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Abstract

Full Text

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SYNTHESIS OF ORGANOTIN OXYGEN-CONTAINING COMPOUNDS OF THE ACETYLENE SERIES

Despite the fact that the first organotin acetylenic compounds containing a triple bond in the α-position with respect to the tin atom were obtained about ten years ago, there is very little information about them in the literature ($^{1-5}$). As for organotin acetylenic oxygen-containing compounds, they have until now almost not been described in the literature. Examples of such substances with a triple bond in the α-position with respect to the tin atom are organotin acetals obtained on the basis of acetylenic acetals (^{6}), and 1,1-diethoxy-3-(triphenylstannyl)-2-propyne, obtained by the interaction of triphenylbromostannane with the silver acetylide of the diethoxy derivative of propargyl aldehyde (^{3}). The rapid development of the chemistry of acetylene and its derivatives prompted us to undertake an investigation of the synthesis and some properties of organotin compounds with a triple bond of the following structure: $R_3SnC \equiv CX$, where $R = C_2H_5$;

$$X = -CH_2CH_2O \; CH - CH_3; \; C_4H_9O$$

$$-CH_2OCH_3; \; -CH_2CO_2OCH = CH_2.$$

In the course of the study, a method was developed for obtaining oxygen-containing organotin compounds with an acetylenic bond in the α-position with respect to the tin atom. Its essence consists in the action of compounds of the acetylene series, containing an acetylenic hydrogen atom, on hexaalkyldistannoxanes.

To illustrate the proposed method, we obtained organotin acetylenic oxygen-containing compounds of the following classes: a) organotin acetylenic acetals, b) organotin acetylenic ethers, and c) organotin acetylenic vinyl ethers, according to the schemes:

$$\text{a) } [(C_2H_5)_3Sn]_2O + 2HC \equiv CCH_2CH_2O(C_4H_9O)CHCH_3 \rightarrow 2(C_2H_5)_3SnC \equiv$$
$$\equiv CCH_2CH_2O(C_4H_9O)CHCH_3 + H_2O.$$

$$\text{b) } [(C_2H_5)_3Sn]_2O{+}2HC \equiv CCH_2OCH_3 \rightarrow 2(C_2H_5)_3SnC \equiv CCH_2OCH_3 + H_2O.$$

$$\text{c) } [(C_2H_5)_3Sn]_2O + 2HC \equiv CCH_2CH_2OCH{=}CH_2 \rightarrow 2(C_2H_5)_3SnC \equiv$$
$$\equiv CCH_2CH_2OCH{=}CH_2.$$

The structure of the compounds obtained was proven by synthesis on the basis of previously developed methods according to the schemes ([7,8]):

$$\text{a) } (C_2H_5)_3SnOCH_3 + HC \equiv CCH_2CH_2O(C_4H_9O)CHCH_3 \rightarrow (C_2H_5)_3SnC \equiv$$
$$\equiv CCH_2CH_2O(C_4H_9O)CHCH_3 + CH_3OH.$$

$$\text{b) } (C_2H_5)_3SnOCH_3{+}HC \equiv CCH_2OCH_3 \rightarrow (C_2H_5)_3SnC \equiv CCH_2OCH_3 + CH_3OH.$$

$$\text{c) } (C_2H_5)_3SnOCH_3 + HC \equiv CCH_2CH_2OCH{=}CH_2 \rightarrow (C_2H_5)_3SnC \equiv CCH_2CH_2OCH{=}$$
$$= CH_2 + CH_3OH.$$

In addition, IR spectra were recorded for the compounds obtained; these are presented in Fig. 1. In the spectra, intense bands with frequencies of 2150 cm^{-1} were found, corresponding to the stretching vibrations of the triple bond, in the α-position to which the tin atom is located ([4]). In the IR spectrum of the organotin acetylenic acetal, in the region of stretching vibrations of the C—O bond, there is a series of intense bands with frequencies of 1136, 1100, and 1046 cm^{-1}, which, according to the literature data ([9]), is specific for compounds containing an acetal group.

Fig. 1. IR spectra

Fig. 1. IR spectra of $(C_2H_5)_3SnC \equiv CCH_2OCH_3$ (1, $d = 0.01$ mm);
$(C_2H_5)_3SnC \equiv CCH_2CH_2O(C_4H_9)OCHCH_3$ (2, $d = 0.01$ mm);
$(C_2H_5)_3SnC \equiv CCH_2CH_2OCH = CH_2$ (3, a—$d = 0.01$ mm,
b—$d = 0.03$ mm)

In the IR spectrum of the organotin vinylacetylenic ether, the vinyl group with a neighboring oxygen atom corresponds to bands with frequencies of 3118 and 3040 cm^{-1}, as well as an intense band with a frequency of 1616 cm^{-1}, having, on the side of the larger wave numbers, two bands characteristic of vinyl ethers with frequencies of 1642 cm^{-1} and 1654 cm^{-1}; the deformational vibration of the terminal CH_2 group corresponds to an intense band with a frequency of 820 cm^{-1} ([10]).

Experimental Part

a) **Synthesis of 1-[4-(triethylstannyl)-3-butynoxy]-1-butoxyethane.**

A mixture of 10.68 g (0.025 g-mol) of hexaethylstannoxane (b.p. 101°/1 mm, n_D^{20} 1.4985) and 8.5 g (0.05 g-mol) of 1-(3-butynoxy)-1-butoxyethane (b.p. 90°/18 mm, n_D^{20} 1.4259, d_4^{20} 0.8813 ([12])) and 8 g of dry benzene was heated for about 6 hours until complete distillation of benzene and the water formed as a result of the reaction at 80-120° and distilled in vacuo. There was isolated 9.8 g (52.2%) of 1-[4-(triethylstannyl)-butyn-3-oxy]-1-butoxyethane, which after repeated distillation had the following constants: b.p. 111-112°/0.3 mm, n_D^{20} 1.4749, d_4^{20} 1.1290, MR_D found 93.52; calculated 94.02.

Found, %: C 51.69, 51.56; H 8.66, 8.65; Sn 31.37, 31.47
Calculated, %: C 51.23; H 8.60; Sn 31.64

A mixture of 23.7 g (0.1 g-mol) of triethylmethoxystannane (b.p. 73°/13 mm, n_D^{20} 1.4758, d_4^{20} 1.3060) and 25.38 g (0.15 g-mol) of 1-(butyn-3-oxy)-1-butoxyethane was heated for 8 h at 100-130°, then distilled in vacuo. There was isolated 26.3 g (70.1%) of 1-[4-(triethylstannyl)-butyn-3-oxy]-1-butoxyethane, b.p. 110-112°/0.3 mm, n_D^{20} 1.4742, d_4^{20} 1.1300.

b) **Synthesis of 3-methoxy-1-(triethylstannyl)-propyne-1.** A mixture of 26.03 g (0.061 g-mol) of hexaethylstannoxane and 5.2 g (0.075 g-mol) of 3-methoxypropyne-1 (b.p. 61°/715 mm, n_D^{20} 1.3947, literature data (11): b.p. 63°/760 mm, n_D^{20} 1.3975) was heated for 4 h at 60-80° and distilled in vacuo. There was isolated 8.57 g (25.6%) of 3-methoxy-1-(triethylstannyl)-propyne-1, which after two distillations had the following constants: b.p. 62-63°/0.55 mm, n_D^{23} 1.4878, d_4^{20} 1.2404, MR_D found 63.84; calculated 64.66.

Found, %: C 43.59, 43.80; H 7.29, 7.19; Sn 42.91, 43.17
Calculated, %: C 43.68; H 7.33; Sn 43.17

A mixture of 11.85 g (0.05 g-mol) of triethylmethoxystannane and 7 g (0.1 g-mol) of 3-methoxypropyne-1 was heated for 8 h at 70° and distilled in vacuo. There was isolated 13.76 g (85.6%) of 3-methoxy-1-(triethylstannyl)-propyne-1, b.p. 62-63°/0.55 mm, n_D^{20} 1.4870, d_4^{20} 1.2400.

c) **Synthesis of 4-vinyloxy-1-(triethylstannyl)-butyne-1.** To 10.68 g (0.025 g-mol) of hexaethylstannoxane was added 4.8 g (0.05 g-mol) of vinyl butyn-1-yl ether (b.p. 100-101°, n_D^{20} 1.4347, d_4^{20} 0.8615 (13)). The reaction mixture was heated for 8 h at 90-110°, then distilled in vacuo. There was isolated 8.46 g (56.3%) of 4-vinyloxy-1-(triethylstannyl)-butyne-1, which after a second distillation had the following constants: b.p. 107.5-108°/2 mm, n_D^{20} 1.4925, d_4^{20} 1.1993. MR_D found 72.87; calculated 73.48.

Found, %: C 47.54, 47.64; H 7.60, 7.40; Sn 38.83, 38.98
Calculated, %: C 47.88; H 7.37; Sn 39.43

17.76 g of triethylmethoxystannane (0.075 g-mol) and 4.8 g (0.05 g-mol) of vinyl butyn-1-yl ether were heated for 8 h at 80-90°, then distilled in vacuo. There was isolated 11.25 g (74.9%) of 4-vinyloxy-1-(triethylstannyl)-butyne-1, b.p. 106-108°/2 mm, n_D^{20} 1.4923, d_4^{20} 1.2002.

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