Synthesis and the structure of tribromo(7-bromobicyclo[4.1.0]hept-7-yl)germane

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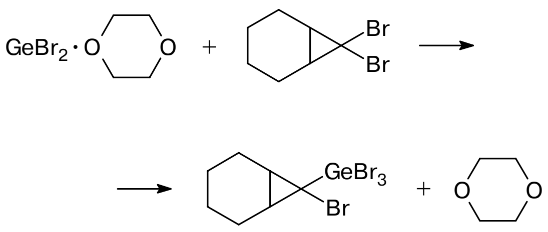
A general procedure was developed for the synthesis of halocyclopropylgermanes. This procedure was used for the preparation of tribromo(7-bromobicyclo[4.1.0]hept-7-yl)germane. The molecular structure was established by GLC-mass spectrometry, ^{1}H NMR spectroscopy, and X-ray diffraction analysis.

Key words: cyclopropylgermanes, synthesis, X-ray diffraction analysis, GLC-mass-spectrometry, ^{1}H NMR spectroscopy.

Trihalocyclopropylgermanes, which are of interest from the chemical standpoint, can realistically be considered as promising starting compounds for the synthesis of new valuable drugs.[1,2] Until recently, data on these compounds have been lacking in the literature due primarily to the difficulties associated with their preparation. The synthesis of the starting trihalogermanes (for example, vinyltrihalogermanes) is a very complicated process. However, even with vinyltrihalogermanes in hand, it is impossible to transform these compounds into cyclopropyltrihalogermanes by the Simmons—Smith reaction because the halogen atoms bound to the germanium atom can also react with zinc.

The insertion of dihalogermylenes at the C—Hal bond of halocyclopropane seemed to be the simplest procedure for this purpose. However, an attempt to insert dibromogermylene, which was generated from the dioxane complex $C_4H_8O_2 \cdot GeBr_2$ at the temperature close to the temperature of its decomposition (140—160 °C), led to the cyclopropane-ring opening yielding alkenylgermane.[3,4] The comprehensive study of this reaction demonstrated that dioxane complexes of dihalogermylenes can enter into insertion reactions at a temperature lower than 100 °C if the duration of the reaction is ~60—70 h.[5,6] The general procedure has been developed for the synthesis of halocyclopropylgermanes, which prevents isomerization of the cyclopropane ring (the reaction temperature is 70—80 °C; the reaction time is 20—25 h).[5]

This procedure was used for the preparation of tribromo(7-bromobicyclo[4.1.0]hept-7-yl)germane (**1**).



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The composition and the structure of compound **1** were established by GLC-mass spectrometry, ^{1}H NMR spectroscopy, and X-ray diffraction analysis (Fig. 1, Table 1). The bicyclo[4.1.0]heptyl fragment consists of the three- and six-membered rings fused at the shared C(2)—C(7) bond. In most of bicyclo[4.1.0]heptane (norcarane) derivatives studied by X-ray diffraction analysis, the C—C bond lengths in the three-membered ring differ from each other and from those observed in nonsubstituted cyclopropane. The length of the C—C bond shared by the three- and six-membered rings is equal to the other C—C bond lengths in the six-membered ring. The remaining two C—C bonds in the three-membered ring are not necessarily equal to each other, sometimes this difference being quite considerable. In this respect, 4,4-dibromotricyclo[5.1.0.0^{3,5}]octane and

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Table 1. Selected interatomic distances and bond angles in molecule **1**

Bond length	d/Å	Bond angle	ω/deg
Br(1)—C(1)	1.926(3)	C—Ge—Br(av.)	111.17(1)
Br—Ge(av.)	2.283(5)	Br—Ge—Br(av.)	107.71(2)
Ge(1)—C(1)	1.920(3)	C(7)—C(1)—C(2)	59.9(2)
C(1)—C(7)	1.508(5)	C(7)—C(2)—C(1)	59.3(2)
C(1)—C(2)	1.530(5)	C(1)—C(7)—C(2)	60.8(2)
C(2)—C(7)	1.517(5)	C(7)—C(1)—Br(1)	121.4(2)
C(3)—C(2)	1.510(5)	C—C—Br(av.)	120.4(2)
C(3)—C(4)	1.536(5)	Br(1)—C(1)—Ge(1)	107.9(2)
C(6)—C(5)	1.517(6)	C(2)—C(3)—C(4)	112.8(3)
C(6)—C(7)	1.530(5)	C(2)—C(7)—C(6)	119.3(3)
C(4)—C(5)	1.521(6)	C(3)—C(2)—C(7)	120.1(3)
		C(3)—C(2)—C(1)	121.8(3)
		C(5)—C(6)—C(7)	115.8(3)
		C(5)—C(4)—C(3)	111.4(3)
		C(4)—C(5)—C(6)	112.0(3)

8,8-dibromo-4-oxatricyclo[5.1.0.0^{3,5}]octane[7,8] are of interest. In the former molecule, the length of the C—C bond shared by the three- and six-membered rings is 1.50 Å, whereas two other C—C bond lengths in the three-membered ring are 1.54 and 1.46 Å (the average accuracy of the determination of the C—C bond lengths is ~0.01 Å). In the latter molecule, these bond lengths are 1.554, 1.493, and 1.493 Å, respectively (the average accuracy of the determination of the C—C bond lengths is ~0.011—0.007 Å). In molecule **1**, the length of the C(2)—C(7) bond shared by the cyclopropyl and cyclohexyl fragments is 1.517 Å and two other C—C bond lengths in the three-membered ring, *viz.*, C(1)—C(2) and C(1)—C(7), are 1.530(5) and 1.508(5) Å, respectively.

The six-membered ring in compound **1** adopts a half-chair conformation. Four carbon atoms, *viz.*, C(5), C(6), C(7), and C(2), are in a single plane (the average deviation is ~0.007 Å). The C(3) and C(4) atoms deviate from this plane by 0.055 and 0.124 Å, respectively. The C(1) atom of the three-membered ring deviates from this plane by 0.352 Å. The dihedral angle between the C(5)—C(6)—C(7)—C(2) and C(3)—C(4)—C(5) planes is 107.1°. The average C—C bond length in the six-membered ring (1.523 Å) is approximately equal to that in cyclohexane. The results of our investigation agree well with the results of electron diffraction studies[9,10] and *ab initio* quantum-chemical calculations[11] for the molecular structure of nonsubstituted norcarane.

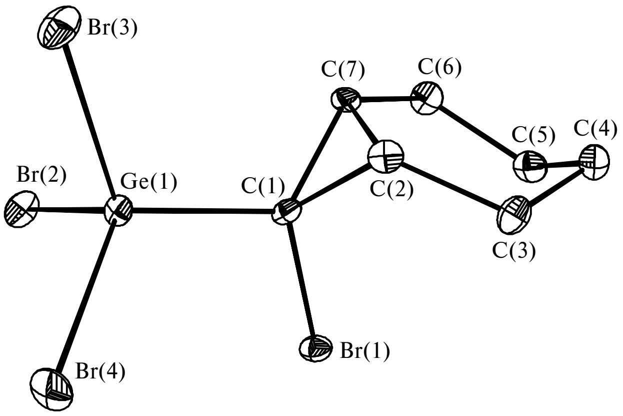

Fig. 1. Molecular structure of tribromo(7-bromobicyclo[4.1.0]hept-7-yl)germane.

The Ge(1)—C(1) interatomic distance is shortened (1.920(3) Å) due, most likely, to the fact that both the germanium and C(1) atoms bear the strong electronegative substituents, such as the bromine atoms. At the same time, the Ge—Br and C(1)—Br(1) interatomic distances are close to those observed in germanium bromides and bromine-substituted alkanes.[12,13] The Br—Ge—Br and Br—C—Ge bond angles are close to the tetrahedral value.

Experimental

The mass spectra of compound **1** were recorded on a Hewlett-Packard HP-5971A GLC-mass spectrometer (EI, 70 eV). The separation was carried out on a 0.032×2500-cm

Table 2. Crystallographic characteristics and details of the refinement of molecule **1**

Parameter	Characteristic
Molecular formula	$C_7H_{10}Br_4Ge$
Molecular weight	486.38
T/K	100
Diffractometer	«Smart 1000K»
Scanning technique	ω Scanning mode
ω Scan step/deg	0.3
Exposition of each frame/s	10
θ Scan range/deg	1.71—30.06
Radiation	MoKα
Wavelength/Å	0.71073
Crystal system	Monoclinic
Space group	$P2_1/c$
a/Å	12.3279(9)
b/Å	7.7637(6)
c/Å	2.9418(10)
α/deg	90
β/deg	104.885(2)
γ/deg	90
V/Å^3	1197.1(2)
Z	4
d_{calc}/mg m^{-3}	2.699
Absorption coefficient/mm^{-1}	15.861
F(000)	896
Total number of	
observed reflections	12678
measured reflections	3476 (R_{int} = 0.0373)
Final R factor	
[$I > 2\sigma(I)$]	
R_1	0.0280
wR_2	0.0604
R factor based on all reflections	
R_1	0.0434
wR_2	0.0646

capillary column with the use of a film (25 μm) of methylphenylsiloxane elastomer DV-5 as the stationary phase.

Analysis was carried out in the temperature-programming mode from 50 to 280 °C at a rate of 7 deg min^{-1} using helium as the carrier gas (0.8 mL min^{-1}). The ^1H NMR spectrum was measured on a Bruker AM-360 spectrometer (360 MHz) in CD_3CN. The details of X-ray diffraction study of a single crystal of **1** are given in Table 2. The structure was solved by the direct method based on all independent reflections. The positions of the hydrogen atoms were revealed from difference electron density syntheses. The structure was refined by the full-matrix least-squares method in the anisotropic-isotropic approximation. All calculations were carried out using the SHELXTL PLUS program package (version 5). The complete tables of the atomic coordinates, thermal parameters, bond lengths, and bond angles were deposited with the Cambridge Structural Database.

Tribromo(7-bromobicyclo[4.1.0]hept-7-yl)germane (1). 7,7-Dibromobicyclo[4.1.0]heptane (21.32 g, 0.0839 mol) and the dioxane complex of dibromogermylene (26.9 g, 0.0839 mol) were placed in a flat-bottom glass flask equipped with a magnetic stirrer and a reflux condenser with a calcium-chloride tube. The reaction mixture was heated at 70—80 °C for 20—25 h (the course of the reaction was monitored based on the disappearance of germanium dibromide dioxanate, which gave a bright-yellow color with water; for this purpose, samples of the reaction mixture, which were taken at regular intervals, were subjected to hydrolysis; 8—10 tests). After completion of the reaction, the resulting mixture was filtered and distilled *in vacuo*. The product with the b.p. 165 °C (3 Torr) and n_D^{30} 1.6117 was cooled to 0 °C. The crystals that precipitated were recrystallized from hexane. Compound **1** was obtained in a yield of 8.0 g (19.6%), b.p. 165 °C (3 Torr), m.p. 67.5—69 °C. ^1H NMR (25 °C, CD_3CN), δ: 1.38 (m, 2 H, CH); 1.62 (m, 1 H, CH_2); 1.80 (m, 1 H, CH_2); 2.14 (s, 6 H, CH_2). MS, *m/z* (I_{rel} (%)): 486 (2) $[M]^+$; 406 (3) $[M-Br]^+$; 313 (22) $[GeBr_3]^+$; 173 (24) $[M-GeBr_3]^+$; 93 (100) $[M-Br-GeBr_3]^+$. Found (%): C, 17.21; H, 2.10; Br, 65.81; Ge, 14.80. $C_7H_{10}Br_4Ge$. Calculated (%): C, 17.29; H, 2.07; Br, 65.71; Ge, 14.93.

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