SYNTHESIS OF 1-GERMATRANOL AND ITS C-SUBSTITUTED DERIVATIVES

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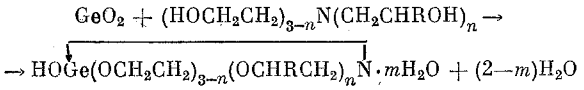
The described method for synthesis of 1-germatranol is based on the hydrolysis of 1-ethoxygermatrane in an aqueous medium [1].

Continuing our investigation in the field of metalloatranes [2-4], we developed a new method for synthesis of 1-germatranol $HOGe(OCHRCH_2)_3N$ (R = H) and its previously unknown C-substituted derivatives (R = CH_3, C_6H_5) directly from germanium dioxide and the corresponding tris(2-hydroxyalkyl)amines according to the scheme*



$$GeO_2 + (HOCH_2CH_2)_{3-n}N(CH_2CHROH)_n \rightarrow$$

$$\rightarrow HOGe(OCH_2CH_2)_{3-n}(OCHRCH_2)_nN \cdot mH_2O + (2-m)H_2O$$

$m = 1$, $n = 0$ (I); $m = 1$, $n = 1$, $R = CH_3$ (II); $m = 0$, $n = 2$, $R = CH_3$ (III); $m = 0$, $n = 3$, $R = CH_3$ (IV); $m = 0$, $n = 1$, $R = C_6H_5$ (V)

The reaction is carried out by boiling of an aqueous solution of tris(2-hydroxyalkyl)-amine with germanium oxide. 1-Germatranol (I) and 3-methyl-1-germatranol (II) are precipitated as monohydrates, and compounds (III)-(V) are precipitated in the anhydrous state. Water can be removed from the monohydrates with heating to 50-60°C in vacuo. The obtained compounds (I)-(V) are crystalline or amorphous substances whose solubility in organic solvents increases with increasing n.

The IR spectra of the C-substituted germatranes contain absorption bands of νOH at 3440-3445 cm^{-1}, ν_{as} Ge—O—C in the region of 1050-1150 cm^{-1}, and ν_s Ge—O at 840-894 cm^{-1}. Pulsational vibration of the $Ge(O—C—C)_3N$ ring is manifested in the region of 545-590 cm^{-1}.

The yields, data of elemental analysis, and physicochemical characteristics of the C-substituted germatranols are given in Table 1.

EXPERIMENTAL

1-Germatranol Hydrate (I). A mixture of 15.4 g of germanium dioxide, 21.9 g of triethanolamine, and 50 ml of water was heated until complete dissolution of GeO_2, and crystals of (I) (20.8 g), which precipitated after cooling of the resulting solution, were filtered, washed with ethyl alcohol, and dried in air. With evaporation of the filtrate, 16.2 g more of the crystals of (I) was recovered. The yield of 1-germatranol hydrate was 37.0 g (99.2%), decomposition temp. 245-260°C, see [1]. Found, %: C 28.39; H 5.86; N 5.69; Ge 27.89. $C_6H_{15}NO_5Ce$. Calculated, %: C 28.40; H 5.96; N 5.52; Ge 28.60.

C-SUBSTITUTED GERMATRANOLS

3-Methyl-1-germatranol Hydrate (II). A mixture of 7.6 g of germanium dioxide, 11.9 g of bis(2-hydroxyethyl)(2-hydroxypropyl)amine, and 20 ml of water was heated until complete dissolution of GeO_2. The crystals that precipitated after cooling of the obtained solution were drawn off, washed with ethyl alcohol, and dried. The yield of (II) was 19.1 g.

3,7-Dimethyl-1-germatranol (III) and 3,7,10-Trimethyl-1-germatranol (IV). A mixture of 0.03 mole of germanium dioxide, 0.03 mole of the appropriate tris(2-hydroxyalkyl)amine,

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*After submission of this article to the editor, a publication appeared [V. F. Mironov, T. K. Gar, N. Yu. Khromova, and O. D. Frid, Zh. Obshch. Khim., 56, 638 (1968)] in which an analogous method is described for the preparation of germatranol, but not of its C-substituted derivatives.

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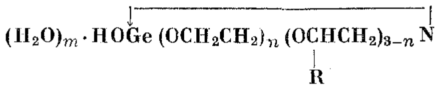
TABLE 1. C-Substituted 1-Germatranol Derivatives 

$(H_2O)_m \cdot HO\overset{\downarrow}{Ge}(OCH_2CH_2)_n(\underset{R}{OCHCH_2})_{3-n}N$

Compound	R	m	n	Yield, %	mp., °C	Empirical formula	Found, %				Calculated, %			
							C	H	N	Ge	C	H	N	Ge
(II)	CH_3	1	2	98.1	135–136	$C_7H_{17}NO_5Ge$	32.30	6.34	5.27	27.47	31.39	6.40	5.23	27.41
(III)	CH_3	0	1	~100	—*	$C_8H_{17}NO_4Ge$	36.52	6.52	5.18	27,57	36,42	6.50	5.31	27.51
(IV)	CH_3	0	0	~100	75–85 **	$C_9H_{19}NO_4Ge$	40.40	6.95	5.04	26.22	38.91	6.89	5.04	26.13
(V)	C_6H_5	0	2	95.6	215–228 (with decomposition)	$C_{12}H_{18}NO_4Ge$	46.42	5,41	4.45	23,19	46.22	5.49	4,49	23,28

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*Amorphous substance.

†Melts incompletely, with subsequent solidification, and decomposes at 140-194°C.

and 20 ml of benzene was added, water was driven off as the azeotrope, the benzene residue was removed under a vacuum of 50-100 mm (bath temp. 50-60°C), and then the reaction product was kept under a vacuum of 5 mm at 25°C for 1 h. The yields of (III) and (IV) were quantitative, 7.91 and 8.34 g, respectively.

3-Phenyl-1-germatranol (V). A mixture of 2.23 g of germanium dioxide, 4.83 g of bis(2-hydroxyethyl)(2-phenyl-2-hydroxyethyl)amine, and 25 ml of water was heated until complete dissolution of germanium dioxide. The white crystalline precipitate (4.75 g) that formed after cooling of the obtained solution was drawn off, washed with ethyl alcohol, and dried in air. With evaporation of the filtrate, 1.63 g more was recovered. The yield of 3-phenyl-1-germatranol was 6.38 g.

CONCLUSIONS

1. A method is proposed for the preparation of 1-germatranols with the general formula $HOGe(OCH_2CH_2)_{3-n}(OCHRCH_2)_nN \cdot mH_2O$ (R = Me, Ph, n = 0-3, m = 0.1) by the reaction of germanium dioxide with tris(2-hydroxyalkyl)amines by heating in an aqueous medium.

2. For the first time, C-substituted 1-germatranols (R = Me, n = 1, m = 1; R = Me, n = 2-3, m = 0; R = Ph, n = 1, m = 0) were obtained and characterized.

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REACTION OF THE SUPERACID $HGeCl_3$ WITH AROMATIC COMPOUNDS.

5.* HYDROGERMYLATION OF BENZENE, TOLUENE, m-XYLENE, AND MESITYLENE AT HIGH PRESSURE†

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The super acid $HGeCl_3$ adds under mild conditions to the aromatic multiple bonds of benzene derivatives with strong electron-donor substituents [3]. However, benzene and the methyl benzenes do not add $HGeCl_3$ under normal conditions although they are capable of exchanging deuterium with $DGeCl_3$ [3].

Since one can expect this reaction to be accelerated by increasing the pressure, we have carried out experiments at 5-14 kbar pressure. Under these conditions it was found that $HGeCl_3$ added comparatively readily, mestylene being hydrogermylated the most smoothly: at 80°C and 10 kbar the conversion reached 100% after 2 h but the reaction product was the corresponding cyclohexene (I) and products of reaction with three molecules of $HGeCl_3$ were completely absent even with excess of the latter.

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*For communication 4, see [1].
†For the preliminary communication, see [2].

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