Synthesis and Characterization of 1-Allyl-3,7,10-trimethylgermatrane and 1-Allylazagermatranes

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The reaction between Br₃GeAll (1) and N(CH₂CHMeOSnBu₃)₃ (2, mixture of isomers) yielded N(CH₂CHMeO)₃GeAll (3) as a mixture of diastereomers. Three azagermatranes of the type N(CH₂CH₂NHR)₃GeAll (9, R = H; 10, R = Me; 11, R = Me₃Si) have been synthesized from the reaction of (Me₂N)₃GeAll (5) with N(CH₂CH₂NHR)₃ (R = H, 6; Me, 7; Me₃Si, 8). Composition and structures of the new compounds were established by elemental analyses, ¹H and ¹³C NMR spectroscopy and mass spectrometry.

Introduction

In the past few years we have been working on the improvement of synthetic routes leading to functionalized germatranes [1 - 4]. Recently, we reported on the synthesis of 1-allylgermatrane and gave a first example of the reaction of this compound with retention of the Ge-C bond [1]. Thus, we became interested in preparing other types of 1-allylgermatranes in order to study the influence of various substituents at the “atrane” moiety regarding the reactivity of the carbon-carbon double bond and of the germanium-carbon bond and the configurational stability of the “atrane” fragment. As part of our studies we synthesized and characterized 1-allyl-3,7,10-trimethylgermatrane 3 and 1-allylazagermatranes, N(CH₂CH₂NHR)₃GeAll 9 - 11.

Results and Discussion

Allyltribromogermane 1 reacts readily with a mixture of isomers of N(CH₂CHMeOSnBu₃)₃ (2) under mild conditions to give 1-allylgermatrane 3 in 81% yield (Scheme 1). After recrystallization from n-pentane 3 (colourless crystals, m. p. 72 - 73 °C) was obtained as a mixture of stereoisomers, 3A (R/S, major component) and 3B (R/S, minor component), which differ in the orientation of the methyl groups relative to the Ge-N bond axis which is evident from the double appearance of all signals in the ¹H and ¹³C NMR spectra.

\[
\text{Br}_3\text{GeAll} + \text{N(CH}_2\text{CHMeO)SnBu}_3\text{)} \\
\text{Bu}_3\text{SnCl} \\
\text{3A (R/S, major component)} \\
\text{3B (R/S, minor component)}
\]

Scheme 1.

Germatrane 3 can also be prepared starting from product 4 as shown in Scheme 2.

\[
\text{AlBr} + \text{GeCl}_3 \rightarrow \text{AlCl}_3 + \text{GeBr}_3 \\
\text{Br}_3\text{Cl} + \text{GeAll} \\
\text{Product 4 (n = 0-3)} \\
\text{3 (2 Enantiomers)}
\]

Scheme 2.

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At the beginning of our work only a few 1-substituted azagermatranes had been published by Verkade et al. [5]; we have shown that the reaction of \((\text{Me}_2\text{N})_3\text{GeAll}\) 5 with \(\text{N}((\text{CH}_2\text{CH}_2\text{NH})_3\) 6 (1.5 h, 60 - 70 °C) leads to 9 (yield 81%) with elimination of \(\text{Me}_3\text{NH}\). Under the same conditions no reaction of 5 with \(\text{N}((\text{CH}_2\text{CH}_2\text{NMe})_3\) 7 took place, and the use of \(\text{N}((\text{NH})_2\text{SO}_4\) as a catalyst [5] in this case led to the formation of polymeric products. We were able, however, to obtain 1-allyl-N,N',N"-trimethyl-azagermatrane 10 by refluxing a toluene solution of 5 d. 1-Allyl-N,N',N"-tris(trimethylsilyl)azagermatrane 11 was prepared analogously (35% after distillation) (Scheme 3).

Compounds 3 and 9 - 11 contain different reactivity centers (C=C-, Ge-C-, N-H-, \(\text{Me}_3\text{Si}-\)bonds) and therefore can be considered as new key molecules in the design of new types of germatranes and azagermatranes.

\(^1\text{H}\) and \(^{13}\text{C}\) NMR spectra are in accord with the suggested structures: in the \(^1\text{H}\) NMR spectrum of germatrane 3 signals of the protons of the NCH\(_2\)CH\(_2\)CH\(_3\)_O groups of the “atrane” framework appear as complex multiplets (ABXM\(_3\) spin system). In this case the composition of mixtures can be examined by \(^{13}\text{C}\) NMR spectroscopy as described earlier for other 1-substituted germatranes [2a, 3, 6]. In the \(^1\text{H}\) NMR spectra of 9 - 11 signals of the methylene protons of the azagermatrane skeleton appear as a set of two pseudo-triplets, forming an \text{AA'BB'} spin system \(J = 5.2 - 6.0\text{ Hz}\). This pattern also is a general feature of the “atrane” framework for azagermatranes [7]. In the \(^{13}\text{C}\) NMR spectra of 9 - 11 the signals of the carbon atoms of the “azatran” skeleton have the expected values [5]; chemical shift data of the proton and carbon atoms of the allyl group are also found in the expected range.

In the mass spectra of 3A the peak of highest intensity at \(m/z\) 262 corresponds to the germatranyl ion resulting from the loss of the apical substituent from the parent ion. This behaviour is analogous to that observed for 1-allylgermatrane [1] and is assumed to reflect the relative bond strength in the Ge-O ring. In contrast to these data, in the mass spectra of 9 and 10 intensities of the azagermatranyl ion are only 8% and 39%, respectively.

**Scheme 3.**

Experimental

All reactions were carried out under argon atmosphere. Solvents were dried by standard methods and distilled prior to use. Elemental analyses were carried out by the Microanalytical Laboratory of the Chemistry Department of the Moscow State University and by the Fachbereich Chemie, Universität Marburg (Heraeus-Rapid-Analyzer). NMR spectra were recorded at 25 °C on Bruker AC 300 and Varian XVR-400 spectrometers, \(\text{C}_6\text{D}_6\) and \(\text{CDCl}_3\) were used as solvents and for internal deuterium lock. Chemical shifts (\(\delta\)) of the \(^1\text{H}\) and \(^{13}\text{C}\) NMR are given in ppm relative to internal TMS. Assignments of the \(^{13}\text{C}\) NMR data were supported by APT experiments. Mass spectra (EI-MS) were recorded on a Varian CH-7a device using electron impact with an ionization energy of 70 eV; all assignments were made with reference to the most abundant isotopes. Melting points are uncorrected.

Allyltribromogermane 1 was synthesized from allylbromide and \(\text{GeBr}_2\)-dioxane according to the literature [1]. Compound 4 (\(\text{Br}_3\text{GeAll}\)) was obtained according to a modified procedure \[9\]. 1-allyltribromogermane 1 was synthesized from allylbromide and \(\text{GeBr}_2\)-dioxane according to the literature [1]. Compound 4 (\(\text{Br}_3\text{GeAll}\)) was obtained according to a modified procedure \[9\].
ture was allowed to warm to room temperature and stirred for 5 h. The reaction mixture was cooled to -78°C and Me₂SiCl (13.0 g, 0.120 mol) was added; the reaction mixture was allowed to warm to room temperature and stirred overnight. Excess of Me₂SiCl and THF was evaporated and the residue was extracted with n-hexane (120 ml). The total volume was reduced to ~ 30 ml, precipitated LiCl was filtered off and residual n-hexane was removed in vacuo. According to NMR spectroscopy the residue was essentially pure Me₂Si-tren 8 (7.51 g, 69%) which was used in further experiments without purification.

1H NMR (CD₆D₆, 400 MHz): $\delta$ = 0.11 (s, 27H, SiMe₃), 0.78 (br s, 3H, NH), 2.35 (m, 6H, SiNCH₂), 2.74 (m, 6H, NCH₂). 13C NMR (CDCl₃): $\delta$ = 20.78, 20.91, 23.41 (CH₃); 25.71 (GeCH₂); 61.78, 62.54, 65.60 (NCH₂); 63.20, 63.94, 65.68 (OCH); 113.23 (=CH₂), 135.72 (=CH). 1H NMR (CDCl₃): $\delta$ = 20.58 (=CH₂), 25.58 (GeCH₂), 59.34 (NCH₂); 62.70 (OCH); 113.06 (=CH₂), 135.42 (=CH). EI-MS, m/z (rel. int., assign.): 262 (100%, M⁺ - H₁). Analysis for C₁₁H₃₀GeN₃ (236.87): $m/z$ 217 (100% (M⁺-GeN²⁺)), 118 (100% (M⁺-GeN⁺)), 52 (73% (M⁺-Ge)).

Analysis for C₁₁H₃₀GeN₃ (236.87): 
Calcd C 44.25 H 10.01 N 17.33%.
Found C 44.25 H 10.01 N 17.33%.

1-Allylazagermatrane 9

A mixture of 5 (1.08 g, 4.4 mmol) and tren 6 (0.61 g, 4.2 mmol) was stirred for 1.5 h at 60-70°C, after which evolution of Me₂NH ceased. Distillation gave 0.78 g (72%) of 9 as a colourless liquid, b.p. 96 - 97°C/0.1 Torr.

1H NMR (CD₆D₆, 400 MHz): $\delta$ = 0.70 (br s, 3H, NH), 1.51 (m, 2H, GeCH₂), 2.21 (t, 6H, NCH₂), 2.72 (t, 6H, NCH₂), 4.80 (m, 2H, =CH₂), 5.88 (m, 1H, =CH). 13C NMR (CDCl₃): $\delta$ = 28.32 (GeCH₂), 38.49 (NCH₂), 52.34 (NCH₂), 111.48 (=CH₂), 138.54 (=CH). EI-MS, m/z (rel. int., assign.): 262 (100%, M⁺), 44 (100%).

Analysis for C₁₁H₃₀GeN₃ (256.87):
Calcd C 42.08 H 7.85 N 21.81%.
Found C 41.64 H 7.38 N 21.56%.

1-Allyl-N,N',N''-trimethylazagermatrane 10

A solution of 5 (2.0 g, 8.1 mmol) and Me₂-tren 7 (1.38 g, 7.3 mmol) in toluene (14 ml) was refluxed for 5 d. Distillation of the reaction mixture gave 1.34 g of 10 as a colourless liquid; yield 61%, b.p. 96 - 97°C/0.1 Torr.

1H NMR (CD₆D₆, 300 MHz): $\delta$ = 1.95 (m, 2H, GeCH₂), 2.04 (t, 6H, NCH₂), 2.44 (t, 6H, NCH₂), 2.52 (s, 9H, CH₃), 2.95 (m, 2H, =CH₂), 6.20 (m, 1H, =CH). 13C NMR (CD₆D₆): $\delta$ = 23.58 (GeCH₂), 38.99 (CH₃), 50.17 (NCH₂), 50.58 (NCH₂), 113.22 (=CH₂), 138.32 (=CH). EI-MS, m/z (rel. int., assign.): 300 (1%, M⁺), 259 (39%, A = M⁺ - All), 58 (100%).

Analysis for C₁₁H₁₆GeN₃ (298.96):
Calcd C 48.21 H 8.77 N 18.74%.
Found C 48.66 H 8.73 N 19.38%.

1-Allyl-N,N',N''-tris(trimethylsilyl)azagermatrane 11

According to the procedure described for 10, 1.14 g (35%) of 11 (b.p. 90-91°C/0.02 Torr) was prepared from 5 (1.86 g, 7.6 mmol) and Me₂-tren 8 (2.50 g, 6.9 mmol).

1H NMR (CD₆D₆, 400 MHz): $\delta$ = 0.13 (s, 27H, Me₃Si), 1.93 (m, 2H, GeCH₂), 2.12 (t, 6H, NCH₂), 2.64 (t, 6H, NCH₂), 4.95 (m, 2H, =CH₂), 6.00 (m, 1H, =CH). 13C NMR (CD₆D₆): $\delta$ = 22.22 (Me₃Si), 32.71 (GeCH₂), 42.04 (NCH₂), 58.43 (NCH₂), 112.90 (=CH₂), 137.24 (=CH). EI-MS, m/z (rel. int., assign.): 262 (100%, M⁺ - All), 44 (100%).

Analysis for C₁₃H₃₆GeN₃Si₃ (473.42):
Calcd C 45.67 H 9.37 N 11.83%.
Found C 45.52 H 8.31 N 11.46%.
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