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COORDINATION COMPOUNDS

# Synthesis, Structure, and Reactivity of Germanium-Containing Derivatives of Substituted Diethanolamines

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**Abstract**—The reaction of dialkanolamines $RN(CH_2CH_2O)(CHR'CHR'OH)$ (R = Me, Ph, $PhCH_2$; R' = H, Ph) with tetraethoxygermane gives either 2,2-diethoxy-1,3,6,2-dioxazagermocanes $RN(CH_2CH_2O)(CHR'CHR'O)Ge(OEt)_2$ or 1,7,9,15-tetraoxa-4,12-diaza-8-germaspiro[7.7]pentadecanes $[RN(CH_2CH_2O)(CHR'CHR'O)]_2Ge$ depending on the reactant ratio. The chemical behavior of the obtained compounds in substitution reactions at germanium was studied. The product structure was confirmed by elemental analysis data and $^1H$, $^{13}C$, and $^{19}F$ NMR spectroscopy. The cyclotrigermanoxane $[MeN(CH_2CH_2O)_2GeO]_3$ was studied by X-ray diffraction.

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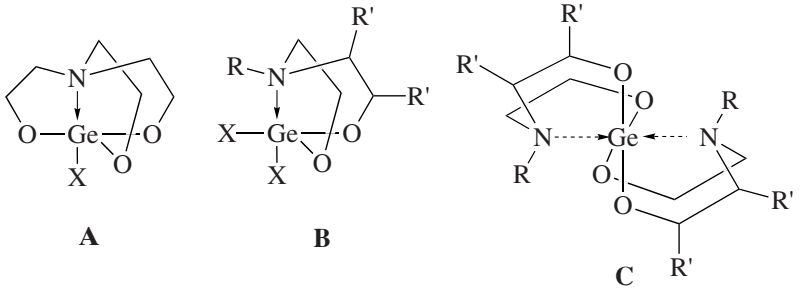
The interest in germanium derivatives is dictated by the extensive industrial use of germanium compounds, in particular, for the design of electronic instruments. Therefore, synthesis and study of previously unknown germanium compounds is important. In recent years, the attention of researchers has been largely concentrated on compounds in which the germanium atom has a nonclassical valence other than four. The molecules containing penta- and hexacoordinated germanium atoms show a broad spectrum of biological activities and find use even now as pharmaceutical drugs [1]. In our opinion, such compounds may also be promising for the design of new materials, in particular, nanostructures.

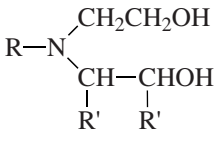
Germatranes A, cyclic ethers of trialkanolamines, are best studied hypercoordinated germanium derivatives [2]. Closely related 1,3,6,2-dioxazagermocanes B, cyclic ethers of dialkanolamines, are less known [3]. In these derivatives, the germanium coordination sphere has been extended through the germanium–nitrogen intramolecular contact whose properties, in particular, the bond strength, are determined by the environment of the atoms forming this bond [4]. As regards the material design, 1,3,6,2-dioxazagermocanes B seem more promising due to the presence of two substituents X at germanium, whose variation would give rise to molecules containing several ocane groups and to complex molecular assemblies. In addition, it has been shown previously that the length of intramolecular germanium–nitrogen bond in 1,3,6,2-dioxazagermocanes, unlike that in germatranes, varies over a broad range (2.080(3)–3.182(1) Å) [3].



**A** **B** **C**

Various synthetic approaches to 1,3,6,2-dioxazagermocanes have been developed. As a result, a broad range of 2,2-diorganyl- (B, X = alkyl, aryl) and 2,2-dihalo-1,3,6,2-dioxazagermocanes (B, X = halogen) have been prepared. The latter compounds seem to be good intermediates for the synthesis of new, more complex 1,3,6,2-dioxazagermocanes B having specified useful properties [5–8]. However, little data have been published on one more class of useful precursors, functionally substituted 1,3,6,2-dioxazagermocanes, in particular, 2,2-dialkoxy

derivatives (B, X = AlkO). Until recently, only compounds containing dialcohol residues as ligands have been reported [9]. It was only in 2006 that we published a paper [10] where demonstrated the existence of 2,2-dialkoxy-1,3,6,2-dioxazagermocanes and developed a preparative method for their synthesis by exchange between 2,2-dihalo-1,3,6,2-dioxazagermocanes and trialkylalkoxystannanes. It is evident that further studies along this line are required in order to develop other approaches to previously unknown 2,2-dialkoxy-1,3,6,2-dioxazagermocanes B, to study their structure and reactivity. It also appears important to continue studies on the chemistry of related compounds, 2,2-dihydroxy-1,3,6,2-dioxazagermocanes and their esters (B, X = OH, OC(O)Y), and 1,7,9,15-tetraoxa-4,12-diaza-8-germaspiro[7.7]pentadecanes (type C), which are called below germaspiro-bis-ocanes for the sake of simplicity. We studied derivatives of five dialkanolamines (**I**–**V**) containing N and C substituents with different electronic and steric properties.



**I–V**

**I**: R = Me, R' = H
**II**: R = $PhCH_2$, R' = H
**III**: R = Ph, R' = H;
**IV**: R = Me, R' = Ph (*erytho*)
**V**: R = Me, R' = Ph (*threo*)

## EXPERIMENTAL

All synthetic operations were carried out under argon using standard Schlenk glassware. The $^1H$, $^{13}C$, and $^{19}F$ NMR spectra were recorded on a Varian XR-400 spectrometer operating at 400, 100, and 376.4 MHz, respectively; $CDCl_3$ served as the solvent and the internal reference. The chemical shifts are referred to TMS.

**6-Methyl-2,2-diethoxy-1,3,6,2-dioxazagermocane (VI).** A solution of $Ge(OEt)_4$ (0.77 g, 3 mmol) and dialkanolamine **I** (0.36 g, 3 mmol) in toluene (15 mL) was refluxed for 5 h. The volatile components were removed in vacuo, and the residual yellow oil was reevaporated under an oil pump vacuum (0.1 mmHg) to give 0.65 g (77%) of compound **VI** as a colorless glassy solid.

$^1H$ NMR ($CDCl_3$, δ, ppm): 1.07–1.12 (m, 6H, $CH_3$); 2.44 (s, 3H, $NCH_3$); 2.54–2.69, 2.66–2.72 (both m, 4H, $NCH_2$); 3.67–3.75, 3.79–3.85 (both m, 8H, $OCH_2$).

$^{13}C$ NMR ($CDCl_3$, δ, ppm): 18.77, 18.84 ($CH_3$); 43.75 ($NCH_3$); 55.18, 57.45 ($NCH_2$, $OCH_2$); 59.41, 60.23 ($2O\underline{C}H_2CH_3$).

$^1H$ NMR ($CDCl_3$, δ, ppm, 50°C): 1.15 (t, 6H, $CH_3$); 2.49 (s, 3H, $NCH_3$); 2.64–2.70, (m, 4H, $NCH_2$); 3.79 (t, 4H, $OCH_2$), 3.90 (q, 4H, $OCH_2$).

For $C_9H_{21}GeNO_4$ anal. calcd. (wt %): C, 38.62; H, 7.56; N, 5.00.

Found (wt %): C, 38.56; H, 7.42; N, 4.82.

**6-Benzyl-2,2-diethoxy-1,3,6,2-dioxazagermocane (VII).** A mixture of $Ge(Oet)_4$ (3.35 g, 13 mmol), dialkanolamine **II** (2.58 g, 13 mmol), and benzene (20 mL) was refluxed for 5 h. The volatile components were removed in vacuo, and the solid residue was washed with ether to give 3.84 g (83%) of compound **VII** as a white solid.

$^1H$ NMR ($CDCl_3$, δ, ppm): 1.22 (t, 6H, $CH_3$); 2.51–2.60, 2.95–3.00 (both m, 4H, $NCH_2$); 3.78–3.84, 4.01–4.08 (both m, 4H, $OCH_2$); 3.97 (br.s, 2H, $CH_2Ph$); 7.30–7.34 (m, 5H, aromatic protons).

$^{13}C$ NMR ($CDCl_3$, δ, ppm): 17.51 ($CH_3$); 49.91, 56.92, 57.43 ($OCH_2$, $NCH_2$); 60.15 ($CH_2Ph$); 128.43, 131.07, 133.33, 139.32 (aromatic carbons).

For $C_{15}H_{25}GeNO_4$ anal. calcd. (wt %): C, 50.61; H, 7.08; N, 3.93.

Found (wt %): C, 49.86; H, 6.88; N, 3.52.

**Reaction of dialkanolamine IV with $Ge(OEt)_4$. *erythro*-6-Methyl-4,5-diphenyl-2,2-diethoxy-1,3,6,2-dioxazagermocane (VIII).** Synthetic operations were carried out as described for **VII** starting from $Ge(OEt)_4$ (1.1 g, 4.3 mmol) and dialkanolamine **IV** (1.17 g, 4.3 mmol). The volatile components were removed in vacuo, and the residue was extracted with ether. The ether-insoluble compound was germaspiro-bis-ocane **IX** ($^1H$ NMR data, the spectra are given below) (0.34 g, 26% in relation to alkanolamine). Removal of the ether from the filtrate gave diethoxigermocane **VIII** (0.59 g, 32%) as a yellow oil.

$^1H$ NMR ($CDCl_3$, δ, ppm): 1.17–1.30 (m, 6H, $CH_3$); 2.22 (s, 3H, $NH_3$); 2.73–2.76, 3.26–3.33 (both m, 2H, $NCH_2$); 3.77 (d, 1H, NCH); 3.69–3.87, 3.94–4.08 (both m, 6H, $OCH_2$); 5.42 (d, 1H, OCH); 7.02–7.14 (m, 10H, aromatic protons).

$^{13}C$ NMR ($CDCl_3$, δ, ppm): 18.62 ($CH_3$); 42.36 ($NCH_3$); 58.40, 59.78, 60.65, 71.86, 73.81 ($OCH_2$, $NCH_2$, NCH, OCH).

**Reaction of dialkanolamine III with $Ge(OEt)_4$ [11].** A mixture of dialkanolamine **III** (0.80 g, 4.4 mmol), $Ge(OEt)_4$ (0.56 g, 2.2 mmol), and toluene (20 mL) was refluxed for 50 h and cooled to room temperature. The volatile compounds (80%) were removed in vacuo, and the residue was collected on a filter, washed with anhydrous ether (2 × 3 mL), and dried in vacuum (0.1 mmHg) to give 0.42 g (44%) of compound **XI** as a white powder. The $^1H$ and $^{13}C$ NMR spectra were consistent with published data [11]. The solvents were removed from the filtrate in vacuo to give a yellow oil, which was a mixture of two compounds: germaspiro-bis-ocane **XI** and diethoxygermocane **XII**. The latter could not be isolated in a pure state.

$^1H$ NMR ($CDCl_3$, δ) (for **XII**): 0.99 (t, 6H, $CH_3$); 3.43 (t, 4H, $NCH_2$); 3.69 (q, 4H, $OCH_2$), 4.09 (t, 4H, $OCH_2$), 6.97–6.93 (m, aromatic protons).

$^{13}$C NMR ($CDCl_3$, δ, ppm) (for **XII**): 18.18, 56.68, 60.95 ($NCH_2$); 63.27 ($OCH_2$); 116.05, 119.90, 128.24, 149.32 (aromatic carbons).

***erythro*-4,12-Dimethyl-2,3,10,11-tetraphenyl-1,7,9,15-tetraoxa-4,12-diaza-8-germaspiro[7,7]pentadecane (IX).** A mixture of dialkanolamine **IV** (2.6 g, 9.7 mmol), $Ge(OEt)_4$ (1.23 g, 4.9 mmol), and benzene (25 mL) was refluxed for 50 h. The volatile compounds were removed in vacuo, and the residue was recrystallized from toluene to give 2.28 g (76%) of compound **IX** as a white powder. The $^1$H and $^{13}$C NMR spectra exhibited signals for three diastereomers, which were not unambiguously assigned.

$^1$H NMR ($CDCl_3$, δ): 2.15, 2.28, 2.33 (all s, 6H, $CH_3N$); 2.44–2.51, 3.33–3.48, 3.96–3.98, 4.18–4.33 (all m, 8H, $CH_2$); 3.46, 3.72 (both d, 2H, $NCH_2$), 5.23 (d), 5.54 (br.s), 6.03 (br.s, 2H, OCH); 6.90–7.09, 7.26–7.34 (both m, 20H, aromatic protons).

$^{13}$C NMR ($CDCl_3$, δ, ppm): 43.31, 43.79, 45.21 ($NCH_3$); 56.44, 57.88, 58.78 ($NCH_2$); 60.87, 61.28 (NCH) (signal for one diastereomer was not observed); 72.53, 74.36, 75.55, 73.64, 75.36, 74.74 (OCH); 125.84, 126.06, 126.19, 126.38, 126.88, 126.95, 127.06, 127.18, 127.28, 127.36, 127.42, 127.84, 127.92, 128.09, 129.29, 130.54, 130.80, 130.91, 141.59, 141.83, 142.51 (aromatic carbons).

For $C_{34}H_{38}GeN_2O_4$ anal. calcd. (wt %): C, 66.46; H, 6.10; N, 4.52.

Found (wt %): C, 66.96; H, 6.00; N, 4.21.

***threo*-4,12-Dimethyl-2,3,10,11-tetraphenyl-1,7,9,15-tetraoxa-4,12-diaza-8-germaspiro[7,7]pentadecane (XIII)** was prepared as described for **X** by refluxing dialkanolamine **V** (0.4 g, 1.5 mmol), $Ge(OEt)_4$ (0.19 g, 0.7 mmol), and benzene (10 mL) for 50 h. Recrystallization from toluene gave 0.38 g (89%) of compound **XIII** as a white powder.

$^1$H NMR ($CDCl_3$, δ): 2.29 (s, 6H, $CH_3N$); 2.41–2.51 (m, 4H, $NCH_2$); 3.61 (d, 2H, NCH), 3.67–3.77 (m, 4H, $OCH_2$); 5.04 (d, 2H, OCH); 7.07–7.13, 7.19–7.26, 7.34 (all m, 20H, aromatic protons).

For $C_{34}H_{38}GeN_2O_4$ anal. calcd. (wt %): C, 66.46; H, 6.10; N, 4.52.

Found (wt %): C, 66.80; H, 6.27; N, 4.58.

**6-Benzyl-2,2-dihydroxy-1,3,6,2-dioxazagermocane (XIV).** $GeO_2$ (1.1 g, 11 mmol) was added in one portion to a mixture of diethanolamine **II** (2.1 g, 11 mmol) and water (10 mL). The mixture was refluxed for 4 h, water was removed at a reduced pressure, and the residue was recrystallized from a methanol/acetone mixture (1 : 3) to give 1.7 g (56%) of compound **XIV** as a white powder.

$^1$H NMR ($CDCl_3$, δ, ppm): 2.44–2.50, 2.92–2.98 (both m, 4H, $NCH_2$); 3.75–3.79, 3.98–4.03 (both m, 4H, $OCH_2$); 4.13 (s, 2H, $CH_2Ph$); 7.19–7.22, 7.29–7.31 (both m, 5H, aromatic protons).

$^{13}$C NMR ($CDCl_3$, δ, ppm): 50.06, 56.81, 57.58 ($OCH_2$, $NCH_2$); 127.87, 128.25, 131.24, 134.12 (aromatic carbons).

For $C_{11}H_{17}GeNO_4$ anal. calcd. (wt %): C, 44.06; H, 5.71; N, 4.67.

Found (wt %): C, 43.80; H, 5.58; N, 4.36.

**2,2-Dihydroxy-6-methyl-1,3,6,2-dioxazagermocane (XV).** Water (3 mL) was added to a solution of germaspiro-bis-ocane **X** (2 g, 6.5 mmol) in toluene (25 mL). The reaction mixture was stirred for 72 h. The volatile compounds were removed in vacuo, and the residue was recrystallized from a methanol/acetone mixture (1 : 3) to give 1.3 g (89%) of compound **XV** as colorless crystals.

$^1$H NMR ($CDCl_3$, δ, ppm): 2.58 (s, 3H, $NCH_3$); 2.65–2.71 (m, 4H, $NCH_2$); 3.75–3.79, 3.85–3.90 (both m, 4H, $OCH_2$).

$^{13}$C NMR ($CDCl_3$, δ, ppm): 44.59 ($NCH_3$); 55.82 ($NCH_2$); 58.10 ($OCH_2$).

According to $^1$H and $^{13}$C NMR data, the filtrate contained dialkanolamine **I**.

**Cyclotrigermanoxane (XVI).** A toluene solution of germaspiro-bis-ocane **X** (0.1 mL) was allowed to stand in air at room temperature for several days. This gave crystals suitable for X-ray diffraction.

**6-Methyl-1,3,6,2-dioxazagermocane-2,2-diyl *bis*(trifluoroacetate) (XVIII).** A solution of $(CF_3CO)_2O$ (0.54 g, 0.24 mmol) in dioxane (10 mL) was slowly added to a solution of 2,2-dichloro-6-methyl-1,3,6,2-dioxazagermocane **XVIII** (0.21 g, 0.8 mmol) in dioxane (10 mL). The trifluoroacetyl chloride evolved was collected in a trap cooled to –78°C. For complete removal of the chloride, the reaction mixture was vigorously stirred for 2 h at 40°C. The resulting solid residue was washed with ether to give 0.31 g (92%) of compound **XVIII** as a white powder.

$^1$H NMR ($CDCl_3$, δ, ppm): 3.01 (s, 3H, $NCH_3$); 3.61 (t, 4H, $CH_2$); 4.81 (t, 4H, $CH_2$).

$^{13}$C NMR ($CDCl_3$, δ, ppm): 41.69 ($CH_3$); 54.78, 61.67 ($CH_2$).

$^{19}$F NMR ($CDCl_3$, δ, ppm): –77.39 (s, $CF_3$).

***erythro*-6-Methyl-4,5-diphenyl-2,2-difluoro-1,3,6,2-dioxazagermocane (XIX).** A solution of $BF_3 \cdot Et_2O$ (0.05 g, 0.33 mmol) in $CH_3CN$ (7 mL) was added dropwise to a solution of 2,2-diethoxygermocane **VIII** (0.21 g, 0.50 mmol) in $CH_3CN$ (3 mL) heated to 50°C. The mixture was stirred at 50°C for 8 h and the volatile compounds were removed in vacuo. Ether (5 mL) was added to the residue and the mixture was stirred for 2 h. The precipitate was collected on a filter and dried in vacuo to give compound **XIX** (0.14 g, 72%) as a white solid. The $^1$H and $^{13}$C NMR spectra exhibited signals for two diastereomers in 3 : 1 ratio.

$^1$H NMR (DMSO-$d_6$, δ, ppm): 2.19, 2.38 (both s, 3H, $CH_3N$); 2.78–2.82, 3.03–3.09 (both m, 2H, $NCH_2$); 3.52–3.61, 3.99–4.05 (both m, 2H, $OCH_2$), 4.11, 4.12 (both d, 1H, NCH); 5.28, 5.58 (both d, 1H, OCH); 6.90–7.02, 7.06–7.09, 7.12–7.16 (all m, 10H, aromatic protons).

$^{13}$C NMR (DMSO-$d_6$, δ, ppm): 54.93, 59.09 ($NCH_3$); 59.85, 61.34 ($NCH_2$); 68.81, 68.95 ($OCH_2$); 72.53, 73.90, 76.14, 79.13 (NCH, OCH); 125.56, 125.90, 127.35, 127.67, 128.00, 130.90, 139.65, 140.59 (aromatic carbons).

$^{19}$F NMR (DMSO-$d_6$, δ, ppm): –143.90 (1F), –141.87 (1F) (GeF).

For $C_5H_{11}F_2GeNO_2$ anal. calcd. (wt %): C, 26.38; H, 4.87; N, 6.15.

Found (wt %): C, 27.03; H, 4.67; N, 6.34.

**Germocane XX.** A solution of 2,2-dihydroxy-6-methylgermocane **XV** (0.22 g, 1 mmol) and 9-hydroxy-9*H*-fluorene-9-carboxylic acid (0.22 g, 1 mmol) in toluene (20 mL) was refluxed for 10 h to give compound **XX** (0.3 g, 72%) as a white solid.

$^1$H NMR ($C_6D_6$, δ, ppm): 2.67 (s, 3H, $NCH_3$); 2.92–2.96, 3.09–3.14 (both m, 4H, $CH_2$); 4.10–4.13 (m, 4H, $CH_2$); 7.14–7.16, 7.34–7.37, 7.45, 7.62 (all m, 8H, aromatic protons).

For $C_{19}H_{19}GeNO_5$ anal. calcd. (wt %): C, 55.12; H, 4.63; N, 3.38.

Found (wt %): C, 55.34; H, 4.67; N, 3.34.

**Reaction of 2,2-dihydroxy-6-methylgermocane XV with menthol.** A solution of 2,2-dihydroxy-6-methylgermocane **XV** (0.46 g, 2 mmol) and *L*-menthol (0.64 g, 4 mmol) in toluene (20 mL) was refluxed for 10 h. According to $^1$H NMR, no reaction took place.

**4-Methyl-12-phenyl-1,7,9,15-tetraoxa-4,12-diaza-8-germaspiro[7,7]pentadecane (XXI).** A mixture of diethanolamine **III** (0.32 g, 1.8 mmol), 2,2-diethoxy-6-methylgermocane (0.50 g, 1.8 mmol), and toluene (20 mL) was refluxed for 25 h and cooled to room temperature. The volatile compounds (80%) were removed in vacuo, and the precipitate was collected on a filter, washed with anhydrous ether (2 × 3 mL), and dried in vacuum (1 mmHg) to give 0.56 g (84%) of compound **XXI** as a white powder.

$^1$H NMR ($CDCl_3$, δ): 2.48 (s, 6H, $NCH_3$); 2.47–2.52, 2.58–2.66 (both m, 4H, $NCH_2$); 3.29–3.33, 3.54–3.59 (both m, 4H, $OCH_2$), 3.36–3.40 (dt, 4H, $NCH_2$); 4.06, 4.10 (both t, 4H, $OCH_2$); 6.60–6.63, 6.80–6.82, 7.13–7.25 (all m, aromatic protons).

$^{13}$C NMR ($CDCl_3$, δ, ppm): 44.19 ($NCH_3$); 52.97, 53.27, 55.06, 57.12, 61.52, 61.97 ($NCH_2$, $OCH_2$); 112.84, 115.85, 128.67, 150.57 (aromatic carbons).

For $C_{15}H_{24}GeN_2O_4$ anal. calcd. (wt %): C, 48.83; H, 6.56; N, 7.59.

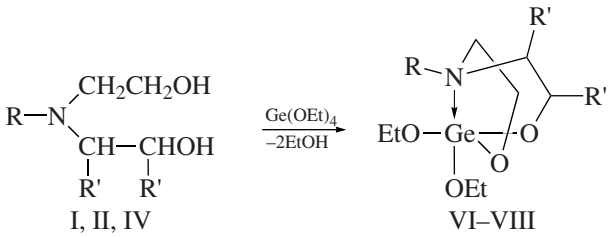
Found (wt %): C, 47.98; H, 6.37; N, 7.38.

**X-ray diffraction study** of compound **XVI** was carried out on a Bruker SMART APEX automated diffractometer at 120 K (Mo$K_\alpha$ radiation, λ = 0.71073 Å, graphite monochromator). The crystals of **XVI** ($C_{15}H_{33}Ge_3N_3O_9$, $M$ = 617.21) are monoclinic, space group $P2_1/c$, $a$ = 10.5973(12) Å, $b$ = 18.002(2) Å, $c$ = 11.8721(13) Å, β = 100.893(3)°, $V$ = 2224.1(4) Å$^3$, $Z$ = 4, $\rho_{calcd}$ = 1.843 g/cm$^3$, μ(Mo$K_\alpha$) = 4.080 mm$^{-1}$, $F$(000) = 1248. The intensities of 12981 reflections (of these, 5295 independent reflections, $R_{int}$ = 0.0354) were measured in the ω scan mode in the range 2.99° < θ < 28.00° (–13 ≤ $h$ ≤ 13, –23 ≤ $k$ ≤ 23, –15 ≤ $l$ ≤ 12). The structure was solved by direct methods (SHELX-86 [12]). All non-hydrogen atoms were refined by full-matrix anisotropic least-squares on $F^2$ (SHELXL-97 [13]). One of the three ocane fragments is rotationally disordered over two positions with an occupancy ratio of 0.59/0.41. All hydrogen atoms (except for disordered ones) were found from a difference Fourier synthesis and refined isotropically. The hydrogen atoms of disordered groups were placed in calculated positions and refined using the riding model. The final $R$ values were $R_1$ = 0.0320 and $wR_2$ = 0.0691 for 4271 reflections with $I > 2\sigma(I)$ and 388 refinement parameters; GOOF = 1.020, $\Delta\rho_{min/max}$ = –0.480/0.713 e Å$^{-3}$.

## RESULTS AND DISCUSSION

2,2-Dialkoxygermocanes were synthesized for the first time using organotin reagents [10]. Previously, the lack of prospects in using the most obvious approach to 2,2-dialkoxygermocanes, transalkoxylation reaction, was apparently based on publication [14] stating that the expected products are not formed in this reaction; rather, germaspirobis(ocane) $[HN(CH_2CH_2O)_2]_2Ge$ was isolated from the reaction mixture.

We studied the reaction of dialkanolamines **I**, **II**, and **IV** with tetraethoxygermane and found that dialkoxygermocanes are formed in satisfactory yields.

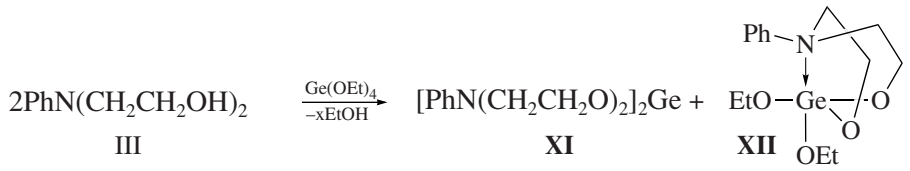



I, II, IV — VI–VIII

+I, VI: R = Me, R' = H; II, VII: R = $PhCH_2$, R' = H
IV, VIII: R = Me, R' = Ph (*erythro*)

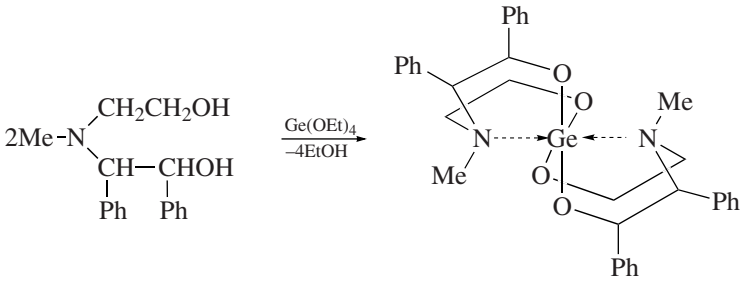
Previously we have shown that the reaction of $Ge(OAlk)_4$ with two equivalents of amino alcohols **I** and **III** gives germaspirobis(ocanes) (C: **X**, **XI**) [11]. Further study of this reaction carried out here has

shown that the reaction of $Ge(OEt)_4$ with **III** yields diethoxygermocane **XII** as a by-product.



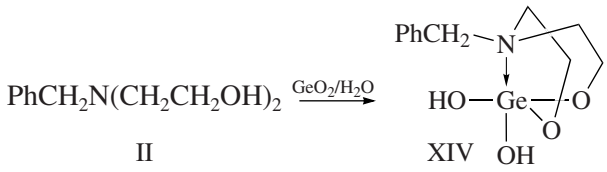

III **XI** **XII**

The reactions of dialkanolamines **IV** and **V** with $Ge(OEt)_4$ in a 2 : 1 ratio give germaspirobis(ocanes) **IX** and **XIII**, respectively, in high yields.



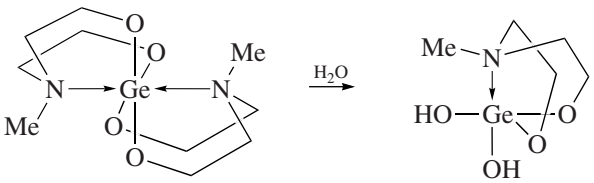

IV, IX: *erythro*; V, XIII: *threo* IX, XIII

2,2-Dihydroxy derivatives can be prepared both by treatment of germanium dioxide with dialkanolamine in the presence of water and by hydrolysis of germaspirobis(ocanes) with excess $H_2O$. Both approaches were used in this study. Dihydroxy derivative **XIV** was obtained in 56% yield by refluxing a mixture of dialkanolamine **II** and $GeO_2$ in water.



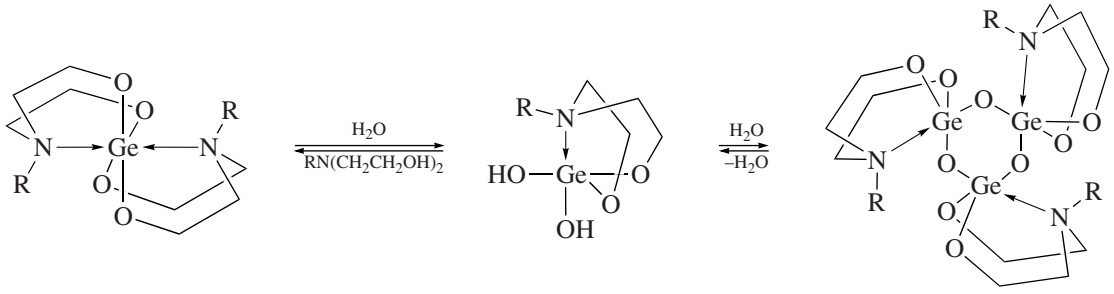

II XIV

The controlled hydrolysis of germaspirobis(ocane) **X** under mild conditions afforded 2,2-dihydroxy derivative **XV** in a high yield.




**X** XV

Compound **XV** was synthesized by the reaction of methyldiethanolamine **I** with $GeO_2/H_2O$ [15]. The transformation of 2,2-dihydroxygermocanes into spirocyclic derivatives or into cyclotrigermoxanes depending on the N-substituent was reported in the literature. The addition of water to these compounds results again in the initial 2,2-dihydroxygermocanes [16].

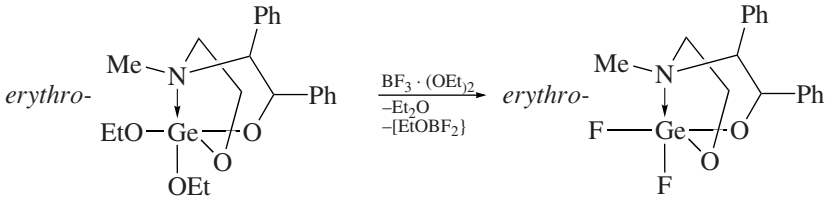


We obtained the crystals of **XVI** (R = Me) upon long-term storage of germaspirobis(ocane) **X** in air and confirmed their structure by X-ray diffraction.

The first representative of a new class of germocanes, 2,2-dicarboxylatogermocane, was prepared by treatment of 2,2-dichloro-6-methyl-1,3,6,2-dioxazagermocane **XVII** with trifluoroacetic anhydride.


**XVII** XVIII

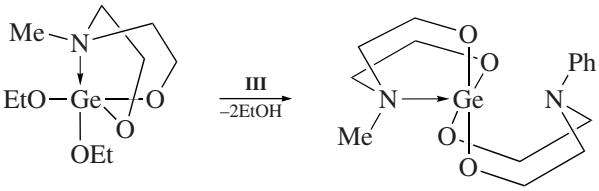
We studied the chemical properties of the compounds synthesized. Previously, we found that 2,2-dihydroxygermocane **XV** undergoes exchange with boron trifluoride etherate to give trifluoro derivative [10]. In this study we showed that the ethoxy groups in 2,2-diethoxygermocanes can be replaced by fluorine atoms.




It was also found that germocane **XV** easily reacts with 9-hydroxy-9*H*-fluorene-9-carboxylic acid to give dispirocyclic derivative **XX**.

However, the reaction of **XV** with two equivalents of L-menthol does not result in the expected dimenthoxygermocane: after 10 h of refluxing in toluene, the reaction mixture still contained only the starting compounds according to $^1$H NMR data.

An important result of this study is the synthesis of unsymmetrical germaspirobis(ocane) **XXI** by the reaction of diethoxy derivative **VI** with 1 equivalent of amino alcohol **III**.

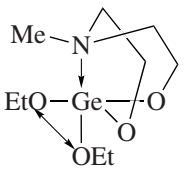



Note that, in the case of similar titanium derivatives, no such unsymmetrical derivatives are formed, but the reactions give mixtures of two symmetrical titanospirobis(ocanes) [17]. The structure of compound **XXI** is discussed in detail below.

The structures of the obtained compounds were confirmed by NMR spectroscopy and, in some cases, by elemental analysis data. Note that preparation of analytically pure samples of 2,2-dialkoxy derivatives is hampered due to their hydrolytic instability and the presence of minor germaspirobis(ocane) impurities. The latter is also true for dihydroxy derivatives.

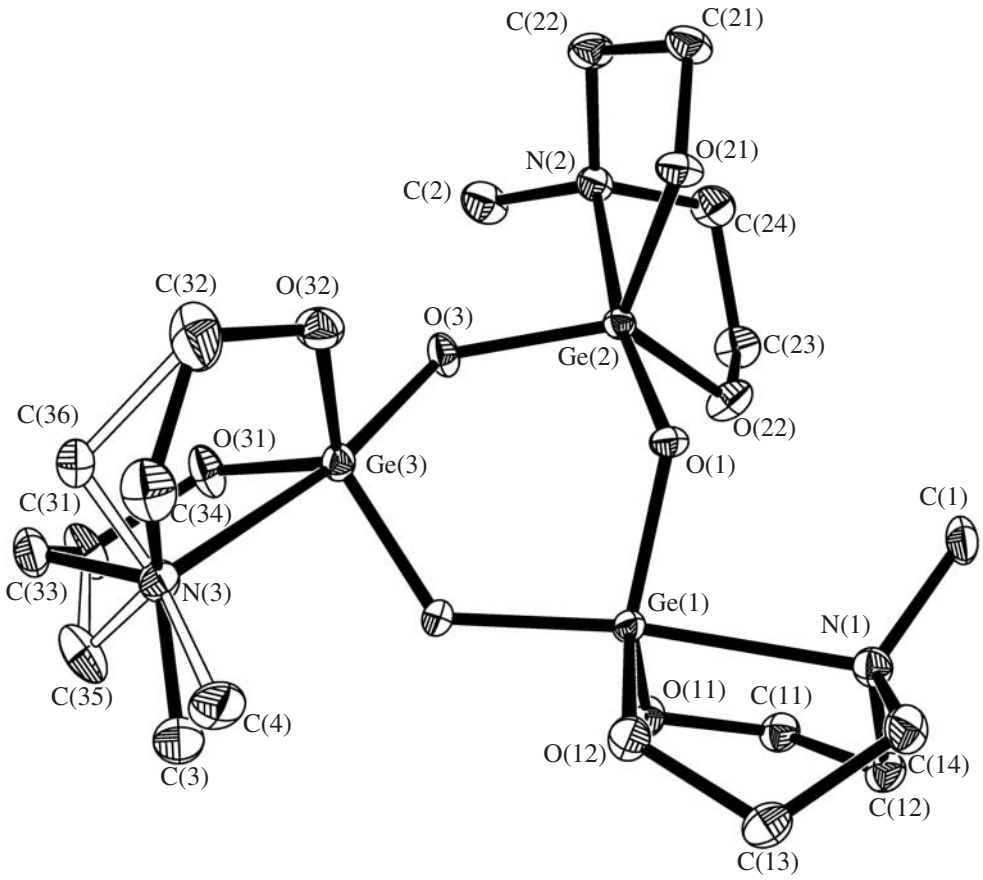
The $^1$H, $^{13}$C, and $^{19}$F NMR data of the prepared germocanes correspond to the proposed structures. A key aspect considered during the NMR study of the product structures in solutions is the presence or absence of transannular interactions. For C-unsubstituted germocanes, the conclusion about the presence of transannular interactions in solution was based on the downfield shift of the proton signals of the $NCH_2$ groups of the ocane cage with respect to those of model compounds (trimethyl silyl ethers of dialkanolamines [10]). For C-substituted ocanes, this conclusion was based on the existence of the compounds as diastereomer mixtures due to the chirality of nitrogen in these compounds with a transannular bond.

An NMR study of germocane **VI** showed the presence of two non-equivalent ethoxy groups. These is due to the absence or difficulty of the conformation exchange of the positions of axial and equatorial EtO groups.




**VI**

As the temperature of recording the spectrum increases to 50°C, the signals of the EtO protons coa-




Molecular structure of compound **XVI**.

Key structural parameters of **XVI**: bond lengths (*d*) and bond angles (ω)

| Bond | *d*, Å | Bond | *d*, Å |
|---|---|---|---|
| Ge ← N | 2.231(2)–2.284(2) | Ge–$X_{ax}$ | 1.794(2)–1.804(2) |
| Ge–O | 1.781(2)–1.795(2) | Ge–$X_{eq}$ | 1.738(2)–1.755(2) |
| Angle | ω, deg | Angle | ω, deg |
| $NgeX_{ax}$ | 169.68(9)–172.96(9) | $OGeX_{eq}$ | 114.8(1)–122.61(9) |
| $NGeX_{eq}$ | 85.67(9)–87.64(9) | $OGeX_{ax}$ | 92.55(9)–95.21(9) |
| NGeO | 80.90(9)–83.06(9) | $X_{ax}GeX_{eq}$ | 100.17(9)–104.43(9) |
| OGeO | 117.05(9)–118.4(1) | CNC | 107.4(5)–115.5(5) |
| | | CNGe | 101.1(3)–118.0(2) |

lesce; thus, the activation energy of conformation transition can be estimated as <15 kcal/mol.

Previously, the hexacoordination of germanium in germaspiro-bis-ocane **X** in a $CDCl_3$ solution and tetracoordination of germanium in **XI** under similar conditions were demonstrated [11]. The germaspirobis(ocanes) **IX** and **XIII** prepared in this work also contain a hexacoordinated germanium atom. Conversely, analysis of the spectral data of unsymmetrical germaspirobis(ocane) **XXI** and their comparison with the data for **X** and **XI** (the proton chemical shifts of **XXI** are similar to those for **X** and **XI**) leads to the conclusion that **XXI** contains a pentacoordinated germanium atom with a strong MeN–Ge bond. Thus, compound **XXI** is the first representative of a germaspirobis(ocane) with a pentacoordinated central atom.

The structure of germocane **XVI** in the solid phase was studied by X-ray diffraction (figure, table). The key structural parameters of **XVI** confirm the trends found previously for germocanes with electron-acceptor substituents at germanium [3]. Compound **XVI** was found to contain rather strong transannular Ge ← N bonds (2.231(2)–2.284(2) Å). In the germocanes with acceptor substituents studied previously, the Ge–N distance varies from 2.080(3) to 2.217(2) Å [3]. Some increase in the Ge ← N distance in **XVI** can be attributed to a decrease in the electron-acceptor properties of oxygen in the Ge–O–Ge group compared with those in the previously studied compounds with Ge–O–Ge and Ge–O–H groups. In addition, this increase may be due to steric reasons, i.e., the presence of three bulky substituents in the $(Ge–O)_3$ six-membered ring.

The coordination polyhedron of each of the three germanium atoms is a slightly distorted trigonal bipyramid. The nitrogen atoms and the Ge–O–Ge oxygen atoms occur in axial (ax) positions, while diethanolamine oxygen atoms and oxygen of the second Ge–O–Ge group occupy equatorial (eq) positions. The $NGeX_{ax}$ angles are nearly linear (169.68(9)°–172.96(9)°). The germanium atom is shifted from the plane formed by equatorial substituents in the direction opposite to nitrogen.

The $Ge–O_{ax}$ distances are much longer than $Ge–O_{eq}$, which confirms the presence of germanium–nitrogen electronic interaction. The nitrogen environment is a slightly distorted tetrahedron. The atoms of all five-membered Ge–O–C–C–N rings do not lie in one plane, the carbon atoms in the α-position to nitrogen being deviated from the root-mean-square plane to the highest extent. The eight-membered Ge–O–C–C–N–C–C–O rings in **XVI** have a "chair–boat" conformation.

## ACKNOWLEDGMENTS

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