Reactions of stannyl carbamates with organochlorosilanes

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

Kuban' State University, 350050 Krasnodar, Russian Federation

Rapid and exothermic reactions of stannyl carbamates with organochlorosilanes result in cleavage of the Sn—O—C bond and afford silyl carbamates in a high yield.

Key words: stannyl and silyl carbamates.

The nucleophilic substitution of the halogen atoms at a silicon atom proceeds extremely readily, which determines the majority of the conversions of organohalosilanes. Organochlorosilanes readily react with hydroxy- and alkoxystannanes, distannoxanes, and other oxygen-containing organotin compounds. In this work we studied their reactions with stannyl carbamates.

Results and Discussion

Previously,[1–4] we have studied some reactions of stannyl carbamates (**1**); the high reactivity of the $Sn-O-\overset{\overset{O}{\|}}{C}-N$ bond system has been established.

New approaches to the synthesis of organic and organotin compounds were found and the applicability of **1** as an efficient stannylating agent was demonstrated.

The high basicity of compounds **1** suggested the possibility of their reactions with organochlorosilanes (**2**). Compounds **1** readily react with **2** to yield carbamates (**3**); the reaction is exothermic and occurs without side processes (Scheme 1).

Scheme 1

$$\underset{\mathbf{1}}{\equiv Sn-O-C(O)NR_2} + \underset{\mathbf{2}}{\equiv SiCl} \longrightarrow \equiv SnCl + \underset{\mathbf{3}}{\equiv SiOC(O)NR_2}$$

It is appropriate to carry out this reaction in aprotic solvents. Pure compounds **3** can be easily isolated by distillation (the yield is up to 80 %).

Organosilicon urethanes containing hydrogen, unsaturated and functional groups, and other substituents at the silicon atom can be prepared in this manner (see, for example, Scheme 2).

The reaction of organotin urethanes with organodichlorosilanes is of considerable interest. The replacement of one of the chlorine atoms in type **2** compounds in the reaction with compounds **1** opens the possibility for synthesizing previously unknown organochlorosilyl carbamates (Scheme 3).

Scheme 2

$$Et_3SnOC(O)NMe_2 + EtSiHCl_2 \longrightarrow \underset{\mathbf{4}}{EtSiH[OC(O)NMe_2]_2} + 2Et_3SnCl$$

$$Et_3SnOC(O)NEt_2 + BuC{\equiv}CSi(Me)(CH{=}CH_2)Cl \longrightarrow$$

$$\longrightarrow \underset{\mathbf{5}}{BuC{\equiv}C(Me)(CH{=}CH_2)SiOC(O)NEt_2} + Et_3SnCl$$

Scheme 3

$$\underset{\mathbf{1}}{\equiv SnOC(O)NR_2} + \underset{\mathbf{6}}{=SiCl_2} \longrightarrow Cl-\overset{\overset{|}{}}{\underset{\underset{|}{}}{Si}}OC(O)NR_2 + \equiv SnCl$$

We studied the reactions of triethyl-, tripropyl-, and tributylstannyl *N,N*-dimethyl and *N,N*-diethylcarbamates with dichlorodimethylsilane. With equimolar amounts of the reagents, trialkylchlorostannanes were prepared in a high yield. However, we failed to separate organochlorosilyl carbamates prepared by this procedure, by distillation *in vacuo*, because these compounds appeared to be unstable on heating. At a reagent ratio of 2:1, both of the chlorine atoms were replaced with carbamoyloxy groups:

$$2R_3SnOC(O)NR'_2 + Me_2SiCl_2 \longrightarrow Me_2Si[OC(O)NR'_2]_2 + 2R_3SiCl$$

Because of the availability of stannyl carbamates, the reaction under investigation can be used in the directed synthesis of different organosilicon urethanes.

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Experimental

***N,N*-Diethylcarbamoyloxytrimethylsilane.** 3.26 g (0.03 mol) of Me_3SiCl was added portionwise to a solution of 6.98 g (0.015 mol) of bis(*N,N*-diethylcarbamoyloxy)dibutylstannane in 30 mL of absolute ether with stirring. The reaction mixture was stirred for 10 min, the solvent was distilled off, and then the residue was distilled *in vacuo*. The yield of *N,N*-diethylcarbamoyloxytrimethylsilane was 3.9 g (68.9 %), b. p. 44—45 °C (3 Torr); n_D^{20} 1.4204 (*cf.* Ref. 5: b. p. 72 °C (13 Torr); n_D^{20} 1.4182). IR, ν/cm^{-1}: 1068 (Si—O—C); 1697 (C=O). Found (%): C, 50.72; H, 10.28; N, 7.29; Si, 14.74. $C_8H_{19}O_2NSi$. Calculated (%): C, 50.75, H, 10.11; N, 7.40; Si, 14.84. In addition, dibutyldichlorostannane was isolated in a yield of 3.9 g (86 %), b. p. 105—110 °C (1 Torr), m. p. 43 °C.

***N,N*-Pentamethylenecarbamoyloxytrimethylsilane** was prepared by a similar procedure from 4.18 g (0.01 mol) of tributyl(pentamethylenecarbamoyloxy)stannane and 1.1 g (0.01 mol) of Me_3SiCl in a yield of 1.73 g (86 %); b. p. 95 °C (8 Torr); n_D^{20} 1.4493 (*cf.* Ref. 6: b. p. 64—65 °C (2 Torr)). IR, ν/cm^{-1}: 1080 (Si—O—C), 1698 (C=O). Found (%): C, 53.12; H, 9.25; N, 7.03; Si, 13.68. $C_9H_{19}O_2NSi$. Calculated (%): C, 53.61; H, 9.48; N, 6.95; Si, 13.92. Besides, tributylchlorostannane was isolated in a yield of 3.26 g (91 %), b. p. 145—148 °C (15 Torr).

***N,N*-Dimethylcarbamoyloxydimethyl(phenylethynyl)silane** was synthesized in a similar manner from 2.9 g (0.009 mol) of *N,N*-diethylcarbamoyloxytriethylstannane and 1.95 g (0.01 mol) of chloro(dimethyl)(phenylethynyl)silane in a yield of 1.6 g (64.5 %), b. p. 158—160 °C (2 Torr). IR, ν/cm^{-1}: 1080 (Si—O—C), 1603 (C_6H_5), 1678 (C=O), 2170 (C≡C). Found (%): C, 65.52; H, 7.99; N, 4.92; Si, 10.14. $C_{15}H_{21}O_2NSi$. Calculated (%): C, 65.41; H, 7.69; N, 5.09; Si, 10.19. Chlorotriethylstannane (2.08 g, 96 %) was also isolated, b. p. 58—60 °C (2 Torr), n_D^{20} 1.5052.

***N,N*-Diethylcarbamoyloxy(methyl)(vinyl)(1-hexynyl)silane (5)** was prepared in a similar manner by reacting 3.43 g (0.012 mol) of *N,N*-diethylcarbamoyloxytriethylstannane with 2.43 g (0.013 mol) of chloro(1-hexynyl)(methyl)(vinyl)silane in a yield of 2.01 g (58 %), b. p. 122—124 °C (3 Torr), d_4^{20} 0.9117, n_D^{20} 1.4637. IR, ν/cm^{-1}: 1080 (Si—O—C), 1610 ($CH=CH_2$), 1700 (C=O), 2200 (C≡C). Found (%): C, 63.21; H, 9.59; Si, 10.67. $C_{14}H_{25}O_2NSi$. Calculated (%): C, 62.87; H, 9.42; Si, 10.50. In addition, chlorotriethylstannane was isolated in a yield of 2.9 g (97 %), b. p. 75—78 °C (3 Torr), n_D^{20} 1.5050.

Bis(*N,N*-dimethylcarbamoyloxy)(phenylethynyl)vinylsilane was synthesized analogously from 4.41 g (0.011 mol) of *N,N*-dimethylcarbamoyloxytributylstannane and 1.05 g (0.0046 mol) of dichloro(phenylethynyl)vinylsilane in a yield of 1.21 g (79 %), b. p. 87 °C (0.01 Torr), n_D^{20} 1.5079. IR, ν/cm^{-1}: 1080 (Si—O—C), 1600 (C_6H_5), 1625 (C=O), 2140 (C≡C). Found (%): C, 58.23; H, 5.92; N, 8.00; Si, 8.12. $C_{16}H_{20}O_4N_2Si$. Calculated (%): C, 57.80; H, 6.06; N, 8.42; Si, 8.44. Tributylchlorostannane was isolated in a yield of 3.3 g (92 %), b. p. 146—148 °C (15 Torr).

Bis(*N,N*-dimethylcarbamoyloxy)ethylsilane (4) was prepared analogously by reacting 6.5 g (0.022 mol) of *N,N*-dimethylcarbamoyloxytriethylstannane with 1.45 g (0.011 mol) of dichloroethylsilane in a yield of 1.2 g (46 %), b. p. 112—113 °C (1 Torr), d_4^{20} 1.0344, n_D^{20} 1.4546. IR, ν/cm^{-1}: 1080 (Si—O—C), 1700 (C=O), 2110 (Si—H).

Bis(*N,N*-diisopentylcarbamoyloxy)dimethylsilane was prepared by adding 8.51 g (0.019 mol) of *N,N*-diisopentylcarbamoyloxytripropylstannane to 0.9 g (0.007 mol) of dichlorodimethylsilane in ether. The yield was 2.12 g (66 %), b. p. 125—127 °C (0.01 Torr), d_4^{20} 1.0748, n_D^{20} 1.4697. IR, ν/cm^{-1}: 1085 (Si—O—C), 1630 (C=O), in $CHCl_3$. Chlorotripropylstannane was isolated in a yield of 3.2 g (81 %), b. p. 113—114 °C (5 Torr), n_D^{20} 1.4981.

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