

The allyl group exchange reaction between tri(substituted allyl) stannyl lithium and (substituted allyl) lithium

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Abstract

Triallylmethylstannane, diallylmethylmethylstannane, allyldimethylmethylstannane, and trimethylmethylstannane were produced by the reaction of triallylstannyl lithium with methyl lithium followed by treatment with iodomethane. The formation of similar mixture of such stannanes was also observed when trimethylstannyl lithium was treated with allyllithium and iodomethane successively. These results indicate that the reaction of tri(substituted allyl)stannyl lithium with (substituted allyl)lithium forms the equilibrium mixture of tri(substituted allyl)stannyl lithiums having all the possible combinations of substituents.

Keywords: Tin; Lithium

1. Introduction

Recently we reported that the triallylstannyl lithium (1a)–allyllithium (2a)-initiated polymerization of 1,3-butadiene gave the star polymer (3), which consisted of three polybutadiene branches and a central tin atom, and the linear polybutadiene (4) (Scheme 1) [1]. On the basis of the facts that the number average molecular weights and molecular weight distribution of the polybutadiene branches of 3 and 4 were almost identical, we proposed the reversible chain transfer mechanism for the polymerization as shown in Scheme 2, in which only 2a was capable of initiating the polymerization of 1,3-butadiene.

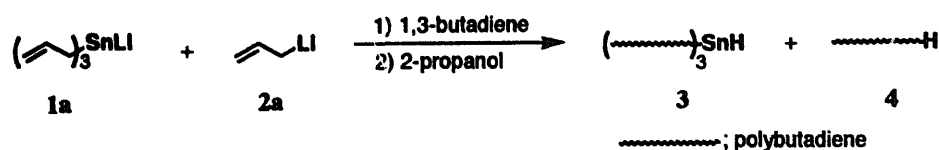
This hypothetical polymerization mechanism is based on the assumption that macroallyl groups of macroallylic anion (5) and tri(macroallyl)stannyl lithium (6) exchange rapidly with each other during the polymerization. It is apparent that such an exchange reaction readily proceeds if 6 exists in equilibrium with di(macroallyl)stannylene (7) and 5.

The preparation of triorganostannyl lithiums and their reactions have been extensively studied, and they are employed for the synthesis of various organotin com-

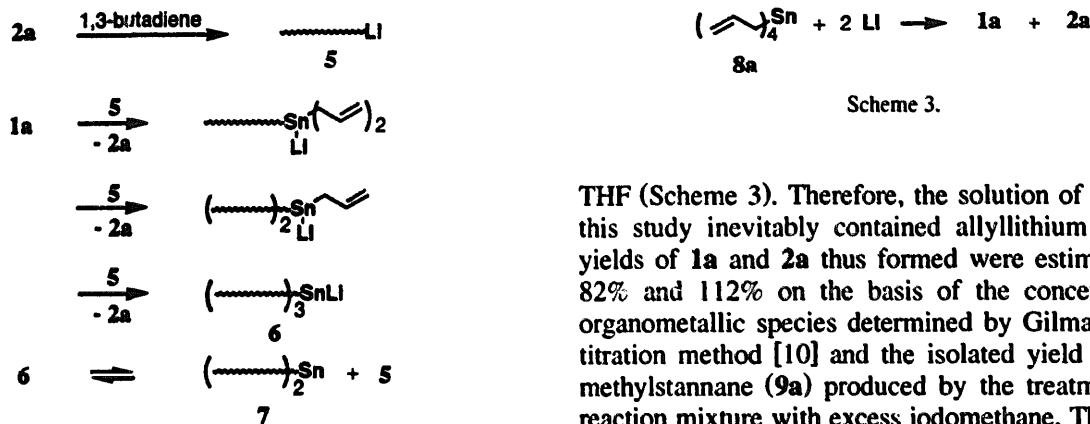
pounds [2] and desulfurizative metallation of organosulfur compounds [3]. However, it is still problematic as to whether triorganostannyl lithium exists in equilibrium with diorganostannylene and organolithium. Blake et al. suggested that tributylstannyl lithium prepared by the reaction of tin(II) chloride with butyllithium in ether dissociates into butyllithium and dibutylstannylene, and hence butyltrimethylsilane is formed by the reaction of tributylstannyl lithium with chlorotrimethylsilane [4]. Kozima and coworkers reported that the decomposition of trialkylstannyl lithium was accelerated by hexaalkyldistannane, and they suggested that partial dissociation of trialkylstannyl lithium into the alkyl lithium–dialkylstannylene complex in a solvent cage plays an important role in the decomposition [5]. Similar dissociation of trimethylstannyl sodium formed by the reduction of hexamethyldistannane with metallic sodium or sodium naphthalenide was observed by Kuivila and coworkers [6]. Creemers et al. also reported that the reaction of unsolvated triphenylstannylmagnesium bromide, which was formulated as dimeric phenylmagnesium bromide and diphenylstannylene coordinated at magnesium, with iodomethane gave diphenylmethylstannyl iodide [7].

In contrast, Tamborski et al. reported that the formation of butyllithium and dibutylstannylene was not detected in a THF solution of tributylstannyl lithium prepared by the reaction of tributylstannyl chloride with

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Scheme 1.



Scheme 3.

Scheme 2.

lithium metal [8], and they also suggested that triphenylstannyl lithium did not exist in equilibrium with diphenylstannylene and phenyllithium [9].

Despite the extensive data on the reactivity and properties of triorganostannyl lithium described above, its reaction with organolithium has not yet been studied. Thus we investigated the allyl group exchange reaction using the combinations of triallylstannyl lithium (**1a**)–methyllithium (**2b**) and trimethyllithium (**1d**)–allyllithium (**2a**).

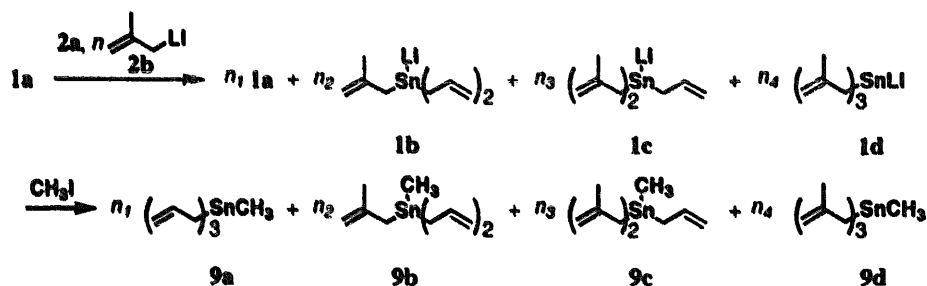
2. Results and discussion

We first examined the reaction of triallylstannyl lithium (**1a**) with methyllithium (**2b**). As we described in a previous paper [1], the preparation of triallylstannyl lithium was successfully achieved by the reduction of tetraallylstannane (**8a**) with an excess amount of lithium metal (2.5 equivalents) at -40°C in

THF (Scheme 3). Therefore, the solution of **1a** used in this study inevitably contained allyllithium (**2a**). The yields of **1a** and **2a** thus formed were estimated to be 82% and 112% on the basis of the concentration of organometallic species determined by Gilman's double titration method [10] and the isolated yield of triallylmethylstannane (**9a**) produced by the treatment of the reaction mixture with excess iodomethane. The fact that the yield of **2a** exceeded the theoretical amount suggested that the further reduction of **1a** with lithium partially occurred. In fact, the formation of a small amount of metallic tin was observed in this preparation. It was confirmed, however, that the use of excess lithium was indispensable for obtaining **1a** in satisfactory yield.

The mixture of **1a** and **2a** prepared by the above procedure was treated with three equimolar amounts of methyllithium (**2b**) at 0°C for 1 min. Then the reaction was quenched by addition of excess iodomethane with cooling within 1 min to determine the structures and quantities of stannyl lithiums formed. The HPLC analysis indicated that four methyltri(substituted allyl)stannanes (**9a**, **b**, **c**, and **d**) were produced by this reaction (Fig. 1). This result clearly shows that the exchange of substituents between **1a** and **2b** readily proceeds by simple mixing of the two reagents. Methyltri(substituted allyl)stannanes (**9**) were isolated by preparative HPLC, characterized, and used to prepare the working-curve for quantitative analysis.

The reactions of the mixture of triallylstannyl lithium (**1a**) and allyllithium (**2a**) with various amounts of



Scheme 4.

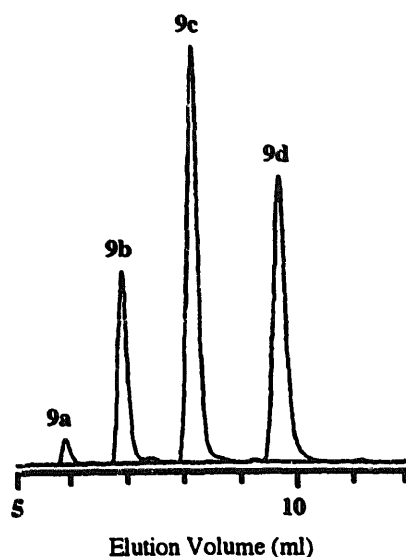
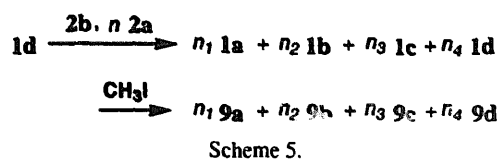


Fig. 1. LiChrospher RP-18 (E) separation of **9**: column $0.4 \times 25 \text{ cm}^2$; eluant $\text{CH}_3\text{CN}-\text{H}_2\text{O}$ (9:1), monitored by UV 254 nm.

methallyllithium (**2b**) were performed (Scheme 4), and the results are summarized in Table 1. The allyl group exchange reaction was completed within 2 min and the ratio of stannylolithiums (**1**) was almost unchanged after 2 h (see runs 1 and 2). As would be expected, it was found that the molar ratio of methallyl-group-substituted stannylolithiums (**1**) increased with increasing quantity of **2b** employed.

In order to confirm whether the above distribution of tri(substituted allyl)lithiums is an equilibrium ratio, the



reaction of trimethallylstannylolithium (**1d**) with allyllithium (**2a**) was studied. The stannylolithium (**1d**) was prepared using tetramethallylstannane (**8b**) and a slight excess of lithium (2.05 equivalents). In this reaction, the formation of tin metal was not observed, and the yields of **1d** and methallyllithium (**2b**) estimated by the methods noted above were close to the theoretical (96% and 88% respectively). The mixture of **1d** and **2b** thus formed was subjected to the allyl group exchange reaction with **2a** (Scheme 5).

We found that a similar allyl group exchange reaction also proceeded between **1d** and **2a**. The results listed in Table 2 indicate the tendency that the formation of triorganostannylolithiums (**1**) possessing more methallyl groups is favored, which was also observed in the reaction of **1a** with **2b**. It is of interest that the molar ratio of **9** obtained by the reaction of **1d** with 4 equivalents of **2a** was almost identical with that of **9** produced by the treatment of **1a** with 4 equivalents of **2b** (see runs 5 in Table 1 and 5 in Table 2). Since the molar quantities of allyl and methallyl groups in all the reactants were the same in both reactions, the above results strongly suggest that **1** and **2** are present in equilibrium. This result clearly supports the reversible chain transfer

Table 1
Reaction of triallylstannylolithium (**1a**)–allyllithium (**2a**)^a with methallyllithium (**2b**)

Run	Methallyllithium (2b) (mmol)	Molar ratio of methyltri(substituted allyl)stannanes (9) (%)				Total yield of 9 (%)
		9a	9b	9c	9d	
1	1	46	41	12	1	82
2 ^b	1	40	43	15	2	— ^c
3	2	10	35	40	15	70
4	3	3	24	44	29	63
5	4	2	19	43	36	50

^a The mixture of **1a** and **2a** employed was prepared using **8a** (1 mmol) and lithium (2.5 mmol). ^b Iodomethane was added after 2 h. ^c Not determined.

Table 2
Reaction of trimethallylstannylolithium (**1d**)–methallyllithium (**2b**)^a with allyllithium (**2a**)

Run	Allyllithium (2a) (mmol)	Molar ratio of methyltri(substituted allyl)stannanes (9) (%)				Total yield of 9 (%)
		9a	9b	9c	9d	
1	1	< 1	5	33	62	93
2 ^b	1	1	7	30	62	— ^c
3	2	1	10	40	49	80
4	3	2	14	42	42	75
5	4	2	19	45	34	70
6 ^b	4	3	21	46	30	— ^c

^a The mixture of **1d** and **2b** employed was prepared using **8b** (1 mmol) and lithium (2.05 mmol). ^b Iodomethane was added after 2 h. ^c Not determined.

mechanism of the polymerization of 1,3-butadiene initiated with the combination of **1a** and **2a**.

Although the mechanism of allyl group exchange is still not clear, the following two pathways should be considered (Scheme 6). The first involves the formation of the five-coordinate tin complex anion (**10**) (Path A) and the second is based on the dissociation of tri(substituted allyl)lithium (**1**) into di(substituted allyl)stannylene (**11**) and (substituted allyl)lithium (**2**) (Path B); the latter has been proposed in the polymerization mechanism. Stannylenes are well-known chemical species and their preparation and properties have been investigated. In contrast, a five-coordinated dimetallo complex such as **10** is as yet unknown and would be a much less stable chemical species if it exists. Therefore, we tentatively assume that Path B is more probable than Path A.

In conclusion, it should be noted that the present reaction is the first example of a substituent exchange reaction between triorganostannyllithium and organolithium, and it is demonstrated that **1** and **2** form an equilibrium mixture of all possible triorganostannyllithiums and organolithiums.

3. Experimental

^1H (400 MHz) and ^{13}C NMR (100 MHz) spectra were measured for a CDCl_3 solution on Jeol GX-400 at room temperature. Chemical shifts are reported (δ scale) from internal tetramethylsilane. IR spectra were recorded on a Jeol Diamond-20; absorptions are reported in wavenumbers. Mass spectra were obtained on a Finnigan mat INCOS 50 spectrometer. Elemental analyses were performed on a Perkin-Elmer 2400II. Preparative HPLC was performed on a Tosoh HLC-8070 using a Merck LiChrospher 100 RP-8 column (10 mm inside diameter, 25 cm length) and $\text{CH}_3\text{CN}-\text{H}_2\text{O}$ (6:4) as eluant. Analytical HPLC was performed using a UV detector (monitored at 254 nm) on a Merck LiChrospher RP-18 (E) column (4 mm inside diameter, 25 cm length)

using $\text{CH}_3\text{CN}-\text{H}_2\text{O}$ (9:1) as eluant. All the reactions were carried out in a dry reaction vessel under argon. Inhibitor-free THF (99.9%, Aldrich) and highly purified lithium metal (99 + %, Honjoh Metal) were used for the preparation of triallylstannyllithium and trimethallylstannyllithium. Tetraallylstannane (**8a**) (Aldrich) was used after distillation under reduced pressure.

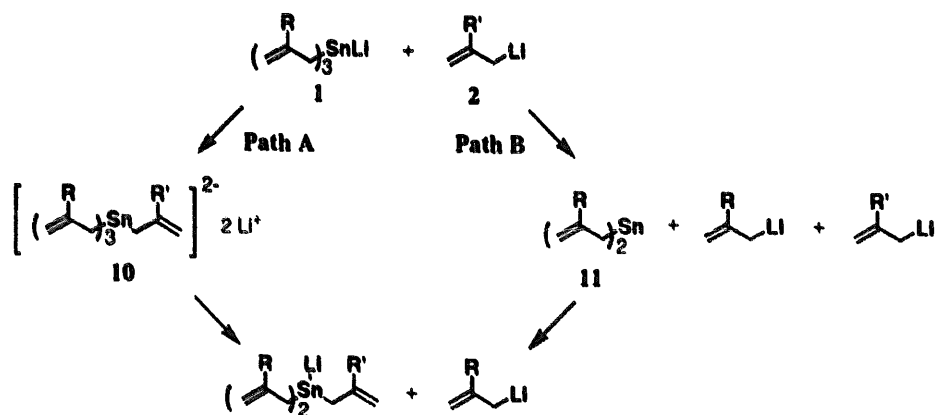
3.1. Preparation of tetramethallylstannane (**8b**)

Tetramethallylstannane (**8b**) was prepared from methallylmagnesium chloride (185 mmol) with tetrachlorostannane (9.6 g, 37 mmol) by a similar procedure employed for the synthesis of tetraallylstannane [11] and purified by distillation (5.7 g, yield 45% based on tetrachlorostannane). **8b**: b.p. $108^\circ\text{C}/3$ mm Hg. MS m/z (relative intensity) 120 (14), 175 (100), 230 (6), 285 (6). IR (neat) 3075, 1631. ^1H NMR 1.69 (d, 12H, $J = 0.8$ Hz), 1.88 (d, 8H, $J = 0.8$ Hz, $J_{\text{Sn-H}} = 64.0$ Hz), 4.50 (d, 4H, $J = 1.2$ Hz), 4.51 (d, 4H, $J = 1.2$ Hz). ^{13}C NMR 22.3, 24.9, 106.9, 145.0. Anal. Found: C, 52.65; H, 8.22. $\text{C}_{16}\text{H}_{28}\text{Sn}$. Calc.: C, 52.22; H, 8.09%.

3.2. Preparation of triallylstannyllithium (**1a**)–allyllithium (**2a**)

To a mixture of tetraallylstannane (**8a**) (283 mg, 1 mmol) and lithium (17.4 mg, 2.5 mmol) was added THF (2 ml) dropwise at -40°C . After the addition was completed, the mixture was further stirred for 7 h at the same temperature to give a dark green solution. The complete disappearance of **8a** was confirmed by HPLC analysis. The total concentration of organolithium species determined by Gilman's double titration method was 0.93 M.

Iodomethane (1 ml) was added to the mixture of **1a** and **2a** prepared by the same procedure and in the same scale described above at -78°C . After being stirred for 15 min, the reaction was quenched by addition of water and the organic layer was extracted with pentane. The



extract was dried (Na_2CO_3) and condensed under reduced pressure to give triallylmethylstannane (**9a**) (210 mg, 82%). Assuming that the yield of **1a** was equal to that of **9a**, the molar ratio of **1a** to **2a** of 1:1.36 and the yield of **2a** (112%) were estimated based on the above results. Since it was found that **9a** is somewhat unstable in air, the analytical sample was prepared on a large scale and isolated by fractionation. **9a**: b.p. $78^\circ\text{C}/8$ mm Hg. MS m/z (relative intensity) 120 (35), 135 (100), 161 (46), 176 (8), 217 (16). IR (neat) 3079, 1639. ^1H NMR 0.13 (s, 3H, $J_{\text{Sn-H}} = 50.0$ Hz), 1.88 (d, 6H, $J = 8.0$ Hz, $J_{\text{Sn-H}} = 64.6$ Hz), 4.72 (d, 3H, $J = 10.4$ Hz), 4.84 (d, 3H, $J = 16.8$ Hz), 5.92 (d, d, t, 3H, $J = 16.8, 10.4, 8.0$ Hz). ^{13}C NMR $-12.5, 16.6, 110.5, 136.8$. Anal. Found: C, 46.63; H, 7.02. $\text{C}_{10}\text{H}_{18}\text{Sn}$. Calc.: C, 46.75; H, 7.06%.

Trimethylstannyl lithium (**1d**)-methallyllithium (**2b**) was prepared by the treatment of tetramethylstannane (**8b**) (339 mg, 1 mmol) and lithium (14.2 mg, 2.05 mmol) at -10°C for 3 h, similar to the preparation of **1a**. The total concentration of organolithium species determined by Gilman's double titration method was 0.81 M. The molar ratio of **1d** to **2b** of 1:0.92 was estimated on the basis of the yield of trimethylmethylstannane (**9d**) obtained by the reaction of **1d** with iodomethane as described above. The yields of **1d** and **2b** were also estimated to be 96% and 88% respectively. The analytical sample of **9d** was obtained by the purification using preparative HPLC. **9d**: MS m/z (relative intensity) 120 (37), 135 (100), 175 (51), 190 (27), 245 (23). IR (neat) 3076, 1631. ^1H NMR 0.14 (s, 3H, $J_{\text{Sn-H}} = 49.6$ Hz), 1.69 (d, 9H, $J = 0.8$ Hz, $J_{\text{Sn-H}} = 11.6$ Hz), 1.88 (d, 6H, $J = 0.8$ Hz, $J_{\text{Sn-H}} = 64.0$ Hz), 4.50 (d, 3H, $J = 1.2$ Hz), 4.51 (d, 3H, $J = 1.2$ Hz). ^{13}C NMR $-11.2, 22.3, 24.8, 106.9, 144.9$. Anal. Found: C, 52.65; H, 8.22. $\text{C}_{13}\text{H}_{24}\text{Sn}$. Calc.: C, 52.22; H, 8.09%.

3.3. Preparation of allyllithium (**2a**)

Butyllithium in hexane (1.65 M, 40 mmol) was added to tetraallylstannane (**8a**) (2.83 g, 10 mmol) at 0°C and the reaction mixture was stirred for 5 h. The resulting precipitate was filtered under argon and washed with three 10 ml portions of pentane, and dissolved in THF (15 ml). The concentration of **2a** (0.70 M) was determined by Gilman's double titration method just prior to use.

Methallyllithium (**2b**) was prepared from tetramethylstannane (**8b**) and butyllithium by the same procedure as described above. The concentration of the THF solution of **2b** used was 0.82 M.

3.4. Allyl group exchange reaction

To a solution of tri(substituted allyl)stannyl lithium (**1**) prepared using tetra(substituted allyl)stannane (**8**) (1

mmol) was added a certain amount of (substituted allyl)lithium (**2**) at 0°C and the reaction mixture was stirred for 1 min. Then the reaction vessel was immersed in a dry ice-methanol bath and iodomethane (1 ml) was added to the reaction mixture within 1 min. After being stirred for 15 min, the reaction was quenched by addition of water and organic materials were extracted with pentane. The extract was dried (Na_2CO_3) and condensed under reduced pressure. The residue was subjected to HPLC analysis. The yields and the ratios of products (**9**) were determined by working-curve method using **9** isolated by preparative HPLC. Diallylmethylstannane (**9b**): MS m/z (relative intensity) 120 (26), 135 (100), 161 (22), 175 (36), 231 (19). IR (neat) 3078, 1624. ^1H NMR 0.12 (s, 3H, $J_{\text{Sn-H}} = 48.4$ Hz), 1.70 (s, 3H, $J_{\text{Sn-H}} = 11.2$ Hz), 1.87 (d, 4H, $J = 7.6$ Hz, $J_{\text{Sn-H}} = 64.8$ Hz), 1.88 (s, 2H, $J_{\text{Sn-H}} = 64.0$ Hz), 4.49 (s, 1H, $J_{\text{Sn-H}} = 28.0$ Hz), 4.51 (s, 1H, $J_{\text{Sn-H}} = 20.8$ Hz), 4.71 (d, 2H, $J = 12.2$ Hz, $J_{\text{Sn-H}} = 32.8$ Hz), 4.83 (d, 2H, $J = 16.6$ Hz, $J_{\text{Sn-H}} = 41.2$ Hz), 5.91 (d, d, t, 2H, $J = 16.6, 12.2, 7.6$ Hz). ^{13}C NMR $-12.0, 17.1, 21.4, 24.8, 106.9, 110.5, 136.9, 145.0$. Anal. Found: C, 48.94; H, 7.30. $\text{C}_{11}\text{H}_{20}\text{Sn}$. Calc.: C, 48.76; H, 7.44%. Allyldimethylmethylstannane (**9c**): MS m/z (relative intensity) 120 (28), 135 (100), 161 (47), 175 (7), 245 (42). IR (neat) 3075, 1624. ^1H NMR 0.12 (s, 3H, $J_{\text{Sn-H}} = 49.6$ Hz), 1.69 (s, 6H, $J_{\text{Sn-H}} = 11.2$ Hz), 1.87 (d, 2H, $J = 7.6$ Hz, $J_{\text{Sn-H}} = 64.8$ Hz), 1.88 (s, 4H, $J_{\text{Sn-H}} = 64.0$ Hz), 4.50 (s, 2H, $J_{\text{Sn-H}} = 25.8$ Hz), 4.52 (s, 2H, $J_{\text{Sn-H}} = 20.8$ Hz), 4.72 (d, 1H, $J = 10.4$ Hz, $J_{\text{Sn-H}} = 28.8$ Hz), 4.83 (d, 1H, $J = 17.2$ Hz, $J_{\text{Sn-H}} = 39.6$ Hz), 5.91 (d, d, t, 1H, $J = 17.2, 10.4, 7.6$ Hz). ^{13}C NMR $-11.6, 17.5, 21.8, 24.9, 106.9, 110.5, 136.9, 145.0$. Anal. Found: C, 50.88; H, 7.83. $\text{C}_{12}\text{H}_{22}\text{Sn}$. Calc.: C, 50.57; H, 7.78%.

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