Aminocarboxylation of organylhalogermanes

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A new method was developed for the synthesis of *O*-trialkylgermylcarbamates by the aminocarboxylation of organylhalogermanes with carbon dioxide and secondary amines.

Key words: trialkylchlorogermanes, trialkylbromogermanes, *O*-trialkylgermylcarbamates, hexaalkyldigermoxanes.

Organoelement esters of dialkylcarbamic acids of Group IVB elements (silicon, germanium, tin) are studied to rather different extent. For instance, *O*-trimethylsilylurethanes are commercial products and used as silylating agents. We have shown that tri(di)alkylstannyl derivatives of carbamic acids can be used for syntheses of different classes of organotin compounds: alkoxystannanes,[1] organotin hydrides,[2] stannylacetylenes,[3] organotin derivatives of CH-acids,[4] and others. Organogermanium esters of dialkylcarbamic acids are also of interest from the viewpoint of synthetic use; however, possibilities of their preparation are limited.[5] Published data on the synthesis of germanium carbamates by the aminocarboxylation of organylhalogermanes with carbon dioxide and secondary amine are lacking, although this method is used for synthesis of both *O*-silylurethanes[6] and *O*-stannylurethanes.[7]

In the present work, in search for a simple and efficient method of synthesis of *O*-trialkylgermylcarbamates **1** we have studied for the first time the aminocarboxylation of trialkylhalogermanes **2**.

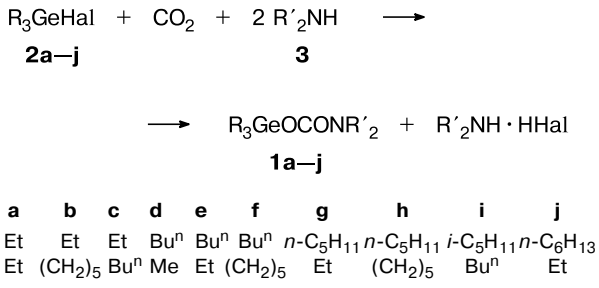
Results and Discussion

We have shown that the aminocarboxylation of organylhalogermanes **2** with carbon dioxide and excess amine **3** occurs readily on slight heating and affords carbamates **1** in a yield of up to 80% (Scheme 1).

It is most likely that the synthesis of carbamates **1** proceeds through intermediate steps of formation of trialkylaminogermanes or dialkylcarbamic acid (Scheme 2, pathways *A* and *B*).

Carbamates **1** can be obtained through the intermediate formation of trialkylaminogermanes **5** when the initial halogermane can easily be transformed by the action of secondary amine[8] into aminogermane **5**, which, as known,[9] affords carbamate by the reaction with carbon dioxide.

Scheme 1



For some organylhalogermanes giving stable complexes **4** with secondary amines (lower trialkylchlorogermanes, dialkylchlorogermanes, *etc.*), transformation *via* pathway *A* is unlikely probable. Pathway *B* is preferential due to the ability of the Ge atom to experience the nucleophilic attack from the carbamoyloxy anion. Indeed, the treatment of salt of dialkylcarbamic acid **6**, which is formed by the reaction of secondary amine **3** with excess carbon dioxide, with organylgermyl halide **2** affords carbamates **1** in good yields. It cannot be excluded that the both possible routes occur simultaneously.

O-Trialkylgermylcarbamates **1** are colorless liquids with weak odor, stable on distillation *in vacuo*, and highly soluble in ether, hydrocarbons, and THF. They are easily decomposed with water but stable on storage in the absence of moisture. Their IR spectra exhibit intense absorption bands at 1660 (C=O) and 860 cm^{-1} (stretching vibrations of the Ge—O bonds).[10] The ^1H NMR spectra contain signals of protons of the alkyl groups bound with the Ge atom at δ 0.8 (CH_3) and 1.1—1.5 (CH_2) and signals of the methylic and methylenic protons at the N atoms at δ 2.6—3.5.

The structure of carbamates **1** was confirmed by elemental analysis data of comparison of their physico-

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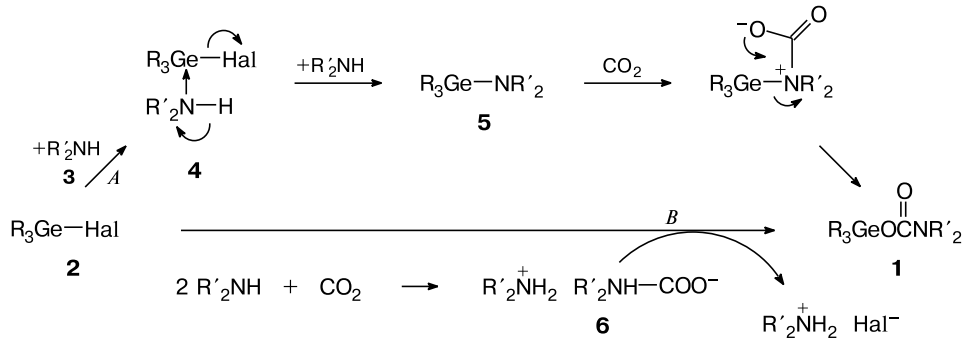
Scheme 2



chemical properties (Table 1) with those described in literature.[5]

Experimental

Initial trialkylchloro- and trialkylbromogermanes were synthesized using known general procedures.[11,12] Anhydrous solvents and secondary amines were distilled prior to use.

IR spectra were obtained on an InfraLum-FT 02 spectrometer (LUMEX Co.) in the frequency interval 4500—350 cm^{-1} (in thin layer and as a suspension in Nujol for liquid and crystalline compounds, respectively).

^1H NMR spectra were recorded on a Tesla BS 587a instrument (80 MHz) in $CDCl_3$ using HMDS as internal standard.

***O*-Tri-*n*-butylgermyl-*N*,*N*-diethylcarbamate (1e).** Carbon dioxide dried by passing through concentrated H_2SO_4 was purged into a solution of diethylamine (6.29 g, 0.086 mol) in anhydrous THF (25 mL) with a rate of 0.5 L min^{-1} at 15—25 °C for 0.5 h. The interaction of the reagents was accompanied by heat release. Then a solution of tri-*n*-butylbromogermane (14 g, 0.043 mol) in THF (20 mL) was added dropwise. Carbon dioxide was purged with stirring into the reaction mixture for 1.5 h at a temperature of the bath of 50—60 °C. On cooling to 20—25 °C the crystalline precipitate was filtered off and washed on the filter with THF. The filtrate was concentrated by evaporation, and the remaining substance was distilled *in vacuo*. Carbamate **1e** was isolated in a yield of 11.08 g (72%).

***O*-Tri-*n*-butylgermyl-*N*,*N*-dimethylcarbamate (1d).** Tetrahydrofuran (50 mL) was placed in a 250-mL reactor equipped

Table 1. Physicochemical parameters of organogermylcarbamates **1a—j**

Compound	B.p. /°C (*p*/Torr)	n_D^{20}	Found / Calculated (%) C	Found / Calculated (%) H	Molecular formula	IR, ν/cm^{-1}	^1H NMR, δ $CH^a_3(CH^b_2)_nGeOCON(CH^c_2)$—$(CH^d_2)_mCH^e_3$
1a*	92 (3)	1.4542	—	—	$C_{11}H_{25}GeNO_2$	1660, 860	—
1b	103 (2)	1.4623	49.49 / 50.07	8.02 / 8.69	$C_{12}H_{25}GeNO_2$	1660, 860	—
1c	130—132 (3)	1.4532	54.83 / 54.28	9.70 / 9.95	$C_{15}H_{33}GeNO_2$	1650, 860	—
1d	100—101 (2)	1.4598	53.65 / 54.28	10.01 / 9.95	$C_{15}H_{33}GeNO_2$	1660, 860	0.87 (t, H_a); 1.36 (m, H_b); 2.62 (s, H_e)
1e**	120 (1)	1.4575	—	—	$C_{17}H_{37}GeNO_2$	1660, 855	0.88 (t, H_a); 1.33 (m, H_b); 2.57 (q, H_c)
1f	125 (3)	1.4651	57.18 / 58.13	9.85 / 9.96	$C_{18}H_{37}GeNO_2$	1650, 850	—
1g	187—189 (10)	1.4592	59.23 / 59.76	10.42 / 10.71	$C_{20}H_{43}GeNO_2$	1660, 860	—
1h	158—160 (3)	1.4588	61.35 / 60.93	10.11 / 10.40	$C_{21}H_{43}GeNO_2$	1655, 850	0.88 (t, H_a); 1.32 (m, H_b, H_d); 3.57 (t, H_c)
1i	225 (2)	1.4622	62.65 / 62.94	10.81 / 11.14	$C_{24}H_{51}GeNO_2$	1660, 850	0.85 (t, H_a); 0.95 (t, H_e); 1.35 (m, H_b, H_d); 2.62 (t, H_c)
1j	170—172 (3)	1.4626	61.54 / 62.22	10.47 / 11.04	$C_{23}H_{49}GeNO_2$	1660, 850	—

* *Cf.* Ref. 9: b.p. 115 °C (5 Torr), n_D^{20} 1.4529.
** *Cf.* Ref. 5: b.p. 120 °C (1 Torr), n_D^{20} 1.4576.

with a bubbler and mechanical stirrer, and gaseous dimethylamine (3.6 g, 0.08 mol) was dissolved in the THF at 20—25 °C. Then CO_2 was purged for 1 h on cooling with ice-cold water, and a solution of tri-*n*-butylchlorogermane (11.16 g, 0.04 mol) in THF (20 mL) was simultaneously added dropwise. The reaction mixture was heated for 30 min at 70 °C with CO_2 purging. On cooling the precipitate was filtered off and washed with THF, the solvent was distilled off, and carbamate **1d** was isolated by distillation *in vacuo* of the residue in a yield of 9.82 g (74%).

***O*-Triethylgermyl-*N*,*N*-diethylcarbamate (1a)** was synthesized similarly to carbamate **1e** from diethylamine (5.8 g, 0.079 mol), triethylgermanium bromide (6.3 g, 0.026 mol), and CO_2 in THF (50 mL). The yield was 4.5 g (62.8%).

***O*-Tri-*n*-hexylgermyl-*N*,*N*-diethylcarbamate (1j)** was synthesized similarly to carbamate **1e** from tri-*n*-hexylgermanium chloride (7.26 g, 0.02 mol), diethylamine (4.4 g, 0.06 mol), and CO_2 in THF (50 mL). The yield was 7.9 g (89%).

O-Trialkylgermylcarbamates **1b**, **1c**, **1f**, **1g**, **1h**, and **1i** were synthesized similarly to carbamate **1e** in 53, 74, 57, 62, 59, and 67% yields, respectively. The physicochemical characteristics of carbamates **1** are presented in Table 1.

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