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Reactions of hexaorganyldigermoxanes with *O*-trimethylsilyl carbamates

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Hexa-*n*-butyl- and hexaisopentyldigermoxanes but not hexaphenyldigermoxane react with *O*-trimethylsilyl *N,N*-diethylcarbamate and trimethylsilyl piperidinocarboxylate to give *O*-triorganylgermyl carbamates.

Key words: hexaalkyldigermoxanes, *O*-trimethylsilyl *N,N*-dialkylcarbamates, *N,N*-dialkylcarbamoyloxy(trialkyl)germanes, *N,N*-diethylcarbamoyloxy(triphenyl)germane.

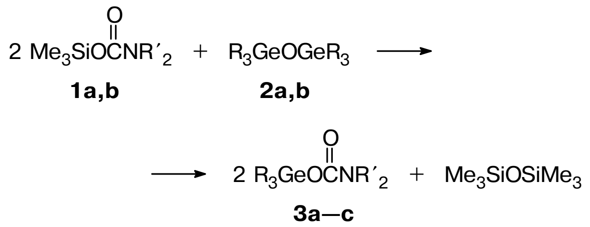
Earlier,[1] we discovered that *O*-trialkylsilyl carbamates react with organotin oxides and organyldistannoxanes to give *O*-di(tri)organylstannyl carbamates.

Taking into account the availability and high reactivities of *O*-trimethylsilyl carbamates (**1**), it was of interest to study their reactions with hexaorganyldigermoxanes (**2**) as a new possible alternative[2] method for the synthesis of *O*-triorganylgermyl carbamates (**3**). Although organogermanium oxides and organyldigermoxanes are less basic and therefore much less reactive than their organotin analogs, they react with some compounds, involving the Ge—O bond.[3]

Results and Discussion

Our study showed that heating of hexaisopentyl- and hexa-*n*-butyldigermoxanes (**2a,b**) at 150—160 °C with equimolar amounts of trimethylsilyl piperidinocarboxylate (**1a**) or *O*-trimethylsilyl *N,N*-diethylcarbamate (**1b**) affords carbamates **3** in up to 60% yield (Scheme 1).

Scheme 1



R = $Me_2CHCH_2CH_2$ (**2a, 3a, 3b**), Bu (**2b, 3c**);
$NR'_2 = N(CH_2)_5$ (**1a, 3a**), NEt_2 (**1b, 3b, 3c**)

Carbamates **3** were identified by IR spectroscopy; their physicochemical constants were also compared with those of compounds obtained by an independent method, namely, by carboxylation of trialkylgermyl halides in the presence of secondary amines[2] (Table 1).

Table 1. Physicochemical constants of carbamates **3a—c**

Compound	B.p. /°C (*p*/Torr)	n_D^{20}	Found / Calculated (%) C	H	N	^1H NMR, δ*
3a	158—160	1.4533	61.24	10.58	3.11	2.52
	(3)		60.93	10.40	3.38	(t)
3b	171—172	1.4564	59.05	10.41	3.18	2.62
	(7)		59.76	10.71	3.49	(q)
3c	120	1.4581	56.92	9.95	3.80	2.63
	(1)		56.73	10.29	3.89	(q)

* Chemical shifts of the signals from the H^x atoms in the ^1H NMR spectra of $R_3GeOC(O)N(CH^x_2R')_2$.

Carbamates **3** are viscous liquids with slight odor. Their IR spectra show an intense absorption band at 1660 cm^{-1} (C=O) and a broad band at 860 cm^{-1} (Ge—O). The ^1H NMR spectra contain signals at δ 2.5—2.6 for the equivalent protons of the N-linked methylene groups. The spectral pattern in the δ range from 0.3 to 1.5 ppm is complicated because multiplets from various groups overlap.

It was established that digermoxanes **2** react with carbamates **1** five to six times more slowly than distannoxanes,[2] the yield of target products **3** being reduced to 50—60% (the yields of *O*-trialkylstannyl carbamates were 70—80%).

When aliphatic radicals in digermoxane **2** are replaced by aromatic ones, no arylgermyl carbamates **3** are formed. Thus, after heating of carbamate **1** with an equimolar amount of hexaphenyldigermoxane (**4**) in toluene and without solvent for 1—5 h only the starting compounds were recovered. This can be due to steric hindrances and lesser basicity and nucleophilicity of digermoxane **4** compared to digermoxanes **2**.

O-Triphenylgermyl *N,N*-diethylcarbamate (**5**) was obtained in 60% yield according to Scheme 2.

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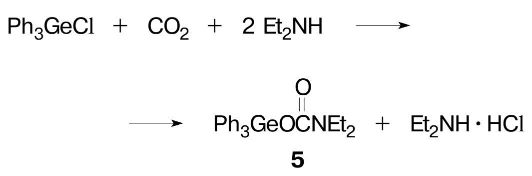
Scheme 2



$$Ph_3GeCl + CO_2 + 2\,Et_2NH \longrightarrow Ph_3GeOC(=O)NEt_2 + Et_2NH \cdot HCl$$

Experimental

The solvents and the starting reagents were thoroughly dried and purified by distillation before use.

The starting hexaorganyldigermoxanes **2** were prepared by alkaline hydrolysis of triorganylgermanium halides.[4] The physicochemical constants of the compounds obtained corresponded to the literature data.[5]

O-Trimethylsilyl carbamates **1** were synthesized by carboxylation of chlorotrimethylsilane in the presence of the corresponding secondary amines in anhydrous benzene.[6]

IR spectra were recorded on a LOMO IKS-29 spectrometer (4200—400 cm^{-1}) with an accuracy of ±5 cm^{-1}.

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

***O*-Trimethylsilyl *N,N*-diethylcarbamate (1b).** Carbon dioxide was bubbled for 0.5 h through a solution of diethylamine (58.5 g, 0.8 mol) in 100 mL of anhydrous benzene with vigorous stirring and cooling with ice water, and then chlorotrimethylsilane (43.4 g, 0.4 mol) was added in small portions. The precipitate that formed was filtered off and washed with benzene. The filtrates were combined and concentrated *in vacuo*, and the residue was fractionated *in vacuo* to give compound **1b** (52.8 g, 70%), b.p. 44—45 °C (3 Torr), n_D^{20} 1.4203. IR, ν/cm^{-1}: 1697 (C=O); 1068 (Si—O—C). *Cf.* Ref. 6: b.p. 36 °C (1.5 Torr), n_D^{20} 1.4202.

Trimethylsilyl piperidinocarboxylate (1a) was prepared analogously from chlorotrimethylsilane (27.2 g, 0.25 mol) and piperidine (42.5 g, 0.5 mol). The yield of **1a** was 46.8 g (66%), b.p. 95 °C (8 Torr), n_D^{20} 1.4493. Found (%): C, 53.14; H, 9.02; N, 6.86; Si, 13.63. $C_9H_{19}NO_2Si$. Calculated (%): C, 53.71; H, 9.45; N, 6.96; Si, 13.96. IR, ν/cm^{-1}: 1690 (C=O); 1080 (Si—O—C). *Cf.* Ref. 7: b.p. 64—65 °C (2 Torr); IR (CCl_4), ν/cm^{-1}: 1675 (C=O).

O*-Triisopentylgermyl *N,N*-diethylcarbamate (3b).** ***A. Dried carbon dioxide was passed through a solution of diethylamine (2.9 g, 0.04 mol) in 50 mL of THF at a rate of 0.5 L min^{-1} for 0.5 h; then, a solution of triisopentylgermyl chloride (6.4 g, 0.02 mol) in 30 mL of THF was added. The reaction mixture was diluted with an equal volume of diethyl ether, and the precipitate that formed was filtered off. The filtrate was concentrated and distilled *in vacuo* to give compound **3b** (5.4 g, 67%), b.p. 171—172 °C (7 Torr), n_D^{20} 1.4564. Found (%): C, 59.05; H, 10.41; N, 3.18. $C_{20}H_{43}GeNO_2$. Calculated (%): C, 59.76; H, 10.71; N, 3.49. IR, ν/cm^{-1}: 1660 (C=O); 860 (Ge—O).

B. A mixture of hexaisopentyldigermoxane (3.7 g, 0.0063 mol) and carbamate **1b** (2.4 g, 0.0126 mol) was heated at 150—155 °C for 3 h. Vacuum fractionation of the reaction mixture gave compound **3b** (2.93 g, 61%), b.p. 145—146 °C (2 Torr), n_D^{20} 1.4546. IR, ν/cm^{-1}: 1660 (C=O); 860 (Ge—O).

Triisopentylgermyl piperidinocarboxylate (3a) was obtained by heating a mixture of hexaisopentyldigermoxane (3.3 g, 0.0056 mol) and carbamate **1a** (2.3 g, 0.0112 mol) at 150—160 °C for 4 h. Vacuum distillation gave compound **3a** (3.2 g, 59%), b.p. 149—150 °C (2 Torr), n_D^{20} 1.4522. IR, ν/cm^{-1}: 1660 (C=O); 860 (Ge—O).

***O*-Tri-*n*-butylgermyl *N,N*-diethylcarbamate (3c)** was obtained analogously from hexa-*n*-butyldigermoxane (1.6 g, 0.003 mol) and carbamate **1b** (1.2 g, 0.006 mol). The yield of **3c** was 1.06 g (49%), b.p. 120 °C (1 Torr), n_D^{20} 1.4576. IR, ν/cm^{-1}: 1660 (C=O); 855 (Ge—O).

***O*-Triphenylgermyl *N,N*-diethylcarbamate (5).** A stirred solution of chlorotriphenylgermane (8.83 g, 0.026 mol) and diethylamine (7.3 g, 0.1 mol) in 50 mL of THF was saturated with dry carbon dioxide at 20—25 °C. The precipitate that formed was filtered off, the filtrate was concentrated, and the residue was recrystallized from pentane to give compound **5** (6.4 g, 59%) as needle-like crystals, m.p. 164 °C. Found (%): C, 66.81; H, 6.12; N, 2.84. $C_{23}H_{25}GeNO_2$. Calculated (%): C, 65.78; H, 5.96; N, 3.34. IR, ν/cm^{-1}: 1650 (C=O); 855 (Ge—O).

Reactions of carbamates 1a,b with hexaphenyldigermoxane (4). ***A.*** A mixture of hexaphenyldigermoxane (**4**) (2.8 g, 4.5 mmol) and carbamate **1b** (1.7 g, 9 mmol) in 10 mL of toluene was kept in an oil bath at 150—160 °C for 4 h. Cooling the reaction mixture gave compound **4** (2.6 g, 93%) as a crystalline precipitate, m.p. 183 °C. (*cf.* Ref. 5: m.p. 183—184 °C).

B. A mixture of hexaphenyldigermoxane (**4**) (2.37 g, 3.8 mmol) and carbamate **1a** (3.05 g, 15.2 mmol) in 10 mL of toluene was kept in an oil bath at 150—160 °C for 5 h. Compounds **4** (2.18 g, 92%, m.p. 183 °C) and **1a** (2.89 g, 95%, b.p. 64—65 °C (2 Torr), n_D^{20} 1.4425) were recovered.

References

1. N. A. Boldyreva, N. V. Komarov, and A. A. Andreev, *Zh. Obshch. Khim.*, 1988, **45**, 1932 [*J. Gen. Chem. USSR*, 1988, **45** (Engl. Transl.)].
2. N. V. Komarov and N. A. Ryzhkova, *Tezisy dokladov Vserossiiskoi konferentsii po metalloorganicheskoi khimii* [*Abstrs., All-Russia Conf. on Organometallic Chemistry*], Nizhnii Novgorod, 1995, **1**, p. 32 (in Russian).
3. R. Ingam, S. Rosenberg, H. Gilman, and F. Rijkens, *Chem. Rev.*, **60**, 459; *Organogermanium Compounds. A Survey of the Literature from January 1950 to July 1960*, Inst. of Organic Chemistry.
4. K. A. Kocheshkov, N. N. Zemlyanskii, N. I. Sheverdina, and E. M. Panov, *Metody elementoorganicheskoi khimii. Germanii, olovo, svinets* [*Methods of Organoelement Chemistry. Germanium, Tin, and Lead*], Nauka, Moscow, 1968, 704 pp. (in Russian).
5. V. F. Mironov and T. K. Gar, *Organicheskie soedineniya germaniya* [*Organogermanium Compounds*], Nauka, Moscow, 1967, 301 pp. (in Russian).
6. D. Knausz, A. Meszticzky, L. Szakacs, B. Csakvari, and K. Ujszaszy, *J. Organomet. Chem.*, 1983, **256**, 11.
7. Y. Yamamoto and D. S. Tarbell, *J. Org. Chem.*, 1971, **36**, 2954.

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