Synthesis and reactivity of germanium heterocycles containing germanium—tin bonds

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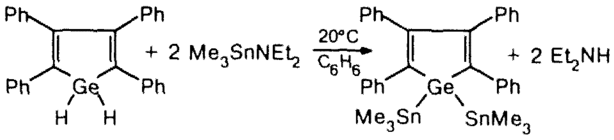
Previously unknown stannyl-substituted germanium heterocycles, 1,1-bis(trimethylstannyl)-2,3,4,5-tetraphenyl-1-germacyclopenta-2,4-diene and 1,1-bis(trimethylstannyl)-3,4-dimethyl-1-germacyclopent-3-ene were synthesized, and their photolysis and chemical transformations were studied.

Key words: stannyl-substituted 1-germacyclopenta-2,4-diene, stannyl-substituted 1-germacyclopent-3-ene, synthesis, reactivity, photolysis, germanium—tin bond cleavage.

Many silicon-, germanium-, and tin-containing heterocycles are convenient sources of short-lived carbene analogs, silylenes, germylenes, and stannylenes.[1–4] Among them, five-membered heterocycles play a special role due to their synthetic accessibility. For example, thermolysis or photolysis of 1-germa(sila)cyclopent-3-enes[5–9] and 7-heteronorbornadienes,[1–4,10–13] which can easily be obtained from the corresponding 1-germa(sila)cyclopenta-2,4-dienes, results in the formation of the corresponding carbene analogs R_2E (E = Si, Ge). Carbene analogs in which the two-coordinated silicon or germanium atom is incorporated into a heterocycle containing multiple carbon—carbon bonds are of special interest, because conjugation effects[14] and various rearrangements[1,15] can take place in these molecules. One of the convenient methods for generating these systems could be based on photolysis of substituted heterocycles containing photolabile E—Sn bonds (E = Si, Ge, Sn). This work is devoted to the synthesis and study of the reactivity of the stannyl-substituted derivatives of 1-germacyclopent-3-ene and 1-germacyclopenta-2,4-diene, which have not been described previously and are potential sources of 1-germacyclopent-3-en and 1-germacyclopenta-2,4-dien-1-ylidenes.

Results and Discussion

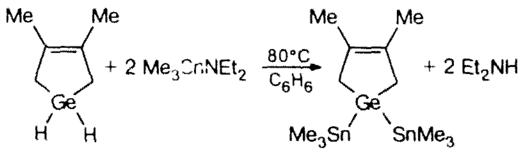
The simplest method for the synthesis of bis(trimethylstannyl)-substituted 1-germacyclopent-3-ene and 1-germacyclopenta-2,4-diene is the reaction of nucleophilic substitution of chlorine in the corresponding dichloro-substituted heterocycles through the action of the Me_3Sn^- ion. However, it turned out that the predominant direction of the reaction of 1,1-dichloro-2,3,4,5-tetraphenyl-1-germacyclopenta-2,4-diene (**1**) with Me_3SnLi is a redox process leading to germanium-containing polymers. Therefore, the reaction of metallation of organogermanium hydrides with Me_3SnNEt_2 [16] was used for insertion of the Me_3Sn group into the organogermanium heterocycle. In fact, it turned out that 2,3,4,5-tetraphenyl-1-germacyclopenta-2,4-diene (**2**) reacts readily with Me_3SnNEt_2 (benzene, 20 °C) to give 1,1-bis(trimethylstannyl)-2,3,4,5-tetraphenyl-1-germacyclopenta-2,4-diene (**3**) in high yield:



2 **3**

Compound **3** is a new representative of germacyclopentadienes (germols)[17,18] and the second germol with a germanium—metal bond (only 1,1-bis(trimethylsilyl)-2,3,4,5-tetraphenyl-1-germacyclopenta-2,4-diene (**4**) has been described previously).[19,20]

A similar method was used for the synthesis of 1,1-bis(trimethylstannyl)-3,4-dimethyl-1-germacyclopent-3-ene (**5**):



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The reaction of germol **2** and 2,3,4,5-tetraphenyl-1-silacyclopenta-2,4-diene (**6**) with Me_3SiNEt_2 was studied to develop a convenient method for synthesis of bis(trimethylsilyl) derivatives of germol and silol. It turned

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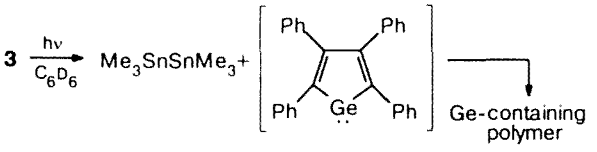
out that in the case of silol **6** the reaction does not occur even under drastic conditions (DMF, 120 °C, sealed tube, 10 h). Under similar conditions, germol **2** reacts with Me_3SiNEt_2, but the only product of this reaction is a germanium-containing polymer. Silylation did not occur with 3,4-dimethyl-1-germacyclopent-3-ene. The initial substances were regenerated after 30 h of boiling of this compound with Me_3SiNEt_2 in toluene.

Unlike germol **4**, which, according to our data, is a photochemically stable compound,* both synthesized compounds **3** and **5**, as expected, turned out to be photolabile. Thus, when heterocycles **3** and **5** in benzene are UV-irradiated with a high-pressure mercury lamp, they decompose with the cleavage of the Ge—Sn bonds. As a result, $Me_3SnSnMe_3$ forms in quantitative yield along with a germanium-containing polymer, which is likely a product of the polymerization of cyclic germylenes **7** and **8**:



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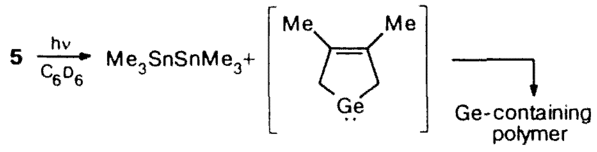

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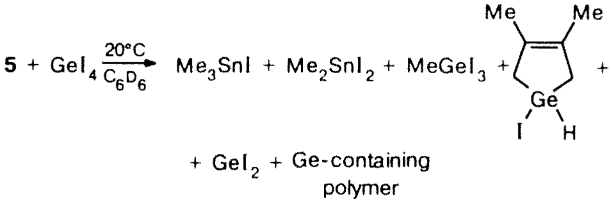
The attempts to trap germylene **7** and **8** by such effective traps as 2,3-dimethylbutadiene and 3,3,6,6-tetramethyl-1-thiacyclohept-4-yne resulted, unfortunately, not in the expected adducts of cycloaddition, but in the products of polymerization of unsaturated reagents under the action of Me_3Sn radicals formed during photolysis of compounds **3** and **5**.

The Ge—Sn bond in heterocycles **3** and **5** is sensitive not only to photoirradiation, but to the action of oxidants as well. It has been established previously that Ge(II) and Ge(IV) halides are efficient oxidants that react with various reducing agents, for example, $Me_3SnSnMe_3$ and *N,N,N',N'*-tetramethyl-*para*-phenylenediamine,[21] in redox processes. It turned out that compounds **3** and **5** are also easily oxidized by the action of the $GeCl_2 \cdot$diox complex (diox is 1,4-dioxane) and GeI_4. The reactions of heterocycle **5** with $GeCl_2 \cdot$diox and GeI_4 occur under mild conditions at room temperature with 100% conversion of the initial heterocycle to form trimethyltin chloride and germanium-containing polymer in quantitative yields in the case of the reaction with $GeCl_2 \cdot$diox:

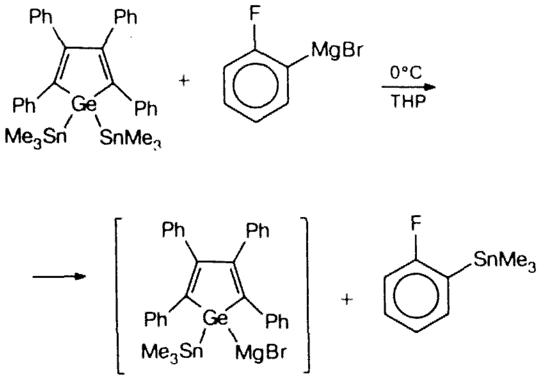
$$\mathbf{5} + GeCl_2 \cdot \text{diox} \xrightarrow[C_6D_6]{20\,^{\circ}C} Me_3SnCl + (GeCl)_x + \text{Ge-containing polymer}.$$

In the case of the reaction of compound **5** with GeI_4, the process is more complicated, resulting in a whole set of products, which were identified by ^1H NMR spectroscopy and GC-MS:



The adducts of the Diels—Alder reaction of germol **3** with alkenes and alkynes, derivatives of 7-germanorbornene and 7-germanorbornadiene, respectively, are of special interest. These bicyclic strained heterocycles could be convenient sources of bis(trimethylstannyl)germylene, which has not yet been studied.

It is known that Diels—Alder reactions of diorganylgermols, *e.g.*, 1,1-dimethyl-2,3,4,5-tetraphenyl-1-germacyclopenta-2,3-diene (**9**) occur most easily when dehydrobenzene generated *in situ* by the action of magnesium on *o*-fluorobromobenzene is used as a dienophile.[10—13,17,18] However, it turned out that the reaction of bis(trimethylstannyl)germol **3** with *o*-fluorobromobenzene in the presence of metallic magnesium (THF, 0°C) proceeds in a different way than the reaction of dimethylgermol **9**. Instead of the expected derivative of 7-germanorbornadiene, GC-MS indicated that the intensely red reaction mixture contained *o*-fluorophenyltrimenthyltin. The formation of this compound attests to the cleavage of the Ge—Sn bond in germol **3** under the action of labile *o*-fluorophenylmagnesium bromide, a precursor of dehydrobenzene (the cleavage of Ge—Ge and Sn—Sn bonds by arylmagnesium halides is described in Ref. 22):



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[*] Prolonged photolysis of compound **5** by light of both high- and low-pressure mercury lamps does not result in noticeable decomposition (hexane, 20 °C, 24 h).

Thus, the extremely labile Grignard reagent from *o*-fluorobromobenzene (*o*-FC_6H_4MgBr) cleaves the Ge—Sn bonds in bis(trimethylstannyl)germol **3** more rapidly than it decomposes to form MgBrF and dehydrobenzene. Unfortunately, we failed to determine unambiguously the structure of another, colored reaction product, which is likely organogermanium Grignard reagent **10**. We are continuing our studies in this area.

Experimental

^{1}H NMR spectra were recorded on Bruker AC 200 (200 MHz) and Jeol-FX 90Q (90 MHz) instruments in C_6D_6. IR spectra were obtained on a Bruker-IFS 113v instrument. GC-MS (electron impact, 70 eV) were recorded on a Finnigan MAT INCOS instrument (column RSL-200, 30 m×0.25 mm). A DRSh-1000 (1 kW) high-pressure mercury lamp was used for photochemical experiments. Solvents were dehydrated by standard procedures.[23] Germanium tetraiodide (chemically pure grade) was purified prior to use by sublimation *in vacuo*. Complex $GeCl_2 \cdot$diox was prepared by the known procedure,[24] Me_3SnNEt_2 was obtained by the procedure described in Ref. 25, and germol **2** was prepared by the procedure described in Ref. 26. 3,4-Dimethyl-1-germacyclopent-3-ene was synthesized by the reduction of 3,4-dimethyl-1,1-dichloro-1-germacyclopent-3-ene by $LiAlH_4$ in ether according to a general procedure[27] (b.p. 141—142 °C; Ref. 27: b.p. 142 °C).

Synthesis of 1,1-bis(trimethylstannyl)-2,3,4,5-tetraphenyl-1-germacyclopenta-2,4-diene (3). A solution of Me_3SnNEt_2 (1 g, 4.22 mmol) in anhydrous C_6H_6 (5 mL) was added to a solution of germol **2** (0.5 g, 1.17 mmol) in anhydrous C_6H_6 with stirring for 15 min at 20 °C in an Ar atmosphere. The reaction mixture was stirred at ~20 °C until the precipitate of germol **2** was completely dissolved (~1 h). Then H_2O (20 mL) was added with stirring, the organic layer was separated, the aqueous layer was extracted with ether (3×10 mL), and the combined organic extracts were dried over $MgSO_4$. After evaporation of the solvent, the residue was treated with 96% ethanol, and crystalline product **3** (0.72 g, 82%) was obtained. An analytically pure sample of compound **3** as lemon-yellow crystals with m.p. 114—116 °C was obtained by recrystallization from ethanol. ^{1}H NMR, δ: 0.34 (s, 18 H, Me_3Sn, $J(^{117,119}Sn—CH_3)$ = 50.4 Hz), 6.9—7.3 (m, 20 H, Ph). IR (KBr pellets), ν/cm^{-1}: 2912 (CH_3), 3051, 3016 ($C—H_{arom}$), 1589, 1485, 1439 (C=C). MS, *m/z*: 759 $[M^+]$, 593 $[M^+—SnMe_3]$, 563 $[M^+—SnMe_3—Me_2]$, 460 $[M^+—Sn_2Me_5]$. Found (%): C, 54.17; H, 5.32; Ge, 9.95; Sn, 30.62. $C_{34}H_{38}GeSn_2$. Calculated (%): C, 54.04; H, 5.03; Ge, 9.67; Sn, 31.26.

Synthesis of 1,1-bis(trimethylstannyl)-3,4-dimethyl-1-germacyclopent-3-ene (5). A solution of Me_3SnNEt_2 (1.64 g, 6.96 mmol) in anhydrous C_6H_6 (10 mL) was added dropwise to a solution of 3,4-dimethyl-1-germacyclopentene (0.6 g, 2.32 mmol) in anhydrous C_6H_6 (20 mL) at 20 °C with stirring in an Ar atmosphere. The reaction mixture was boiled for 6 h, then water (20 mL) was added. The organic layer was separated, the aqueous layer was extracted with C_6H_6 (2×30 mL), and the combined organic extracts were dried over $CaCl_2$. After the solvent was distilled off, the residue was distilled *in vacuo*. Compound **5** (0.54 g, 48%) with b.p. 90 °C (2 Torr) was obtained. ^{1}H NMR, δ: 0.35 (s, 18 H, Me_3Sn, $J(^{117,119}Sn\text{-}CH_3)$ = 48.3 Hz), 1.80 (s, 6 H, $-CH_3$), 2.22 (s, 4 H, $-CH_2$-, $J(^{117,119}Sn\text{-}Ge\text{-}CH_2\text{-})$ = 31.5). IR (in a thin layer), ν/cm^{-1}: 1651 (C=C), 2978, 2909 (CH_3). MS, *m/z*: 482 $[M]^+$, 467 $[M-Me]^+$, 400 $[(Me_3Sn)_2Ge]^+$, 385 $[(Me_3Sn)_2Ge-Me]^+$, 319 $[M-SnMe_3]^+$, 237 $[Me_3SnGe]^+$, 165 $[Me_3Sn]^+$. Found (%): C, 30.13; H, 6.01; Ge, 14.94; Sn, 48.84. $C_{12}H_{28}GeSn$. Calculated (%): C, 29.88; H, 5.81; Ge, 15.06; Sn, 49.26.

General procedure of photolysis. A solution of a substrate (0.2 mmol) in dry degassed benzene (0.5 mL) was irradiated in an Ar atmosphere with the UV light of a high-pressure mercury lamp in a quartz NMR-tube (20 °C, 6 h). The liquid products were recondensed in a high vacuum in a vessel cooled with liquid nitrogen. Volatile $Me_3SnSnMe_3$ was formed in quantitative yield (according to the data of GC-MS and ^{1}H NMR spectroscopy). The residue is a germanium-containing polymer.

Photolysis in the presence of a tenfold excess of a trapping agents of germylenes (2,3-dimethylbutadiene, 3,3,6,6-tetramethyl-1-thiacyclohept-4-yne) was performed in a similar way.

Reaction of compound 5 with complex $GeCl_2 \cdot$diox. A solution of $GeCl_2 \cdot$diox (64 mg, 0.2629 mmol) and heterocycle **5** (61.8 mg, 0.1285 mmol) in anhydrous C_6D_6 (0.5 mL) was stirred at ~20 °C in an Ar atmosphere. The reaction was entirely complete in 2 days (monitored by ^{1}H NMR spectra). The precipitate of germanium subchlorides $(GeCl)_x$ that formed was filtered off, and the liquid products from the filtrate were recondensed in a high vacuum. Volatile Me_3SnCl was formed in quantitative yield according to the data of ^{1}H NMR spectroscopy and GC-MS. The residue is a germanium-containing polymer.

Reaction of compound 5 with GeI_4. A solution of heterocycle **5** (33.9 mg, 0.07 mmol) and GeI_4 (86 mg, 0.148 mmol) in anhydrous C_6D_6 (0.5 mL) was stirred at ~20 °C in an Ar atmosphere. The reaction was entirely complete in 2 days. The precipitate of GeI_2 that formed was filtered off, and the liquid products from the filtrate were recondensed in a high vacuum. The volatiles (according to ^{1}H NMR spectroscopy and GC-MS) are Me_3SnI, Me_2SnI_2, $MeGeI_3$, and 3,4-dimethyl-1-iodo-1-germacyclopent-3-ene (**11**) in a ratio 0.4 : 1 : 1 : 0.2. MS of compound **11**, *m/z*: 283 $[M]^+$, 156 $[M—I]^+$, 201 $[GeHI]^+$. The nonvolatile residue is a germanium-containing polymer.

The reaction of germol **3** with *o*-fluorobromobenzene in the presence of magnesium (THF, 0 °C) was performed by a procedure[10,11] described for the synthesis of the 7-germanorbornadiene derivative from dimethylgermol **9** and dehydrobenzene.

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