

# Synthesis and X-Ray Crystal Structure Analysis of (–)-1-Menthoxygermatrane

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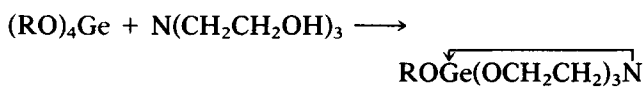
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## ABSTRACT

A solvate complex of (–)-1-menthoxygermatrane with chloroform (**1**) was obtained by reaction of (–)-menthoxytriethylstannane with 1-bromogeratrane in chloroform. The crystal and molecular structure of **1** was established by X-ray analysis.

## INTRODUCTION

The main synthetic approach for 1-alkoxygermatranes has been the transesterification of tetraalkoxygermanes with trialkanolamines [1, 2].



R = Me, Et, Pr

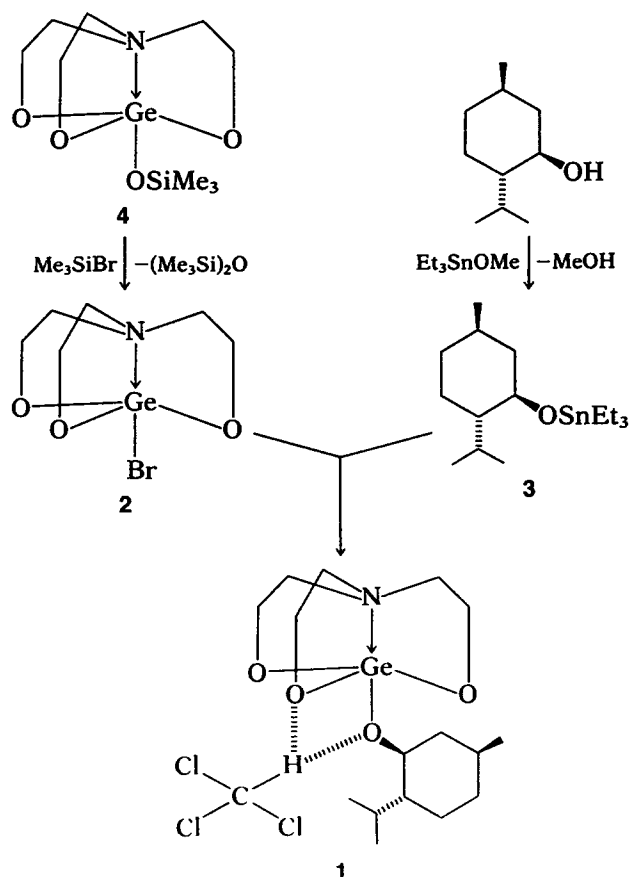
This method is restricted, however, to the synthesis of simple alkoxygermatranes, as tetraalkoxygermanes with more complex groups R are not easily accessible [3]. Exchange reactions between the halogermanes and functional IVB group compounds have been widely studied in a series of triethyl- and triarylhalogermanes [4] and have been successfully applied to synthesize various functional germanes, such as alkoxygermanes [4]. The reactivity of 1-halogeratranes has not been studied in a similar way. We tried to obtain 1-alkoxygermatranes starting from 1-bromogeratrane.

## RESULTS AND DISCUSSION

(–)-1-Menthoxygermatrane was obtained as a solvate complex **1** by reaction of 1-bromogeratrane (**2**) with (–)-menthoxytriethylstannane (**3**) at room temperature, using chloroform as the solvent. (–)-1-Menthoxygermatrane is the only compound that forms the solvate complex with chloroform, whereas, in the case of R = CH<sub>3</sub>, C<sub>2</sub>H<sub>5</sub>, cyclohexyl, pentalactonyl, and so on, the formation of solvate complex with chloroform was not observed. Until now, the type of complex that we studied, that is, a hydrogen bonded complex of chloroform with the atrane skeleton that could be subjected to X-ray analysis, has not been described in the literature. Here we report for the first time the solvate complex of (–)-1-menthoxygermatrane with chloroform, as established by X-ray analysis. Compound **2** was synthesized by the reaction of trimethylbromosilane with 1-trimethylsiloxygermatrane (**4**) using *m*-xylene as the solvent. (–)-Menthoxytriethylstannane (**3**) was obtained by a transesterification reaction of triethylmethoxystannane with (–)-menthol.

The <sup>1</sup>H NMR spectrum of **1** was obtained in DMSO-d<sub>6</sub> solution. The methylene proton signals of the germatrane skeleton appeared as two markedly broadened triplets at δ = 2.83 (NCH<sub>2</sub>) and δ = 3.65 (OCH<sub>2</sub>), forming the (AA'XX') spin system. The signal of chloroform appeared at δ = 8.31, and the signal of the menthoxy group appeared as a multiplet in the normal range of the spectrum. In the <sup>13</sup>C NMR spectrum, the signals of the carbon atoms of the atrane skeleton appeared at δ = 50.64 (NCH<sub>2</sub>) and δ = 56.09 (OCH<sub>2</sub>); the signal of the carbon atom of the menthoxy group attached to the oxygen at δ = 71.42 and that of chloroform at δ = 79.46.

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The composition and structure of **1** was confirmed by X-ray crystallographic methods. Bond lengths and bond angles are listed in Tables 1 and 2 respectively; Table 3 contains the atomic coordinates. The menthoxygermatrane molecule forms a solvate complex with chloroform (Figure 1) in such a way that the hydrogen atom of the solvent molecule has an apparent interaction with atoms O1 and O4, with interatomic distances H201–O1 2.35(9) Å and H201–O4 2.46(9) Å, indicating hydrogen bonding between the chloroform molecule and (-)-1-menthoxygermatrane. The fragment O1, O4, H201, C20 is almost planar; the sum of the bond angles O1–H201–O4 63(3)°, O1–H201–C20 151(9)°, and O4–H201–C20 143(9)° is 357°. The coordination polyhedron of the germanium atom is a trigonal bipyramid, with the nitrogen atom and the oxygen atom of the menthoxy group in the apical positions and the oxygen atoms of the atranic framework in the equatorial positions. The germanium atom is displaced 0.18 Å from the equatorial plane defined by O1, O2, O3 toward O4. The Ge···N intramolecular distance (2.149 Å) is almost the same as in 1-hydroxygermatrane (2.146 Å) [5] and can be compared to the longer (2.24 Å) bond in alkyl- and arylgermatranes and to the shorter (2.09 Å) bond in bromo-germatrane. This comparison thus demonstrates that dGeN does not diminish with increasing electro-

**TABLE 1** Selected Bond Lengths (Å)<sup>a</sup> in Complex **1**

Ge	O1	1.776(6)	O4	C10	1.428(11)
Ge	O2	1.760(7)	N1	C1	1.498(12)
Ge	O3	1.790(6)	N1	C3	1.463(14)
Ge	O4	1.767(6)	N1	C5	1.487(14)
Ge	N1	2.150(7)	C1	C2	1.517(14)
O1	C2	1.417(11)	C3	C4	1.53(2)
O2	C4	1.437(13)	C5	C6	1.50(2)
O3	C6	1.405(11)			

<sup>a</sup>Figures in parentheses are estimated standard deviations in the least significant digits.

negativity of the other atoms bonded to Ge as has been suggested [6].

### Crystal Structure Determination

The data were collected on an Enraf Nonius CAD-4 diffractometer (Mo-K $\alpha$ , graphite monochromator,  $\omega$ -scan). The crystals have a space group P2<sub>1</sub>2<sub>1</sub>2<sub>1</sub> with a unit cell  $a = 10.606(2)$ ,  $b = 10.745(2)$ ,  $c = 20.083(4)$ ,  $Z = 4$ ,  $D_{\text{calc}} = 1.43 \text{ g}\cdot\text{cm}^{-3}$ ,  $\mu = 16.931 \text{ cm}^{-1}$ . A total of 2555 unique reflections were recorded in the range  $2\theta < 52^\circ$ , of which 1659 had  $I > 3\sigma(I)$ . The structure was solved by direct methods using MULTAN [7]. The refinement of the non-hydrogen atoms was carried out in the anisotropic full matrix version. The hydrogen atoms were held at fixed positions found in the difference Fourier synthesis and eventually refined with isotropic temperature factors; the final residual factor was  $R = 0.046$ .

The atomic coordinates of all atoms including the hydrogen atoms are deposited with the Cambridge Crystallographic Data Centre.

### EXPERIMENTAL

Melting points and boiling points are uncorrected. Proton NMR spectra were recorded on a Varian XR-400 (400-MHz) spectrometer, with tetramethylsi-

**TABLE 2** Selected Bond Angles (°)<sup>a</sup> in Complex **1**

O1	Ge	O2	119.0(4)	Ge	O4	C10	121.7(5)
O1	Ge	O3	119.0(3)	Ge	N1	C1	104.1(5)
O1	Ge	O4	90.7(3)	Ge	N1	C3	105.0(6)
O1	Ge	N1	83.8(3)	Ge	N1	C5	104.6(6)
O2	Ge	O3	118.9(3)	C1	N1	C3	115.5(8)
O2	Ge	O4	97.6(3)	C1	N1	C5	111.3(8)
O2	Ge	N1	84.7(3)	C3	N1	C5	114.9(8)
O3	Ge	O4	99.0(3)	N1	C1	C2	104.5(8)
O3	Ge	N1	84.1(3)	O1	C2	C1	109.8(7)
O4	Ge	N1	174.5(3)	N1	C3	C4	106.4(8)
Ge	O1	C2	117.6(5)	O2	C4	C3	110.3(9)
Ge	O2	C4	117.4(6)	N1	C5	C6	108.5(9)
Ge	O3	C6	118.7(6)	O3	C6	C5	111.4(9)

<sup>a</sup>Numbers in parentheses are estimated standard deviations in the least significant digits.

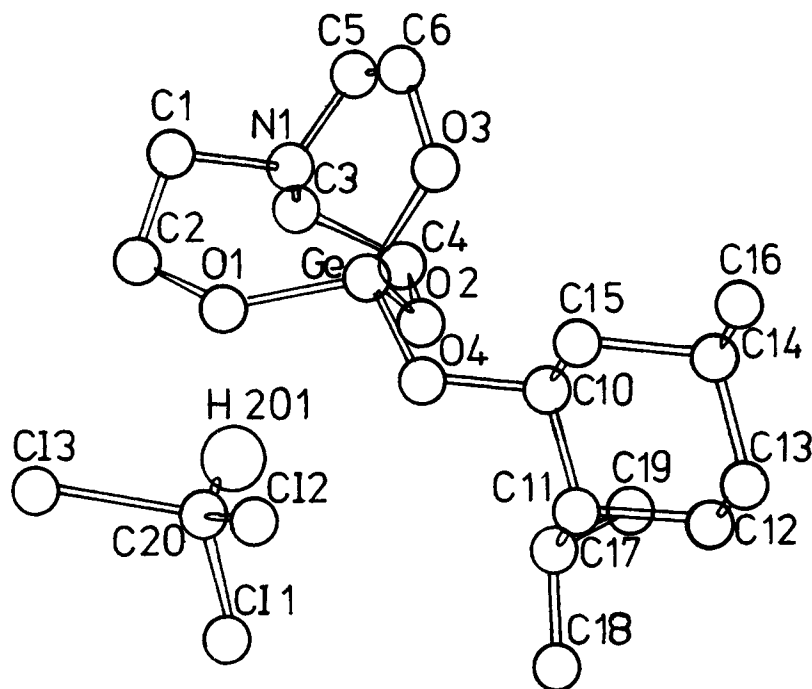
**TABLE 3** Positional Parameters in Complex 1

Atom	$x^a$	$y^a$	$z^a$	$B(A^2)^{a,b}$
Ge	0.58530(9)	0.25476(9)	0.04836(4)	2.55(1)
C11	0.2240(3)	0.6912(4)	0.9395(3)	7.7(1)
C12	-0.0437(3)	0.6953(3)	0.9302(2)	6.76(9)
C13	0.0750(6)	0.6622(3)	1.0569(2)	9.5(1)
O1	0.5844(8)	0.1495(5)	-0.0198(3)	3.3(1)
O2	0.7300(7)	0.3167(6)	0.0756(3)	3.9(2)
O3	0.4424(6)	0.3335(6)	0.0701(3)	3.6(1)
O4	0.5765(8)	0.1296(5)	0.1053(3)	3.3(1)
N1	0.5975(8)	0.3940(6)	-0.0282(3)	3.0(1)
C1	0.554(1)	0.328(1)	-0.0899(5)	4.2(3)
C2	0.6095(9)	0.1984(8)	-0.0839(4)	3.0(2)
C3	0.730(1)	0.433(1)	-0.0283(6)	4.4(3)
C4	0.774(1)	0.429(1)	0.0441(6)	4.3(2)
C5	0.506(1)	0.491(1)	-0.0076(6)	4.8(3)
C6	0.399(1)	0.4297(9)	0.0286(5)	3.6(2)
C10	0.551(1)	0.1491(9)	0.1743(5)	3.4(2)
C11	0.635(1)	0.060(1)	0.2150(5)	3.8(2)
C12	0.597(1)	0.070(1)	0.2889(5)	5.8(3)
C13	0.458(1)	0.040(1)	0.3011(6)	5.3(3)
C14	0.376(1)	0.133(1)	0.2624(5)	4.3(3)
C15	0.410(1)	0.1279(9)	0.1885(5)	3.8(2)
C16	0.237(1)	0.107(1)	0.2714(6)	6.6(4)
C17	0.778(1)	0.085(1)	0.2036(5)	4.7(3)
C18	0.853(1)	-0.022(2)	0.2291(9)	8.3(4)
C19	0.827(1)	0.207(1)	0.2331(7)	7.2(4)
C20	0.084(1)	0.630(1)	0.9732(7)	5.7(3)

<sup>a</sup>Numbers in parentheses are estimated standard deviations.

<sup>b</sup>Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as:  $\exp[-0.25\{h^2a^2B(1,1) + k^2b^2B(2,2) + l^2c^2B(3,3) + 2hkaB(1,2) + 2hlcB(1,3) + 2klcB(2,3)\}]$ , where a, b, and c are reciprocal lattice constants.

The hydrogen atoms were refined isotropically.

**FIGURE 1** Structure of 1 showing the atom numbering scheme.

lane used as an internal standard.  $^{13}\text{C}$  NMR spectra were recorded on a Bruker WP-80 (20.1-MHz) spectrometer, with tetramethylsilane used as an internal standard. Chemical shifts are in ppm downfield from TMS.

### (-)-Menthoxotriethylstannane (3)

A mixture of (-)-menthol (5.0 g, 32 mmol) and methoxytriethylstannane (8.3 g, 35 mmol) was heated for 30 min at 100°C with distillation of methanol formed during the course of the reaction. The product was removed by vacuum distillation, yielding 10.8 g (93%) of compound (3): bp 130–131°C at 2 mm Hg,  $n_D^{20}$  1.4850,  $\alpha_D^{21}$  - 39.48 ( $c = 6.1$ ,  $\text{CHCl}_3$ ). Anal. Calc. for  $\text{C}_{16}\text{H}_{34}\text{OSn}$ : C, 53.21; H, 9.49; Sn, 32.86. Found: C, 52.84; H, 9.20; Sn, 33.19. Results by  $^{13}\text{C}$  NMR,  $\delta$  ( $\text{CDCl}_3$ ), 6.23, 10.03, 16.24, 21.38, 22.57, 23.69, 23.67, 32.33, 35.29, 48.65, 52.26, and 74.28.

### 1-Bromogeriatrane (2)

To a two-necked roundbottomed flask (50 mL) fitted with a dropping funnel, reflux condenser, and magnetic stirrer, a solution of 1-trimethylsilyloxygeriatrane (4) [8] (6.16 g, 2 mmol) in 30 mL of *m*-xylene was placed. To the solution, trimethylbromosilane (6.12 g, 4 mmol) was added dropwise with stirring at room temperature. When the addition was completed the reaction mixture was refluxed; after 30 min the solid precipitate had dissolved, and the reaction mixture became a clear solution. About 15 min later a white crystalline product started to precipitate. After refluxing further for 1 h and then cooling the flask, the product was collected by filtration and washed two times with pentane ( $2 \times 5$  mL). After drying in vacuo the yield was 5.1 g (85%) of compound (2): mp 202–204°C (dec.) (lit. [9] mp 200°C (dec.)).

### (-)-1-Menthoxogeriatrane· $\text{CHCl}_3$ (1)

Into a two-necked roundbottomed flask (25 mL) a solution of 1-bromogeriatrane (2) (0.83 g, 2.8 mmol) in chloroform (3 mL) was placed. (-)-Menthoxotriethylstannane (1.1 g, 3 mmol) was added dropwise with stirring at room temperature. After almost 50 h a fine crystalline compound was obtained. After collecting by filtration, washing with chloroform ( $2 \times 3$  mL), and drying in vacuum, the yield was 0.85 g (82%) of 1: mp 182–183°C,  $\alpha_D^{21}$  - 23.93 ( $c = 1.63$ , DMSO). Anal. Calc. for  $\text{C}_{17}\text{H}_{32}\text{Cl}_3\text{GeNO}_4$ : C, 41.38; H, 6.54; Ge, 14.71. Found: C, 40.80; H, 6.70; Ge, 15.05. Results by  $^1\text{H}$  NMR,  $\delta$  (DMSO,  $d_6$ ) 2.83 (6H, t,  $\text{NCH}_2$ ), 3.65 (6H, t,  $\text{OCH}_2$ )  $J$  5–6 Hz; by  $^{13}\text{C}$  NMR,  $\delta$  (DMSO,  $d_6$ ), 56.09 ( $\text{OCH}_2$ ), 50.64 ( $\text{NCH}_2$ ), 71.42, 50.55, 45.60, 34.52, 31.20, 24.45, 22.80, 22.40, 21.29, 16.07 (menthoxy group) and 79.46 ( $\text{CHCl}_3$ ).

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