressure, mm	n_D^{20}	d_4^{20}	MR_D found	MR_D calc.	C, % found	C, % calc.	H, % found	H, % calc.	Sn, % found	Sn, % calc.	Yield, %
12	$(C_2H_5)_3SnOCH_2C{\equiv}CH$	80–81	5	1.4660	1.2870	58.92	60.01	41.7	41.5	6.8	6.9	44.8	45.7	31
13	$(C_2H_5)_3SnOCH(CH_3)C{\equiv}CH$	73	3	1.4830	1.2375	63.45	64.28	43.39	43.68	7.25	7.31	43.12	43.17	40
14	$(C_2H_5)_3SnOC(CH_3)_2C{\equiv}CH$	83	2	1.4755	1.1851	68.59	69.27	45.48	45.71	8.02	7.67	41.47	41.07	26
15	$(n\text{-}C_3H_7)_3SnOCH(CH_3)C{\equiv}CH$	92	1	1.4785	1.1544	77.80	78.17	49.61	49.24	8.39	8.26	37.04	37.44	17
16	$(n\text{-}C_3H_7)_3SnOC(CH_3)_2C{\equiv}CH$	109	4	1.4735	1.1168	83.22	82.80	51.04	50.79	8.32	8.51	35.34	35.85	10
17	$(n\text{-}C_4H_9)_3SnOCH(CH_3)C{\equiv}CH$	117	3	1.4785	1.1009	91.58	92.16	53.64	53.51	8.97	8.97	33.06	33.05	68
18	$(n\text{-}C_4H_9)_3SnOC(CH_3)_2C{\equiv}CH$	118	2	1.4740	1.0867	96.69	98.56	54.65	54.71	9.22	9.18	31.85	31.81	31
19	$(C_2H_5)_3SnOCH_2C{\equiv}CSn(C_2H_5)_3$	160	5	1.5145	1.3541	103.18	103.7	38.40	38.60	6.70	6.88	51.40	51.20	81
20	$(C_2H_5)_3SnOCH(CH_3)C{\equiv}CSn(C_2H_5)_3$	132	1	1.5160	1.3242	107.56	108.32	39.43	40.06	7.11	7.14	49.84	49.48	70
21	$(C_2H_5)_3SnOC(CH_3)_2C{\equiv}CSn(C_2H_5)_3$	138	2	1.5005	1.2969	112.09	112.96	41.02	41.34	7.43	7.35	47.91	48.09	77
22	$(n\text{-}C_3H_7)_3SnOCH(CH_3)C{\equiv}CSn(C_3H_7\text{-}n)_3$	165	1	1.4970	1.2139	135.95	136.14	46.99	46.81	8.04	8.22	41.58	42.02	52
23	$(n\text{-}C_3H_7)_3SnOC(CH_3)_2C{\equiv}CSn(C_3H_7\text{-}n)_3$	172	4	1.4925	1.2073	139.01	139.74	47.92	47.78	8.27	8.37	41.22	41.07	73
24	$(n\text{-}C_4H_9)_3SnOCH(CH_3)C{\equiv}CSn(C_4H_9\text{-}n)_3$	200	3	1.4875	1.1558	—	—	51.42	51.88	8.94	9.02	36.98	36.62	12
25	$(n\text{-}C_4H_9)_3SnOC(CH_3)_2C{\equiv}CSn(C_4H_9\text{-}n)_3$	198	2	1.4890	1.1277	169.49	168.62	51.98	52.50	9.12	9.05	35.60	35.84	63
26	$(C_2H_5)_3SnC{\equiv}C{-}CH{=}CHOC_4H_9$	107–108	0.5	1.5098	1.1760	83.65	82.40	51.10	51.10	7.98	7.96	35.27	35.07	98
27	$(C_2H_5)_3SnC{\equiv}C{-}CH(CH_3)OCH(OC_4H_9)CH_3$	120	2	1.4722	1.1075	94.84	94.41	51.09	51.24	8.41	8.54	31.77	31.68	70
28	$(C_2H_5)_3SnC{\equiv}C{-}C(CH_3)_2OCH(OC_4H_9)CH_3$	112	1.5	1.4670	1.0727	100.6	99.24	52.40	52.48	8.76	8.75	30.60	30.54	62

Bis-(tri-*n*-propylstannyl)acetylene. To 2.32 g (0.048 gram-mole) of sodium acetylide in 15 ml of abs. ether, with stirring, is added a solution of 24.6 g (0.048 gram-mole) of hexa-*n*-propyldistannoxane in 25 ml of ether. The organic layer is separated from the precipitate and distilled. This gives 24.6 g (92%)

of bis-(tri-*n*-propylstannyl)acetylene with b.p. 188–189°/6 mm, n_D^{20} 1.5040, d_4^{20} 1.2461. Found MR 122.7, calculated 123.09.

$C_{20}H_{42}Sn_2$.	Found %:	Sn 45.92
	Calculated %:	Sn 45.64

In addition, 1.1 g of tri-*n*-propylstannylstannane is isolated, with b.p. 78°/4 mm, n_D^{20} 1.4780.

Triethylstannyldiacetylene. To a solution of 15.5 g of diacetylene in 70 ml of abs. ether, cooled to −20, −30°, 52 g of hexaethyldistannoxane is gradually added, and the mixture is left overnight and distilled. This gives 15.5 g (50%) of triethylstannyldiacetylene with b.p. 60°/1 mm, n_D^{20} 1.5262, d_4^{20} 1.2626. MR found 61.98, calculated 60.95.

$C_{10}H_{16}Sn$.	Found %:	C 47.45; H 6.31; Sn 44.04
	Calculated %:	C 47.50; H 6.33; Sn 46.56

In addition, 26.1 g (46.4%) of bis-(triethylstannyl)diacetylene is isolated, with b.p. 156°/0.5 mm, n_D^{20} 1.5483, d^{20} 1.3646. MR found 107.5, calculated 105.53.

$C_{16}H_{30}Sn_2$.	Found %:	C 42.40; H 6.58; Sn 52.1
	Calculated %:	C 41.79; H 6.57; Sn 51.62

Triethylstannylethynylvinyldiethylamine. In an apparatus with a Dean-Stark trap are placed 11.7 g (0.27 gram-mole) of hexaethyldistannoxane, 6.1 g (0.05 gram-mole) of ethynylvinyldiethylamine, and 50 ml of benzene, and the mixture is heated until the water and benzene have been completely removed. On distillation, 6.59 g (80%) of the substance is obtained, with b.p. 125–126°/1.5 mm; n_D^{20} 1.5470, d_4^{20} 1.1648.

Found %:	C 51.10; H 7.96; Sn 35.94; N 4.1
Calculated %:	C 51.22; H 8.28; Sn 36.2; N 4.27

Interaction of hexaethyldistannoxane with triethylethynylstannane. A mixture of 5.5 g (0.013 gram-mole) of hexaethyldistannoxane and 3 g (0.013 gram-mole) of triethylethynylstannane is stirred for 10 hours and distilled. This gives 5.2 g of ethyldistannoxane with b.p. 150–151°/3 mm, n_D^{20} 1.5010, and 2.3 g of bis-(triethylstannyl)acetylene with b.p. 155–156°/13 mm, n_D^{20} 1.5080.

Interaction of triethylethynylstannane with triethylstannanol. Into a flask fitted with a magnetic stirrer and a gas outlet tube connected to a cylinder for measuring gas are placed 3.6 g (0.016 g/mole) of triethylstannanol, and 3.7 g (0.016 gram-mole) of triethylethynylstannane is added. Evolution of acetylene

(360 ml) begins immediately. This gives 6.5 g (98%) of hexaethyldistannoxane with b.p. 145–146°/12 mm, n_D^{20} 1.4990.

Irkutsk Institute of Organic Chemistry
Siberian Branch of the Academy of Sciences of the USSR

Received
6 I 1965

REFERENCES

1. M. F. Shostakovskii, N. V. Komarov, V. K. Misyunas, *Izv. AN SSSR, OKhN*, **1962**, 368.

2. N. V. Komarov, M. F. Shostakovskii, V. K. Misyunas, Author' s Certificate No. 163176 (1964).

3. M. F. Shostakovskii, N. V. Komarov et al., *Izv. AN SSSR, ser. khim.*, **1964**, 1102.

4. M. F. Shostakovskii, N. V. Komarov et al., *DAN*, **161**, No. 2 (1965).

5. M. F. Shostakovskii, N. V. Komarov et al., *DAN*, **158**, 918 (1964).

6. N. V. Komarov, M. F. Shostakovskii, I. S. Guseva, Author' s Certificate No. 158573 (1963).

7. M. F. Shostakovskii, N. V. Komarov, I. S. Guseva, Author' s Certificate No. 148409 (1962).

8. N. V. Komarov, I. S. Guseva, Author' s Certificate No. 164598 (1964).

9. E. A. Gastilovich, D. N. Shigorin, N. V. Komarov, *Optics and Spectroscopy*, **16**, No. 1, 46 (1964).

Note: Figure translations are in progress. See original paper for figures.