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Preliminary Communication

New approach to 1-(phenylethynyl)germatranes and 1-(phenylethynyl)-3,7,10-trimethylgermatrane. Reactions of 1-(phenylethynyl)germatrane with *N*-bromosuccinimide and bromine

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Abstract

Reaction of $N(CH_2CHRO)_3GeBr$ (**2a, b**) with $LiC{\equiv}CPh$ affords $N(CH_2CHRO)_3GeC{\equiv}CPh$ (**1a**, **b**) (**a**, R = H; **b**, R = Me). Compound (**1b**) was also obtained by treatment of $Cl_3GeC{\equiv}CPh$ (**3**) with $N(CH_2CHMeOSnEt_3)_3$ (**4**). (**1a**) reacts with *N*-bromosuccinimide to yield $N(CH_2CH_2O)_3GeC(Br)_2C(O)Ph$ (**5**). *Cis*-$N(CH_2CH_2O)_3GeC(Br){=}C(Br)Ph$ (**6**) is formed by the reaction of **1a** with Br_2 in equivalent amounts. All compounds were characterized by ^1H- and ^{13}C-NMR spectroscopy and mass spectrometry. Single crystal structures of **1a** and **6** were determined by X-ray diffraction studies. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Germatrane; Crystal structure; Alkyne; Bromination

1. Introduction

Recently we have reported an efficient approach for the synthesis of various functionally substituted germatranes by transesterification reaction between trihalogermanes and organotin derivatives of tris-(2-hydroxyalkyl)amines [1,2]: 1-(Phenylethynyl)-germatrane (**1a**) was obtained via this method [3]. More recently we have developed an alternative simple and effective method for the preparation of germatranes using reactions of easily available $N(CH_2CHRO)_3GeX$ (X = Br, $OSiMe_3$, OTf) with lithium reagents [4]. In this article we describe our studies of the same procedure for synthesis of 1-(phenylethynyl)germatranes, $N(CH_2CHRO)_3GeC{\equiv}CPh$ (**1a**, R = H; **1b**, R = Me). We focussed our attention on the chemical transformations of some germatranes as reactive precursors for new types of germatranes. Viewing the synthetic usability of **1** for functionalized germatranes, we have investigated reactions of germatrane $N(CH_2CH_2O)_3GeC{\equiv}CPh$ (**1a**) with *N*-bromosuccinimide (NBS) and bromine.

2. Results and discussion

Reactions of THF solutions of $LiC{\equiv}CPh$ with a suspension of 1-bromogermatranes (**2a**,**b**) [5] in toluene for 48 h at room temperature afford, after work-up, germatranes **1a** and **1b** (**1a**: R = H, **1b**: R = Me) in yields 70 and 65%, respectively, as shown in Eq. (1).

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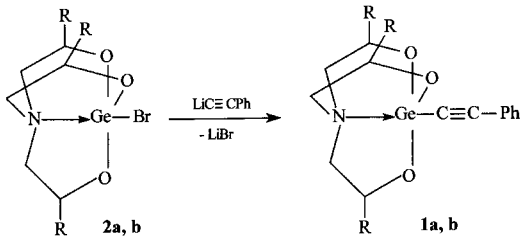
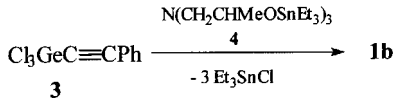


(1)

NMR control shows the absence of degradation products of the 'atrane' fragment.

Compound **1b** was synthesized also using the 'organotin route' for the formation of the atrane framework (Eq. (2)).

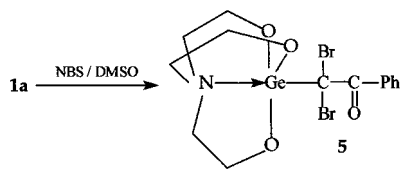


(2)

Two types of reactions of 1-(phenylethynyl)germatrane **1a** have been examined: the first is the reaction of **1a** with *N*-bromosuccinimide (NBS), another reaction is the addition of bromine.

Earlier we reported a reaction of 1-vinylsilatrane with NBS/H_2O to form a bromohydrin, $N(CH_2CHRO)_3SiCH(Br)CH_2OH$ with subsequent transformation of the latter into a silatranylacetaldehyde, $N(CH_2CHRO)_3SiCH_2CHO$ [6]. Here we have studied the reaction with NBS for the functionalization of **1a**.

Treatment of **1a** with NBS in DMSO provided, after aqueous work-up, germatranyldibromoacetophenone **5** with yield 68% (Eq. (3)).



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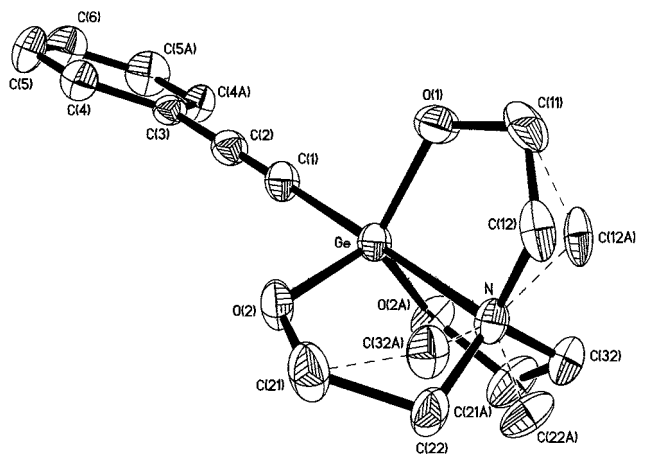
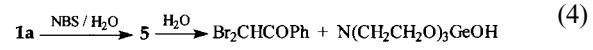


Fig. 1. Molecular structure of **1a**. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Ge–N 2.178(6), Ge–C(1) 1.920(8), Ge–O(1) 1.768(5), Ge–O(2) 1.793(4), C(1)–C(2) 1.19(1), C(1)–Ge–N 179.4(3), C(2)–C(1)–Ge 179.5(7), C(1)–C(2)–C(3) 179.8(7).

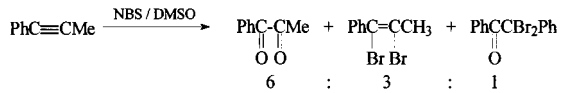
The structure of **5** is consistent with a carbonyl stretching vibration at 1661 cm^{-1} in the IR spectrum and with an intensive peak of $[C_6H_5C{\equiv}O]^+$ at m/z 105 in the mass spectrum.

When the reaction of **1a** with NBS was carried out in water, ketone **5**, accompanied by dibromoacetophenone and 1-hydroxygermatrane (Eq. (4)) as a result of Ge–C bond cleavage, has been obtained ^{1}H-NMR monitoring showed full conversion of ketone **5** to hydrolysis products (3 months, $H_2O/CDCl_3$).

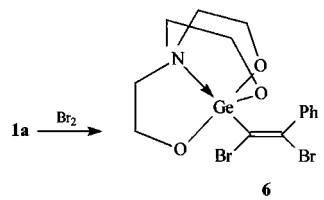


(4)

Our results contrast with data for reactions of NBS with acetylenes containing only organic substituents. For instance, diphenylacetylene reacts with NBS/DMSO with the formation of dibenzyl in high yield. Under the same conditions unsymmetrically substituted acetylene, e.g. methylphenylacetylene, gives a mixture of three products with the predominance of α-diketone [7].



NMR control showed the absence of a corresponding α-diketone and 1,2-dibromoethylene (**6**) in the reaction products (3). We were able to obtain **6** by treatment of **1a** with bromine (Eq. (5)). The Z-isomer was obtained exclusively and no traces of the E-isomer could be detected (NMR spectra) in the reaction mixture and the *cis*-structure of **6** was determinated by X-ray diffraction studies.



(5)

The result of reaction (5) is a rare example of the formation of a Z-isomer in the electrophilic bromination of alkynes [10].

Mechanism of the bromination reaction with alkynes was discussed [7–10]. At the moment we are unable to explain significant differences in the reaction pathways of organic and organometallic substituted ethynyls, but may be caused by specific stereoelectronic properties of the germatranyl group. Further studies to investigate the mechanism are in progress.

1b, **5** and **6** were characterized by elemental analysis, ^{1}H- and ^{13}C-NMR spectroscopy and mass spectrometry.

Structures of **1a** and **6** were confirmed by a single crystal X-ray analysis.

The main geometrical parameters of **1a** (Fig. 1) are close to those previously reported for the same

molecule in the structure of its chloroform solvate (**7**) [3]. The structure of **7** was measured at 150 K and the atrane moiety in **7** did not display any kind of disorder. In contrast, C_α atoms of the atrane skeleton in molecule **1a** are disordered over two positions related to each other by a mirror plane.

The molecular structure of **6** is shown in Fig. 2. The coordination polyhedron of the germanium atom in **6** is typical for germatrane derivatives [1,2a–c,3] and represents a distorted trigonal bipyramid with N and C atoms in the apical positions and the three oxygen atoms in equatorial positions. The germanium atom is displaced by 0.20 Å from a plane defined by three oxygen atoms. The bond angle at the N–Ge–C fragment is almost linear (178.0(7)°) and the N–Ge distance (2.23(1) Å) is within the normal range for germatranes containing a N–Ge–C moiety (2.16–2.32 Å) [3,11].

All five-membered rings Ge–O–CH_2–CH_2–N of the atrane skeleton in structure **6** are disordered over two positions with approximately equal occupancies and adopt an envelope conformation. Atoms C(21), C(211), C(22), C(221), C(23) and C(231) (all in β-position to the nitrogen atom) occupy 'flap' sites while the C_α atoms sit on the base envelope planes (C_β-envelope). It should be noted that germatranes without C_β-substituents usually possess C_α-envelope conformation. The C_β-envelope conformation was previously reported for structures of 3,7,10-methyl substituted germatranes only [2c].

3. Experimental

3.1. General comments

All solvents were dried by standard methods and distilled before use. Solutions of LiC≡CPh in THF were commercially obtained. Reactions with lithium reagents were carried out under argon atmosphere using standard Schlenk techniques. **2a**, **2b** [5], **3** [12] and **4** [1] were prepared according to the literature. NMR spectra were recorded at 25°C on Bruker AC 300 and Varian VXR 400 spectrometers, $CDCl_3$ and C_6D_6 were used as solvents and for internal deuterium lock. Chemical shifts in the ^{1}H- and ^{13}C-NMR spectra are given in ppm relative to internal TMS. Elemental analyses were carried out by the Microanalytical Laboratory of the Chemistry Department of the Moscow State University. Mass spectra (EI-MS) were recorded on a VARIAN CH-7a device using electron impact ionisation at 70 eV; all assignments were made with reference to the most abundant isotopes.

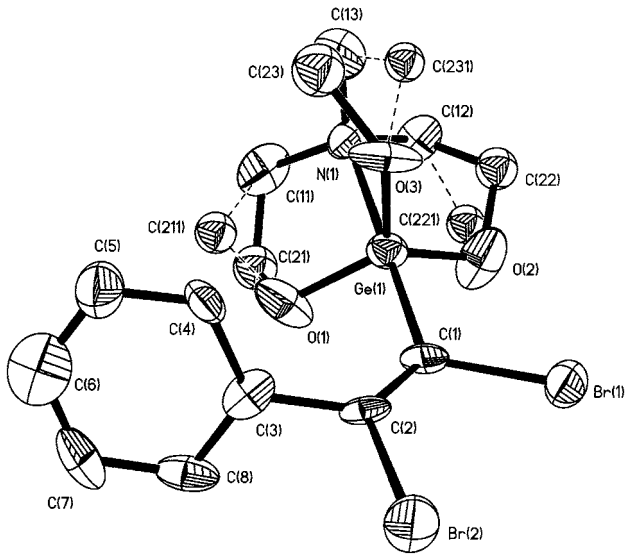


Fig. 2. Molecular structure of **6**. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Ge(1)–N(1) 2.23(1), Ge(1)–C(1) 1.98(2), Ge(1)–O(1) 1.78(1), Ge(1)–O(2) 1.75(1), Ge(1)–O(3) 1.75(1), C(1)–C(2) 1.30(2), C(1)–Ge(1)–N(1) 178.0(7).

3.2. Reactions of 1-bromogermatranes *2a*, *b* with *LiC≡CPh*

3.2.1. Synthesis of *1-(phenylethynyl)-3,7,10-trimethylgermatrane* *1b*

A 1M solution of LiC≡CPh in THF (2.14 ml, 2.14 mmol) was added to a suspension of **2b** (0.73 g, 2.14 mmol) in toluene (30 ml) at room temperature (r.t.). The reaction mixture was stirred for 24 h at r.t., then 2/3 of the volatiles were evaporated in vacuo. A precipitate was filtered off and volatiles were removed in vacuo. To the residue pentane (20 ml) was added and the mixture stored at −30°C for 20 h. A white solid was filtered off and dried in vacuo (1 Torr) for 3 h. After sublimation (100°C/0.05 Torr) 0.54 g, (70%) of **1b** was obtained. ^{1}H-NMR (C_6D_6): δ 0.80–3.9 ($ABXM_3$ system of NCH_2CHMeO group protons), 6.7–7.0, 7.3–7.5 (2m, C_6H_5, 5H); ^{13}C-NMR (C_6D_6): 20.60, 20.71, 21.13, 23.22 (CH_3); 58.97, 62.13, 62.45, 63.36, 63.82, 64.46, 65.90, 66.28 (NCH_2, OCH); 90.12, 90.13 (GeC≡); 98.72, 98.75 (C≡); 124.40, 124.41, 132.44, 132.45 (aromatic C; 4 signals at 127–128 ppm are crossed with signals of C_6D_6); two diastereomers. EI MS *m/e* (rel. int.): [M^+] 363 (1.74); [M^+–CH_3CHO] 319 (12.74); [M^+–2 CH_3CHO] 275 (4.0); [M^+–PhC≡C] 262 (1.08); [M^+–PhC≡C–CH_3CHO–$CH_2CH(CH_3)O$] 160 (100). Anal. Found: C, 56.78; H, 6.63; Ge, 20.50. Calc. for $C_{17}H_{23}GeNO_3$ (361.96): C, 56.41; H, 6.40; Ge, 20.05%.

3.2.1.1. 1-(Phenylethynyl)germatrane ***1a***. Synthesis of **1a** was analogous to that of **1b** (Section 3.2.1) except that 1-bromogermatrane **2a** was used instead of **2b**.

Yield 65%. ^{1}H- and ^{13}C-NMR data in $CDCl_3$ are consistent with those already published [3].

3.3. Synthesis of 1-(phenylethynyl)germatrane **1b** by reaction of **3** with **4**

A solution of $Cl_3GeC{\equiv}CPh$ **3** (4.2 g, 15 mmol) in 20 ml of CHCl3 was added dropwise to a solution of $N(CH_2CHMeOSnEt_3)_3$ **4** (12.89 g, 16 mmol) in 10 ml of $CHCl_3$. The reaction mixture was stirred for 4 h at r.t., then hexane (10 ml) was added and the precipitate was filtered off, washed with cold hexane (5×10 ml) and dried in vacuo (2 Torr) for 2 h. Yield: 5.1 g (94%).

3.4. Reactions of **1a** with NBS

3.4.1. Reaction of **1a** with NBS (1:2) in DMSO. Synthesis of 2,2-dibromo-2-germatranyl-1-phenyl-1-ethanone **5**

NBS (0.28 g, 1.57 mmol) was added to a solution of **1a** (0.25 g, 0.78 mmol) in DMSO (5 ml). The reaction mixture was stirred for 24 h at r.t. and water (50 ml) was added. The reaction mixture was extracted with $CHCl_3$ (20 ml), the extract was washed with water (3×15 ml) and dried ($MgSO_4$). $CHCl_3$ was removed in vacuo. The residue was recrystallized from chloroform/hexane, dried in vacuo to give 0.26 g (68%) of **5** as a colourless solid, m.p. 155–156°C. IR (nujol): ν 1661 cm^{-1} (C=O). ^{1}H-NMR ($CDCl_3$): δ 2.89 (t, NCH_2, 6H); 3.89 (t, OCH_2, 6H); 7.33–7.47, 8.34–8.38 (2m, C_6H_5, 5H); ^{13}C-NMR ($CDCl_3$): δ 40.97 (CBr_2); 53.20 (NCH_2); 57.51 (OCH_2); 127.64, 131.24, 132.62, 132.79 (aromatic C); 190.10 (C=O). EI MS m/e (rel. int.): [M^+] 495 (11); [$A{=}M^+{-}CBr_2COC_6H_5$] 220 (100); [A–$2CH_2O$] 160 (14); [A–$3CH_2O$] 130 (14); [C_6H_5CO] 105 (38). Anal. Found: C, 33.78; H, 3.23; Ge, 14.30. Calc. for $C_{14}H_{17}Br_2GeNO_4$ (495.69): C, 33.92; H, 3.46; Ge, 14.64%.

3.4.2. Reaction of **1a** with NBS (1:2) in water.

NBS (0.49g, 2.8 mmol) was added to a suspension of **1a** (0.45 g, 1.4 mmol) in water (10 ml). The reaction mixture was stirred for 48 h at r.t., then water was removed in vacuo. ^{1}H-NMR spectra of the residue (0.92 g) showed the presence of **5** and $Br_2CHCOPh$ (9:1) and succinimide (δ 2.4 ppm). ^{1}H- and ^{13}C-NMR data of $Br_2CHCOPh$ in $CDCl_3$ are consistent with those already published [8].

A solution of **5** in $CDCl_3$ (not dried prior to use) was stored in a NMR tube for 3 months. ^{1}H-, ^{13}C-NMR data showed complete hydrolysis of germatrane **5** resulting in the formation of $Br_2CHCOPh$ and $N(CH_2CH_2O)_3GeOH$; ^{1}H-, ^{13}C-NMR data of the latter in $CDCl_3$ are consistent with those already published [1].

3.5. Reaction of **1a** with bromine. Synthesis of cis-1,2-dibromo-2-phenyl-1-germatranylethene **6**

A solution of bromine (0.10 g, 0.63 mmol) in CCl_4 was added to a solution of **1a** (0.2 g, 0.63 mmol) in $CHCl_3$ (10 ml). The reaction mixture was stirred for 4 h at r.t. and solvents were removed in vacuo. Hexane (5 ml) was added to the residue. A white solid was filtered off and recrystallized from toluene to give 0.17 g (55%) of **6**, m.p. 191–192°C. IR (nujol): ν 1560–1580 cm^{-1} (C=C). ^{1}H-NMR ($CDCl_3$): δ 2.72 (t, NCH_2, 6H); 3.55 (t, OCH_2, 6H); 7.2–7.3, 7.4–7.5 (2m, C_6H_5, 5H); ^{13}C-NMR ($CDCl_3$): δ 52.45 (NCH_2); 56.94 (OCH_2); 134.59 (PhC=); 126.40 (GeC=); 127.17, 128.22, 129.14, 142.89 (aromatic C). EI MS m/e (rel. int.): [M^+] 479 (0.2); [M^+–Br] 400 (30); [$A{=}M^+{-}CBrCBrC_6H_5$] 220 (100); [A–CH_2O] 190 (36); [A–$2CH_2O$] 160 (37); [C_8H_5Br] 180 (49); [A–CH_2O–CH_2CH_2O] 146 (87); [A–$3CH_2O$] 130 (14). Anal. Found: C, 35.33; H, 3.42; N, 2.72. Calc. for $C_{14}H_{17}Br_2GeNO_3$ (479.69): C, 35.05; H, 3.57; N, 2.92%.

3.6. X-ray crystallographic study of **1a** and **6**

Crystal data for **1a**: $C_{14}H_{17}NO_3Ge$, M = 319.88, orthorhombic, $a = 14.597(9)$, $b = 9.823(5)$, $c = 9.643(7)$ Å, $V = 1383(2)$ Å^3, space group $Pnma$, $Z = 4$, $D_{calc} = 1.537$ g cm^{-3}, $F(000) = 656$, μ(Mo–K_α) = 2.219 mm^{-1}, colorless block with dimensions ca. $0.4 \times 0.2 \times 0.1$ mm. A total of 3547 reflections (1291 unique) were measured on an Enraf-Nonius CAD4 diffractometer (graphite monochromatized Mo–K_α radiation, $\lambda = 0.71073$ Å) at r.t. Data were collected in the range $2.53 < \theta < 24.98$ ($-3 \le h \le 17$, $-11 \le k \le 2$, $-11 \le l \le 8$) using ω–scan mode. The structure was solved by direct methods [13] and refined by full-matrix least-squares on F^2 [14] with anisotropic thermal parameters for all non-hydrogen atoms. All H atoms were placed in calculated positions and refined using a riding model. The atrane skeleton was found to be disordered over two positions with equal occupancies. Final residuals were $R_1 = 0.0508$, $wR_2 = 0.1062$ for 761 reflections with $I > 2\sigma(I)$ and 112 parameters. Goodness-of-fit = 0.965, maximum $\Delta\rho = 0.632$ e × Å^{-3}.

Crystal data for **6**: $C_{14}H_{17}NO_3GeBr_2$, M = 479.69, monoclinic, $a = 9.288(2)$, $b = 10.256(2)$, $c = 17.061(7)$ Å, $\beta = 97.66(3)°$, $V = 1611(1)$ Å^3, space group $P2_1/n$, $Z = 4$, $D_{calc} = 1.978$ g cm^{-3}, $F(000) = 936$, μ(Mo–K_α) = 6.873 mm^{-1}, colorless block with dimensions ca. $0.3 \times 0.1 \times 0.05$ mm. A total of 2188 reflections (1964 unique) were measured on an Enraf-Nonius CAD4 diffractometer (graphite monochromatized Mo–K_α radiation, $\lambda = 0.71073$ Å) at r.t. Data were collected in the range $1.30 < \theta < 21.97$ ($-9 \le h \le 9$, $0 \le k \le 10$, $0 \le l \le 17$) using ω–scan mode. The structure was solved by direct methods [13] and refined by full-matrix least-squares on F^2 [14] with anisotropic thermal

parameters for all non-hydrogen atoms except disordered carbon atoms. All H atoms were placed in calculated positions and refined using a riding model. The atrane skeleton was found to be disordered over two positions with equal occupancies. Final residuals were $R_1 = 0.0723$, $wR_2 = 0.1447$ for 994 reflections with $I > 2\sigma(I)$ and 188 parameters. Goodness-of-fit = 0.989, maximum $\Delta\rho = 0.717$ e $\times$ Å^{-3}.

4. Supplementary material

Crystallographic data (excluding structure factors) for the structures reported here have been deposited with the Cambridge Crystallographic Data Centre CCDC nos. 147346 (**1a**) and 140561 (**6**). Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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