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Abstract

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ON THE INTERACTION REACTION BETWEEN STANNANOLS AND ACETYLENES

A. E. Favorskii and one of the authors of the present work ([1–3]) studied in detail the interaction of acetylenes of various structures with hydroxyl-containing compounds and showed that, in an alkaline medium, simple vinyl ethers are formed. In the absence of catalysts, vinylation of alcohols is not observed.

The present investigation is a further development of the work of Favorskii and his school on the study of acetylene chemistry and is devoted to elucidating the nature of the interaction between acetylenes and stannanols. It seemed of considerable interest to study this reaction and to compare the behavior of stannanols in it with that of alcohols and silanols, and in this way to obtain new information on the chemical nature of the compounds under study and on the role of the tin atom.

Earlier we ([4]) established that stannanols, unlike alcohols and silanols, exchange the hydroxyl group for an organic radical upon interaction with organomagnesium compounds.

$$R_3SnOH + R'MgBr \rightarrow R_3SnR'.$$

Taking this fact into account, as well as the information that stannanols are typical bases ([5–7]), one could expect a different direction for the reaction between acetylenes and stannanols. And indeed it turned out that, instead of organotin vinyl ethers, whose formation should be expected according to the Favorskii–Shostakovskii scheme,

$$R_3SnOH + HC \equiv CH \rightarrow R_3SnOCH = CH_2,$$

$$R_3SnOH + HC \equiv C{-}R' \rightarrow R_3SnOCH = CHR' + R_3SnOC = CH_2,$$

$$\begin{array}{c} \\ | \\ R' \end{array}$$

in reality tin-acetylene stannanes are obtained ([8,9]). The interaction proceeds according to a scheme entirely different from that of the vinylation of alcohols and silanols, and resembles the reaction of neutralization of acids by bases,

$$R_3SnOH + HC \equiv CR' \rightarrow R_3SnC \equiv CR' + H_2O,$$

where $R = CH_3, C_2H_5, C_3H_7, C_4H_9$, etc.; $R' = H, Na, CH = CH_2, C_4H_9, C_6H_5$,

$$-\overset{|}{C}-OH, \qquad -\overset{|}{C}-OCH(OR)CH_3$$

etc., and is reduced to the reaction of the hydroxyl group of stannanols with the active acetylenic hydrogen. A distinctive feature of the reaction under study is that it proceeds in the absence of a catalyst.

The formation of acetylenic stannanes is evidently due to donor–acceptor interaction of the unshared electron pairs of the oxygen atom of stannanols with the mobile acetylenic hydrogen and of the π-electrons of the acetylenic bond with the vacant $5d$-orbitals of the tin atom

$$R_3SnOH + HC \equiv CR' \rightarrow \left[\begin{array}{c} R_3Sn{-}\ddot{O}H \\ \uparrow \quad \downarrow \\ R'{-}C \equiv C{-}H \end{array}\right] \rightarrow R_3SnC \equiv CR' + H_2O.$$

The mechanism of the reaction under study presupposes an electrophilic attack by the acetylenic hydrogen on the oxygen atom of the stannanols.

$$R_3Sn^+ - \overset{(-)}{O} + \overset{(+)}{H}\,[:C{\equiv}CR']^{(-)} \longrightarrow R_3Sn^{(+)} - OH \xrightarrow{[R'C{\equiv}C]^{(-)}} R_3SnC{\equiv}CR' + H_2O$$

And indeed, as the acidity of the acetylenic hydrogen increases, the reaction rate rises and the yields of acetylenic organotin compounds increase. If the interaction of acetylene with stannanols proceeds under pressure and at a temperature of 100–120°, then with phenyl- and vinylacetylenes the reaction proceeds excellently under ordinary conditions at room temperature.

In contrast to the reaction under study, the vinylation of organic alcohols consists in their addition to the acetylenic bond and is determined by the mobility of the hydrogen atom of the alcoholic group. The mechanism of formation of vinyl ethers of alcohols and silanols, unlike that of stannanols, is based on nucleophilic attack by an alkoxide ion on the acetylenic bond ([10])

$$\overset{(+)}{HC}{\equiv}\overset{(-)}{CH} \xrightarrow{RO^-} R - OCH = \overset{(-)}{C}H \xrightarrow{H^{(+)}} ROCH = CH_2,$$

$$CH_3-\overset{(+)}{C}\equiv\overset{(-)}{C}H \xrightarrow{RO^-} CH_3-C=\overset{(-)}{C}H \xrightarrow{H^{(+)}} CH_3-C=CH_2, \quad \underset{OR}{|} \quad \underset{OR}{|}$$

$$C_6H_5-\overset{(-)}{C}\equiv\overset{(+)}{C}H \xrightarrow{RO^-} C_6H_5-\overset{(-)}{C}=CHOR \xrightarrow{H^{(+)}} C_6H_5=CHOR,$$

and, in this connection, the rate of addition of alcohols to the acetylenic bond depends on the nucleophilicity of the attacking ion.

More detailed data on the interaction of acetylenes with stannanols will be published in subsequent communications.

Tri-*n*-propylethynylstannane. Into a stirred autoclave of 0.25 l capacity are placed 31.8 g of tri-*n*-propylstannanol (m.p. 31°), acetylene is introduced under a pressure of 15–18 atm, and the mixture is heated at 100–120° until absorption of acetylene ceases. After completion of the reaction, the contents of the autoclave are transferred to a distillation apparatus and fractionated in vacuo. This gives 8.85 g (37%) of tri-*n*-propylethynylstannane, b.p. 91° at 10 mm; n_D^{20} 1.4780; d_4^{20} 1.1555; MR_D found 67.1, calculated 67.16.

Found, %:	*C* 41.73; *H* 7.01; *Sn* 51.28
$C_{11}H_{22}Sn$. Calculated, %:	*C* 41.60; *H* 6.98; *Sn* 51.45

In addition, 18.8 g (61%) of unreacted tri-*n*-propylstannanol is isolated in a mixture with bis-(tri-*n*-propyl) oxide, b.p. 154–155° at 3.5 mm, with n_D^{20} 1.4932.

In an analogous manner, triethylvinylethynylstannane and tri-*n*-butylethynylstannane were obtained; their physicochemical constants are presented in Table 1.

Triethylvinylethynylstannane. Into a round-bottom flask of 50 ml capacity, equipped with a mechanical stirrer and a gas outlet tube connected to a dry-ice trap, are placed 11.14 g of triethylstannanol and 7 g of previously cooled (−5–0°) vinylacetylene. The mixture is stirred for 6–8 h at room temperature. Dissolution of the stannanol and evolution of water are observed. After completion of the synthesis, the reaction mixture is distilled in vacuo to give 8.07 g (62.8%) of triethylvinylethynylstannane, b.p. 78–79° at 3 mm; n_D^{20} 1.5085; d_4^{20} 1.2180. Literature data ([11]): b.p. 89.5–90° at 10 mm; n_D^{20} 1.5098; d_4^{20} 1.2181. In addition, 1.7 g of unreacted triethylstannanol is isolated.

Table 1

Physicochemical constants of the synthesized compounds

No.	Compound	b.p., °C (mm)	n_D^{20}	d_4^{20}	MR found	MR calc.	C, % found	C, % calc.	H, % found	H, % calc.	Sn, % found	Sn, % calc.	Yield, %
1	$(C_2H_5)_3SnC\equiv CH$	60 (15)	1.4770	1.2455	52.4	53.2	41.79	41.61	7.19	6.99	51.42	51.41	21.7
2	$(n\text{-}C_3H_7)_3SnC\equiv CH$	94 (10)	1.4780	[illegible]	67.1	67.16	48.53	48.39	8.01	8.12	43.28	43.45	37
3	$(n\text{-}C_4H_9)_3SnC\equiv CH$	100–101 (3)	1.4767	[illegible]	80.63	84.61	53.53	53.39	8.92	8.95	37.32	37.67	20.3
4	$(C_2H_5)_3SnC\equiv C–CH=CH_2$*	78–79 (3)	1.4938	[illegible]	[illegible]	—	—	—	—	—	—	—	62.8
5	[illegible]	100–101 (3)	[illegible]	[illegible]	[illegible]	[illegible]	52.19	52.21	8.11	8.09	39.45	39.70	60
6	$(n\text{-}C_4H_9)_3SnC\equiv C–CH=CH_2$	135–136 (3.5)	1.4955	[illegible]	[illegible]	89.92	56.42	56.34	8.86	8.86	34.83	34.80	50
7	$(C_2H_5)_3SnC\equiv CSn(C_2H_5)_3$**	136–137 (5)	1.5089	[illegible]	[illegible]	97.21	—	—	—	—	—	—	62.1
8	$(n\text{-}C_3H_7)_3SnC\equiv CSn(C_3H_7\text{-}n)_3$	178–179 (3)	1.5040	[illegible]	[illegible]	123.09	—	—	—	—	45.92	45.64	53.5
9	$(n\text{-}C_4H_9)_3SnC\equiv CSn(C_4H_9\text{-}n)_3$	204 (3)	1.4888	[illegible]	[illegible]	153.05	—	—	—	—	39.76	39.34	55.8
10	[illegible]	142 (5)	1.4775	[illegible]	[illegible]	[illegible]	50.27	49.91	8.30	8.31	32.44	32.91	86.7
11	[illegible]	120 (2)	1.4722	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	8.41	8.54	31.77	31.68	89.3
12	[illegible]	112 (1.5)	1.4670	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	8.76	8.75	30.60	30.54	78

* Literature data (11): b.p. 89.5–90° at 10 mm, n_D^{20} 1.5098, d_4^{20} 1.2181.
** Literature data (12): b.p. 294° at 760 mm, 123° at 0.05 mm, n_D^{20} 1.5089, d_4^{20} 1.3411.

In a similar manner, tri-n-propylvinylethynylstannane and tri-n-butylvinylethynylstannane, presented in Table 1, were synthesized.

Bis-(triethylstannyl)acetylene. Into the apparatus for the synthesis are placed 0.135 g-mol of sodium acetylide in 100 ml of absolute ether, and, with stirring at room temperature, a solution of 30 g (0.135 g-mol) of triethylstannanol in 50 ml of anhydrous ether is added. A slight warming of the mixture

occurs. To complete the reaction, the contents of the flask are heated at 30–35° for 10–12 h. The mixture is filtered, the precipitate is washed with anhydrous ether, the ether is distilled off from the filtrate, and the remaining substance is distilled in vacuo. This gives 18.2 g (62.1%) of a substance with b.p. 136–137° at 5 mm; n_D^{20} 1.5089; d_4^{20} 1.3430; MR_D found 96.87, calculated 97.21. Literature data (12): b.p. 294° at 760 mm and 123° at 0.05 mm; n_D^{20} 1.5089; d_4^{20} 1.3411.

By the reaction of tri-*n*-propyl- and tri-*n*-butylstannanols with sodium acetylide, bis-(tri-*n*-propylstannyl)acetylene and bis-(tri-*n*-butylstannyl)acetylene were obtained; their constants are given in Table 1.

3-Triethylstannylpropyn-2-butyl acetal. In a three-necked round-bottom flask of 100 ml capacity, fitted with a reflux condenser, thermometer, and Dean–Stark trap, are placed 20 g of triethylstannanol and 28 g of propyn-2-butyl acetal in 50 ml of benzene. The contents of the flask are heated at 85–90° and collected in the Dean–Stark trap ···

an azeotropic mixture of benzene and water. The remaining substance is distilled in vacuum. This gives 28 g (86.7%) of a substance with b.p. 142° at 5 mm; n_D^{20} 1.4775; d_4^{20} 1.1363; MR_D found 89.84, calculated 89.78.

Found, %:	C 50.27; H 8.30; Sn 32.44
$C_{15}H_{30}SnO_2$. Calculated, %:	C 49.91; H 8.31; Sn 32.91

Analogously, 3-triethylstannyl-1-methylpropyn-2-butyl acetal and 3-triethylstannyl-1,1-dimethylpropyn-2-butyl acetal, presented in Table 1, were obtained.

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