ATRANES

XIV. 1-Organylgermatranes*

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A method has been developed for the synthesis of the previously unknown 1-organylgermatranes $RGe(OCH_2CH_2)_3N$ (R is alkyl or aryl). It is based on the cleavage of the polymeric products of the hydrolysis of organyltrihalogermanes with triethanolamine in the presence of an alkali-metal hydroxide. Four 1-organylgermatranes have been obtained by this method and characterized. The parameters of the elementary cells of the crystals of these compounds have been determined by X-ray structural analysis.

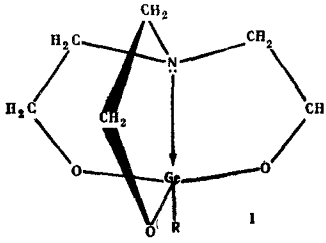
Only one paper in the literature has been devoted to germanium derivatives of trialkanolamines [2], and this described the products of the transesterification of tetralkoxygermanes with triethanolamine, i.e., 1-alkoxygermatranes. It also mentions the possibility of the transesterification of 1-ethoxygermatrane with higher alcohols. In addition, a patent [3] mentions the preparation of water-soluble compounds of germanium by the action of triethanolamine on tetrachlorogermane. However, the nature of these compounds was not established.

Continuing our study of atranes, we have developed a method for synthesizing the previously unknown 1-organylgermatranes (I) [4–6] which is based on the cleavage of the polymeric products of the hydrolysis of organyltrihalogermanes, polyorganylgermasesquioxanes, with triethanolamine in the presence of an alkali-metal hydroxide as catalyst. The reaction takes place in the following way:

$$1/n(RGeO_{1.5})_n + (HOCH_2CH_2)_3N \rightarrow RGe(OCH_2CH_2)_3N + 1.5H_2O$$

$$R = CH_3,\ C_2H_5,\ C_6H_5,\ \alpha\text{-}C_{10}H_7$$

The synthesis was effected by continuous azeotropic distillation with a suitable inert solvent (xylene) of the water liberated in the reaction of triethanolamine with the organylgermasesquioxane. The I formed crystallized out directly from the reaction mixture and was purified by recrystallization.



I

The compounds I synthesized consisted of colorless crystalline substances with higher melting points than the corresponding 1-organylsilatranes. The solubility of compounds I is similar to that of the analogous silatranes; they are readily soluble in halogenated hydrocarbons. 1-Alkylgermatranes are also readily soluble in water while the 1-aryl derivatives are sparingly soluble.

The yields, melting points, and analytical data of the compounds I obtained are given in Table 1.

The presence of an intramolecular Ge ← N coordination bond in compounds I is confirmed by the high values of the dipole moments (~6–7 D) and by the results of PMR spectroscopy, which will be published separately.

1-Phenylgermatrane exhibits a physiological action similar to that of phenylsilatrane but is approximately 100 times less toxic (LD_{50} for white mice, 48 mg/kg)*.

The symmetry, translation groups, and the parameters of the elementary cells of the crystals of methyl-, ethyl-, phenyl-, and α-naphthylgermatranes have been

Table 1

1-Organylgermatranes (I)

R	Mp, °C	Empirical formula	Found, %				Calculated, %				Yield of unpurified substance %
			C	H	N	Ge	C	H	N	Ge	
CH_3	158–159	$C_7H_{15}GeNO_3$	35.80	6.63	6.23	30.94	35.96	6.47	5.99	31.04	85
C_2H_5	146–147	$C_8H_{17}GeNO_3$	39.00	7.05	6.00	29.32	38.77	6.93	5.65	29.29	70
C_6H_5	232–232,5	$C_{12}H_{17}GeNO_3$	49.07	5.96	4.74	24.85	48.72	5.79	4.73	24.53	89
α-$C_{10}H_7$	263–263,5	$C_{16}H_{19}GeNO_3$	55.46	5.51	4.11	20.74	55.55	5.54	4.05	20.98	84

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*For communication XIII, see [1].

*The pharmacological study of I was carried out by A. A. Kimenis. Detailed information on the physiological action of the atranes will be published in subsequent communications.

determined by X-ray structural analysis. The experimental data were obtained with copper radiation by the rocking and rotation method [1].

It has been established that the crystals of 1-methylgermatrane are monoclinic ($\beta = 122°$ C) while the other three compounds are rhombic. The elementary cells of the crystals of all four compounds I are primitive. The parameters of the elementary cells are given in Table 2. Preliminary data on the crystal structure of 1-ethylgermatrane have been given in a previous paper [7].

EXPERIMENTAL

The initial alkyltrihalogermanes were prepared by direct synthesis, that is, by the reaction of the corresponding alkyl halides with elementary germanium in the presence of metallic copper [8]. The aryltrihalogermanes were obtained by a method published previously [9, 10] from the corresponding aryl iodides and a germanium tetrahalide in the presence of metallic copper.

The hydrolysis of the organyltrihalogermanes was carried out with a 25% aqueous solution of KOH which was added in small portions to the trihalogermane until the reaction was weakly alkaline. For the formation of water-soluble alkylgermoxanes, a solution of the hydrolyzate was used for the synthesis of I. The insoluble arylgermanes were filtered off, washed with water, and dried in the air. They were used in this form for the synthesis of compounds I.

1-Methylgermatrane. A flask fitted with a stirrer and a reflux condenser connected with a water trap was charged with the hydrolyzate obtained from 8.40 g (0.026 mole) of CH_3GeBr_3, and then 3.73 g (0.025 mole) of triethanolamine and 50 ml of xylene were added. The mixture was heated until no more water separated in the trap, which required 1/2 hr. As the water separated from the reaction mixture, a white precipitate of potassium bromide precipitated. The hot mixture was filtered and the residue was washed with hot xylene. When the filtrate was slowly cooled, it deposited crystals of 1-methylgermatrane, which were filtered off, washed with petroleum ether, and dried in vacuum. Yield 4.96 g (85%), mp 156-158° C. After recrystallization from xylene, mp 158-159° C.

1-Ethylgermatrane was obtained similarly from a hydrolyzate of $C_2H_5GeCl_3$.

1-Phenylgermatrane. A mixture of 9.70 g (0.056 mole) of phenylgermasesquioxane, 8.33 g (0.055 mole) of triethanolamine, 200 ml of xylene, and 0.1 g of KOH was heated to the boil until no more water separated in the trap (in 1/2 hr, 1.4 ml of H_2O, 93% of theoretical, separated). The hot solution obtained was filtered and slowly cooled. It deposited crystals of 1-phenylgermatrane which were treated as in the preceding example. Yield 14.70 g (89%), mp 230-231° C. After recrystallization from xylene, mp 232-232.5° C.

1-α-Naphthylgermatrane was obtained similarly to 1-phenylgermatrane from (α-$C_{10}H_7GeO_{1.5}$).

Table 2

Crystallographic Parameters of the 1-Organylgermatranes

$RGe(OCH_2CH_2)_3N$

R	a, Å	b, Å	c, Å	β
CH_3	7.60	9.69	14.38	122°
CH_3CH_2	9.34	16.75	6.72	
C_6H_5	13.19	18.63	10.09	
α-$C_{10}H_7$	9.57	14.54	10.64	

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