

Brief Communications

Synthesis of alkoxyastannanes by reactions of *O*-(organylstannyl) carbamates with alcohols

N. V. Komarov, N. A. Ryzhkova, and A. A. Andreev*

*Kuban State University,
149 ul. Stavropol'skaya, 350040 Krasnodar, Russian Federation.
Fax: +7 (861 2) 69 9502. E-mail: silan@chem.kubsu.ru*

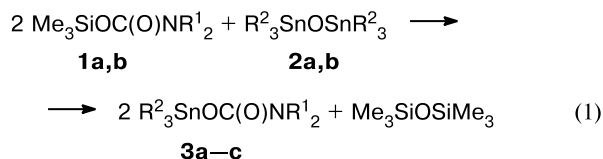
Reactions of *O*-(organylstannyl) carbamates with alcohols afford alkoxyastannanes and proceed most completely on heating in an excess of alcohol. The reactions provide a new approach to the synthesis of difficultly accessible alkoxyastannanes.

Key words: organotin carbamates, *O*-organylstannyl *N,N*-dialkylcarbamates, organyl-alkoxyastannanes, diorganylalkoxyastannanes.

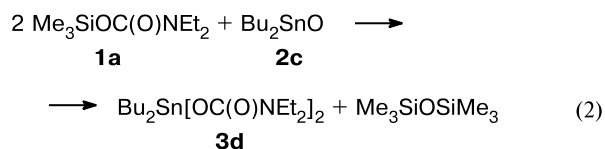
Earlier,^{1–5} we have described the reactions of *O*-organostannyl *N,N*-dialkylcarbamates with alk-1-yne, β -dicarbonyl compounds, secondary amines, sodium borohydride, and organochlorosilanes. The reactivity of organotin carbamates differs from that of alkyltin carboxylates due to the influence of the amino group on carboxyl. Based on this fact, new approaches to the construction of the Sn–C, Sn–H, Sn–O, *etc.* bonds were proposed, which hold promise for organometallic synthesis. We have also developed new procedures for the preparation of organotin carbamates, which makes these compounds more accessible.^{3,6}

In the present study, we examined the reactions of organotin carbamates with alcohols as an alternative approach to the synthesis of alkoxyorganylstannanes. Reactions with aliphatic alcohols are untypical of organotin carboxylates. However, the structural features of organotin derivatives of *N,N*-dialkylcarbamic acids as well as the data on their reactivity obtained earlier^{1–5} give grounds to expect that these compounds would react with weak

OH-acids, such as alkanols. The starting *O*-di(tri)organylstannyl carbamates were prepared by the reactions of *O*-trimethylsilyl carbamates with organotin oxides and hexaorganyldistannoxanes⁶ (Eqs (1) and (2), respectively). Compound **3b** was synthesized in the present study for the first time.

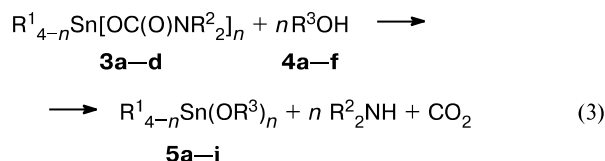


NR¹₂ = NEt₂ (**1a**, **3a**, **3b**), N(CH₂)₅ (**1b**, **3c**);
R² = Et (**2a**, **3a**), Bu (**2b**, **3b**, **3c**)



Results and Discussion

We found that *O*-organylstannyl carbamates **3** efficiently react with alcohols **4** on heating above 100 °C. Apparently, the reaction proceeds through the mechanism of nucleophilic substitution at the Sn atom to form the corresponding organylalkoxyastannanes **5** and *N,N*-dialkylcarbamic acids, which decompose under the conditions of reaction (3) with elimination of secondary amine and CO₂.



$n = 1$ (**3a–c**, **5a,b,d–f,g,h**), 2 (**3d**, **5c,i**);
 $\text{R}^1 = \text{Et}$ (**3a**, **5a,b,d,e,g**), Bu^n (**3b,c**, **5c,f,h,i**);
 $\text{R}^2 = \text{Pr}$ (**4a, 5d**), Bu^n (**4b, 5a,f,i**), Bu^t (**4c, 5e**), Bu^i (**4d, 5e**),
 Bn (**4e, 5h**), *cyclo*-C₆H₁₁ (**4f, 5b,c**);
 $\text{NR}^2_2 = \text{NEt}_2$ (**3a,b,d**), $\text{N}(\text{CH}_2)_5$ (**3c**)

The yields of triorganylalkoxyastannanes may be as high as 95%. Diorganyldialkoxyastannanes were prepared in somewhat lower yields (60–75%) due to their lower thermal stability and partial decomposition in the course of vacuum distillation.

Primary, secondary, and tertiary alcohols differ slightly in reactivity. The temperature is of decisive importance in these reactions. The use of higher-boiling alcohols makes it possible to decrease the reaction time and prepare the reaction products in higher yields. The use of an excess of alcohol also increases the conversion of the starting *O*-organylstannyl carbamates. The reaction conditions and the yields of the products are given in Table 1.

Organylalkoxyastannanes are colorless liquids, which are readily hydrolyzed with water, including atmospheric moisture, and can be involved in various transformations at the Sn–O bond.

Alkoxyastannanes **5** were identified by elemental analysis and IR spectroscopy as well as by comparing their physicochemical parameters with the published data (Table 2).

The IR spectra of the compounds synthesized have a broad absorption band at 1075–1070 cm⁻¹ corresponding to C–O stretching vibrations.

The reaction under consideration can be used as a convenient procedure for the preparation of various organylalkoxyastannanes. This method is free from the known drawbacks, in particular, there is no need to separate finely dispersed precipitates of sodium halides, which presents difficulties, in the case of the synthesis of organylalkoxyastannanes from sodium alkoxides and alkyltin halides¹² or to use difficultly accessible stannylated amines.¹³

Experimental

The solvents and starting compounds were thoroughly dried and purified by distillation.

The IR spectra were recorded on an IKS-29 spectrometer (LOMO) in the frequency range of 4200–400 cm⁻¹ (accuracy was ±5 cm⁻¹).

The ¹H NMR spectra were measured on a Tesla BS 587a instrument (80 MHz) in CDCl₃ with HMDS as the internal standard.

O-Trimethylsilyl carbamates **1a,b** were synthesized by carboxylation of trimethylchlorosilane in the presence of the corresponding secondary amines in anhydrous benzene according to a known procedure.¹²

Carbamates **3a,c,d** were prepared from silyl carbamates **1** according to a procedure described in our earlier study.⁶

Tributylstannyl *N,N*-diethylcarbamate (3b). A mixture of carbamate **1a** (3.4 g, 0.018 mol) and hexabutylstannoxane (5.36 g, 0.009 mol) was heated at 160–180 °C (oil bath) for 0.5 h. Vacuum distillation afforded compound **3b** in a yield of 5.33 g (73%), b.p. 129–130 °C/2 Torr, n_D^{20} 1.4748, d_4^{20} 1.1233. Found (%): C, 50.68; H, 8.88; N, 3.71; Sn, 29.73. C₁₇H₃₇NO₂Sn. Calculated (%): C, 50.27; H, 9.18; N, 3.45; Sn, 29.22. IR (in a thin layer), ν/cm^{-1} : 1628 (C=O). ¹H NMR, δ : 3.14 (m, >N–CH).

Table 1. Conditions of the synthesis of alkoxyastannanes **5a–i**

Reaction product 5	Yield (%)	Starting <i>O</i> -stannyl carbamate	Starting alcohol	Reaction conditions		
				Molar ratio 3 : 4	<i>T</i> /°C	τ /h
Bu ⁿ OSnEt ₃ (5a)	86	Et ₃ SnOC(O)NEt ₂ (3a)	Bu ⁿ OH (4b)	15 : 80	100	0.5
<i>cyclo</i> -C ₆ H ₁₁ OSnEt ₃ (5b)	84	3a	<i>cyclo</i> -C ₆ H ₁₁ OH (4f)	10 : 90	120	1.0
(<i>cyclo</i> -C ₆ H ₁₁ O) ₂ SnBu ₂ (5c)	69	Bu ₂ Sn[OC(O)NEt ₂] ₂ (3d)	4f	14 : 30	120	0.5
Pr ⁿ OSnEt ₃ (5d)	58	3a	Pr ⁿ OH (4a)	13 : 126	100	1.0
Bu ^t OSnEt ₃ (5e)	70	3a	Bu ^t OH (4c)	4 : 12	110	0.5
Bu ⁿ OSnBu ₃ (5f)	93	Bu ₃ SnOC(O)NEt ₂ (3b)	4b	9.5 : 31	130	0.75
Bu ^t OSnEt ₃ (5g)	34	3a	Bu ^t OH (4d)	11 : 110	90	1.0
BnOSnBu ₃ (5h)	95	Bu ₃ SnOC(O)N(CH ₂) ₅ (3c)	BnOH (4e)	3.2 : 16	120	1.0
(Bu ⁿ O) ₂ SnBu ₂ (5i)	60	3d	4b	7.2 : 72	100	0.25

Table 2. Physicochemical parameters of alkoxytannanes **5a–i**

Compound	M.p./°C (p/Torr)	n_D^{20}	d_4^{20}	Found (%)			Published data			
				Calculated			B.p./°C (p/Torr)	n_D^{20}	d_4^{20}	Reference
				C	H	Sn				
5a	95–97 (7)	1.4680	1.1922	42.70 43.05	9.04 8.67	42.14 42.54	—	—	—	
5b	81–82 (2)	1.4913	1.2208	47.95 47.25	8.79 8.59	38.26 38.91	120–124 (5)	1.4923	—	7
5c	128 (0.5)	1.4812	1.1138	55.12 55.70	9.22 9.35	27.17 27.52	—	—	—	
5d	76 (6)	1.4687	1.2258	—	—	—	83–84 (8)	1.4660	1.2019	8
5e	76–77 (1)	1.4660	1.1007	42.85 43.05	8.90 8.67	42.38 42.54	—	—	—	
5f	139–141 (4)	1.4670	1.0854	—	—	—	124–128 (3)	1.4688	—	9
5g	113 (36)	1.4630	1.1632	—	—	—	132–135 (112)	1.4672	—	10
5h	138–140 (1)	1.5106	1.1449	57.24 57.45	9.02 8.63	30.03 29.88	—	—	—	
5i	132–134 (1)	1.4699	1.2159	50.85 50.68	9.41 9.56	31.09 31.30	160 (3)	—	1.2056	11

Butoxytriethylstannane (5a). Carbamate **3a** (5 g, 15.5 mmol) and *n*-butyl alcohol (6 g, 0.08 mol) were placed in an apparatus for vacuum distillation. The reaction mixture was heated at 100 °C (temperature of an oil bath) for 0.5 h. After removal of a low-boiling fraction by vacuum distillation, compound **5a** was isolated in a yield of 3.72 g (86%), b.p. 95–97 °C/7 Torr, d_4^{20} 1.1922, n_D^{20} 1.4680. Found (%): C, 42.70; H, 9.04; Sn, 42.14. $C_{10}H_{24}OSn$. Calculated (%): C, 43.05; H, 8.67; Sn, 42.54. IR, ν/cm^{-1} : 1070 (Sn–O–C).

Cyclohexyloxytriethylstannane (5b). A mixture of carbamate **3a** (3.2 g, 0.01 mol) and cyclohexanol (10 g, 0.09 mol) was heated at 120 °C for 1 h on an oil bath with protection from atmospheric moisture. Excess alcohol was removed by vacuum distillation and compound **5b** was obtained in a yield of 2.56 g (84%), b.p. 81–82 °C/2 Torr, d_4^{20} 1.2208, n_D^{20} 1.4913 (*cf.* lit. data⁷: b.p. 120–124 °C/5 Torr, n_D^{20} 1.4923).

Dicyclohexyloxydibutylstannane (5c) was prepared analogously by heating a mixture of dibutylstannyl bis(*N,N*-diethylcarbamate) **3d** (6.57 g, 0.014 mol) and cyclohexanol (3.31 g, 0.03 mol) at 100–120 °C (temperature of an oil bath) for 0.5 h under argon. Vacuum distillation afforded compound **5c** in a yield of 4.15 g (68.7%), b.p. 128 °C/0.5 Torr, d_4^{20} 1.1138, n_D^{20} 1.4812. Found (%): C, 55.12; H, 9.22; Sn, 27.17. $C_{20}H_{40}O_2Sn$. Calculated (%): C, 55.70; H, 9.35; Sn, 27.52. IR, ν/cm^{-1} : 1075 (Sn–O–C).

References

- A. A. Andreev, N. A. Boldyreva, and N. V. Komarov, *Zh. Obshch. Khim.*, 1986, **56**, 1664 [*J. Gen. Chem. USSR*, 1986, **56** (Engl. Transl.)].
- N. A. Boldyreva, N. V. Komarov, and A. A. Andreev, *Zh. Obshch. Khim.*, 1988, **58**, 1179 [*J. Gen. Chem. USSR*, 1988, **58** (Engl. Transl.)].
- N. A. Boldyreva, N. V. Komarov, and A. A. Andreev, *Zh. Obshch. Khim.*, 1987, **57**, 2801 [*J. Gen. Chem. USSR*, 1987, **57** (Engl. Transl.)].
- N. A. Boldyreva, A. A. Andreev, and N. V. Komarov, *Zh. Obshch. Khim.*, 1988, **58**, 1181 [*J. Gen. Chem. USSR*, 1988, **58** (Engl. Transl.)].
- N. V. Komarov, N. A. Ryzhkova, and A. A. Andreev, *Izv. Akad. Nauk, Ser. Khim.*, 1994, 313 [*Russ. Chem. Bull.*, 1994, **43**, 293 (Engl. Transl.)].
- N. A. Boldyreva, N. V. Komarov, and A. A. Andreev, *Zh. Obshch. Khim.*, 1988, **58**, 1932 [*J. Gen. Chem. USSR*, 1988, **58** (Engl. Transl.)].
- G. A. Razuvaev and N. S. Vyazankin, *Zh. Obshch. Khim.*, 1960, **30**, 2498 [*J. Gen. Chem. USSR*, 1960, **30** (Engl. Transl.)].
- I. F. Lutsenko and S. V. Ponomarev, *Zh. Obshch. Khim.*, 1961, **31**, 2025 [*J. Gen. Chem. USSR*, 1961, **31** (Engl. Transl.)].
- R. K. Ingam, C. D. Rosenberg, and M. Gilman, *Chem. Rev.*, 1960, **60**, 510.
- G. A. Razuvaev, N. S. Vyazankin, and E. S. D'yachkovskaya, *Zh. Obshch. Khim.*, 1962, **32**, 2161 [*J. Gen. Chem. USSR*, 1962, **32** (Engl. Transl.)].
- C. I. Zhivukhin, E. D. Dudikova, and Ter-Sarkisyan, *Zh. Obshch. Khim.*, 1962, **32**, 3059 [*J. Gen. Chem. USSR*, 1962, **32** (Engl. Transl.)].
- D. Knausz, A. Meszticzky, L. Szakacs, B. Csakvari, and K. Ujszaszy, *J. Organomet. Chem.*, 1983, **256**, 11.
- J. C. Pommier and M. Pereyre, in *Organotin Compounds: New Chemistry and Applications*, Ed. J. J. Zuckerman, *Adv. Chem. Ser.*, American Chemical Society, Washington, 1976, No. 157, p. 82.
- J. D. Kennedy, W. McFarlane, P. J. Smith, R. F. M. White, and L. Smith, *J. Chem. Soc., Perkin Trans. 2*, 1973, 1785.

Received April 12, 2003;
in revised form December 3, 2003