

GERMATRANES AND THEIR ANALOGS.

SYNTHESIS, STRUCTURE,

AND REACTIVITY. (REVIEW)*

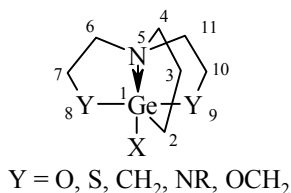
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Results on the synthesis of germatranes and their analogs, the chemical behavior of these compounds, and the characteristics of the transannular germanium–nitrogen bond in these compounds are reviewed and classified.

Keywords: azagermatranes, germanium, germatranes, hypervalent interaction.

One of the challenges in chemistry is the investigation of the nature of the chemical bond. Compounds with nonclassical interactions are of particular interest. The range of substances containing such bonds that have been investigated in recent times includes organic derivatives of silicon, germanium, and tin with an extended coordination sphere, in which hypervalent bonding of the atoms in the molecule occurs. Many of these compounds play an important role in the study of the general relationships governing nucleophilic substitution reactions and also have a wide range of biological activity. In this series the cyclic pentacoordinated derivatives of the 14 group elements – metallatranes (M = Si, Ge, Sn) have attracted particular attention. The silatranes, which have been the subject of a series of reviews [1-3], have been investigated most systematically. Recently a considerable number of papers have been published on the synthesis, structure, and properties of germatranes. Unfortunately, the number of reviews has been limited to isolated examples concerned with a specific region in the chemistry of these compounds [2, 4, 5].

We are presenting a review in which published data on the synthesis of these derivatives, investigation of their chemical properties, and study of the transannular germanium–nitrogen bond in germatranes and their analogs (germatranes containing hydrocarbon substituents in the atrane skeleton, homogermatranes, germatranones, aza-, thia-, and carbagermatranes) are summarized. The literature up to 2001 was analyzed.



* Dedicated to Professor E. Lukevics in connection with his 65th birthday.

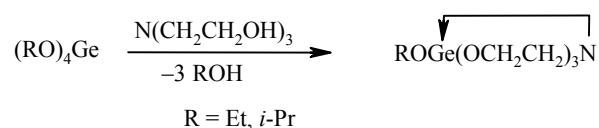
M. V. Lomonosov Moscow State University, Moscow, Russia; e-mail: SSK.SSK@mail.com. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 11, pp. 1451-1486, November, 2001. Original article submitted September 14, 2001.

1. METHODS OF THE ATRANE FRAGMENT GENERATION

Several methods for generation of the atrane fragment have been used for the preparation of metallatranes known at the present time. These methods can be divided into two groups: a) with the use of trialkanolamines in the pure form; b) with the use of trialkanolamine derivatives (silyl or stannyl ethers, trisodium salts, or other metallatranes).

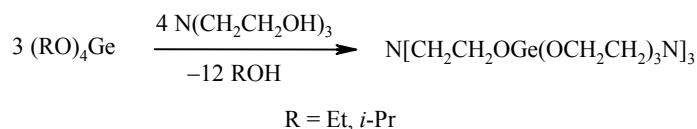
1.1. Reactions of Germanium-containing Compounds and Trialkanolamines

1.1.1. Transalkoxylation. Historically the first and the most often used method (method a) for the generation of the atrane fragment of germatranes is transalkoxylation, i.e., the reaction of tri- or tetraalkoxygermanes with trialkanolamines. The synthesis of germatranes by this method was first described in 1965 [6].

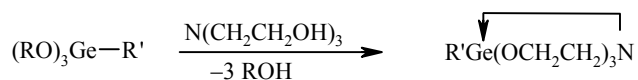


Almost simultaneously with this communication Voronkov and co-workers published a review on the synthesis and structure of metallatranes, in which the synthesis of 1-methoxy-, 1-ethoxy-, and 1-*n*-butoxygermatranes by this method from the corresponding tetraalkoxygermanes was mentioned (with reference to the authors' unpublished data) [7]. It should be mentioned that, in contrast to silicon, catalysis by strong bases (sodium hydroxide, potassium hydroxide) was not used for transesterification in the case of germanium [8].

Mironov and co-workers showed that not only 1-alkoxy- but also 1-chloro- and 1-organylgermatranes can be synthesized similarly using the corresponding alkoxides [9]. The reaction was carried out in dry benzene with distillation of an azeotropic mixture (benzene and alcohol). In [9] eight germatranes were obtained by this method: 1-chloro-, 1-methoxy-, 1-ethoxy-, 1-propoxy-, 1-isopropoxy-, and 1-iodomethylgermatrane, bis(1-germatranyl)methane, and ethyl β -(1-germatranyl)propionate. This made it possible to form an opinion about the wide use of transesterification in the synthesis of germatranes. However, a substantial disadvantage of the method is the extremely low stability of the initial alkoxygermanes to hydrolysis. It should be noted that a compound containing three germatrane fragments in one molecule is formed in the reaction of a large excess of triethanolamine (TEA) with germanium tetraalkoxides [9].



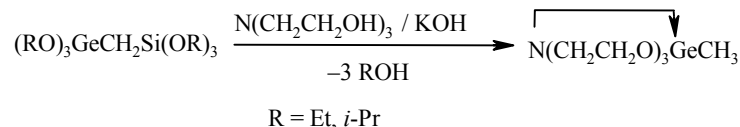
Generation of the germatrane fragment by transalkoxylation was used successfully for the synthesis of 1-substituted germatranes by various groups of researchers [10-45].



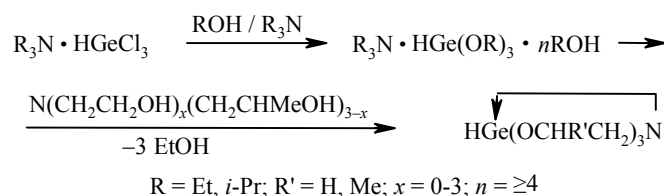
R' = alkyl, cycloalkyl, adamantyl, arylalkyl, alkenyl, arylalkenyl, aryl, heteroaryl, alkynyl, halogenoalkyl, cyanoalkyl, amidomethyl, aminocarbonylmethyl, aminocarbonyloxymethyl, silylalkyl, thiocyanato

1-(1-Adamantyl)germatranes containing methyl substituents in the germatrane fragment were obtained by this method. The yields of the substituted germatranes were lower than in the case of the unsubstituted analog [13].

It should be noted that if compound containing $\text{Si}(\text{OR})_3$ and $\text{Ge}(\text{OR})_3$ groups is reacted with triethanolamine the Si–C bond is broken quantitatively in the presence of the catalytic amounts of potassium hydroxide required for the formation of silatrane [30].

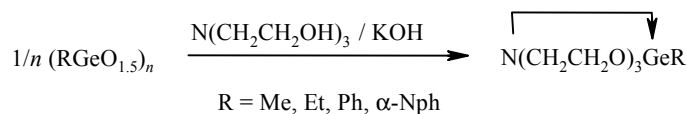


1-Hydrogermatranes were obtained by this method. The aminates of trialkoxygermanes were used as initial germanium-containing compounds [46, 47]. It was shown that the most suitable was the complex of triisopropoxygermane with triethylamine, formed during the reaction of the aminate complexes of trichlorogermane and alcohol. The complex is readily soluble in hydrocarbons and can be brought into reaction with trialkanolamines without isolation [47].



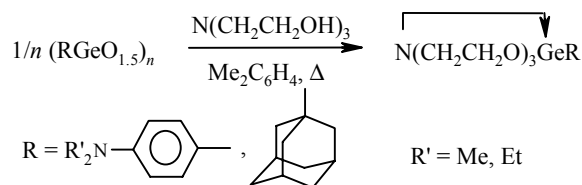
The low yield of 1-hydrogermatranes (27-44%) should be noted. The authors explained this by the formation of polymeric products from decomposition of the initial trialkoxyaminates.

1.1.2. Reaction of Polyorganogermasesquioxanes with Trialkanolamines. Polyorganogermasesquioxanes, the products from partial hydrolysis of organyltrichlorogermanes, were first used for the formation of germatranes by Voronkov and co-workers in 1968 [48]. In this work 1-organylgermatranes unknown at that time were synthesized with yields of 80-90%.

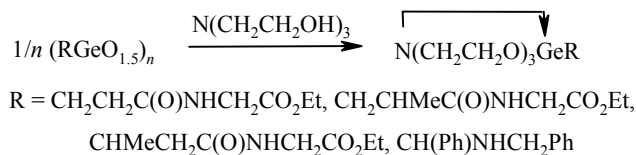


It should be pointed out that the reaction of polyorganogermasesquioxanes with trialkanolamines requires much more drastic conditions (catalysis by potassium hydroxide and boiling in xylene) than transalkoxylation. Like the presence of the water released in the reaction, this can lead to cleavage of the Ge–C bond and the formation of a polymer. The method can, therefore, only be used for the synthesis of a limited number of germatranes in which the Ge–C bond is stable to heat and hydrolysis.

This conclusion is also supported by the data from other papers [32, 49]. Whereas the yield in the case of *para*-substituted derivatives of aniline amounts to about 50% (without the use of the potassium hydroxide catalyst), in the case of the adamantyl substituent it falls to 15% (in the presence of potassium hydroxide).



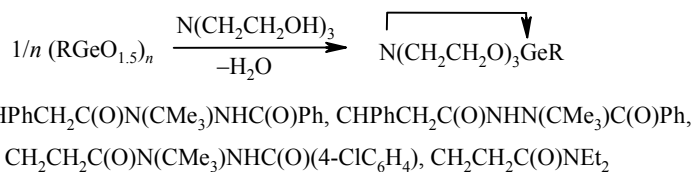
By treating the polyorganogermasesquioxanes with triethanolamine in boiling ethanol or benzene it is also possible to isolate another series of organylgermatranes [36, 50-54].



In [55] the reaction of the corresponding polyorganogermasesquioxanes with triethanolamine, leading to β-(1-germatranyl)-substituted propionic acids [which rearrange to germocines (see section 2.2) under the conditions of synthesis], was described.

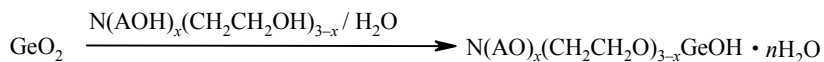
The method can also be used for the synthesis of germatranes containing substituents in the atrane skeleton. When polyphenylgermasesquioxanes are boiled with 2-phenyl- or 2,2'-diphenylethanolamine or triisopropanolamine in toluene in the presence of catalytic amounts of potassium hydroxide germatranes substituted in the atrane fragment are formed with yields of 67, 49, and 34% respectively (lower than in the case of the unsubstituted analog, 89%) [56].

Recently a series of papers were published, demonstrating that 1-substituted germatranes can be formed from germasesquioxanes by treatment with triethanolamine in the presence of dehydrating media (P₄O₁₀, molecular sieves). In this case the reaction takes place at room temperature [57, 58].



In reaction with triethanolamine polyorganogermasesquioxanes can be replaced successfully by polyorganogermasesquisulfides [59].

1.1.3. Reaction of Germanium Dioxide with Trialkanolamines. The most widely used method for the synthesis of 1-hydroxygermatrane and its C-substituted derivatives is the reaction of germanium dioxide with aqueous solutions of trialkanolamines. The yields in this reaction amount to 80-100%.

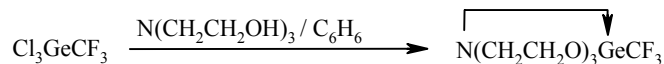


A	x	n	References
—	0	1	[60, 61]
CH ₂ CHMe	1	0.1	[60-62]
CH ₂ CHMe	2	0	[61, 62]
CH ₂ CHMe	3	0	[61, 62]
CH ₂ CHPh	1	0	[61, 62]
CH ₂ CH ₂	1	0	[63]
CH(CO ₂ H)CH ₂	1	0	[64]
CH(CO ₂ H)CH(Me)	1	0	[64]

Depending on the condition of synthesis, the obtained 1-hydroxygermatranes may contain crystal water. The hydrates of 1-hydroxy- and 1-hydroxy-3-methylgermatrane readily lose the water when heated at 50-60°C under vacuum [61].

1.1.4. Reaction of Trichloro- and Tris(dimethylamino)germanes with Trialkanolamines. There are other methods for the generation of a germatrane fragment, but they are used much more rarely than the methods described above.

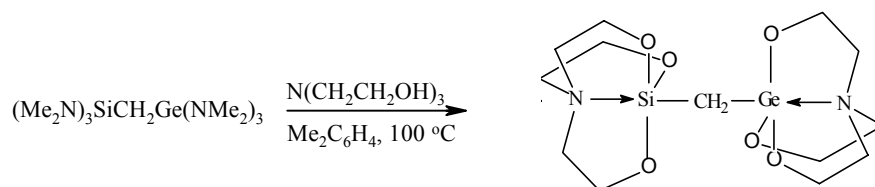
In [65] 1-trifluoromethylgermatrane was obtained with a 45% yield by the reaction of triethanolamine and CF_3GeCl_3 . The released HCl forms a salt with the triethanolamine.



An analogous reaction was recently used for the synthesis of 1-chlorogermatrane [66].

During the treatment of RGeCl_3 with triethanolamine or $\text{N}(\text{CH}_2\text{CHMeOH})_3$ in the presence of catalytic amounts of potassium hydroxide 1-substituted germatranes are formed with high yields [67].

It was found that the Ge–N bonds (like Si–N bonds) in $(\text{Me}_2\text{N})_3\text{SiCH}_2\text{Ge}(\text{NMe}_2)_3$ are sufficiently labile for cleavage by triethanolamine [30].

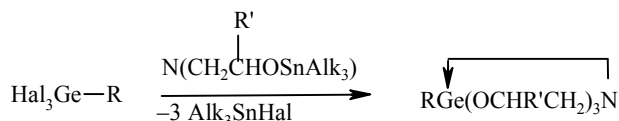


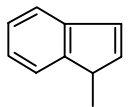
The rate and degree of reaction depend on the substituent at the germanium atom [68]. According to NMR spectroscopy, whereas the reaction takes place instantaneously in the case of $\text{MeGe}(\text{NMe}_2)_3$, with $t\text{-BuGe}(\text{NMe}_2)_3$ it goes to the extent of only 60% after boiling for 44 h in C_6D_6 .

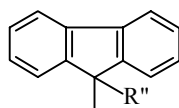
1.2. Reaction of Germanium-containing Compounds with Na, B, Si, and Sn Derivatives of Trialkanolamines

The creation of the atrane fragment by the reaction of trihalogenogermanes and trialkylstannyl ethers of trialkanolamines was first used for the synthesis of 1-(5-cyclopentadienyl)germatrane [69, 70]. The reaction was carried out at reduced temperature in *n*-hexane; the product was isolated with a yield of 98%. The same method was used for the synthesis of 1-chloro-, 1-vinyl-, 1-ethynyl-, 1-phenylethynyl-, and 1-cyclohexylethynylgermatranes. The yields of the recrystallized compounds were 60-70% [71].

Using an organotin method, Zaitseva and co-workers obtained a wide range of germatranes with various substituents both at the germanium atom and in the atrane fragment. The yields in all cases (except 1-hydrogermatrane, 44%) were close to quantitative [72-79].

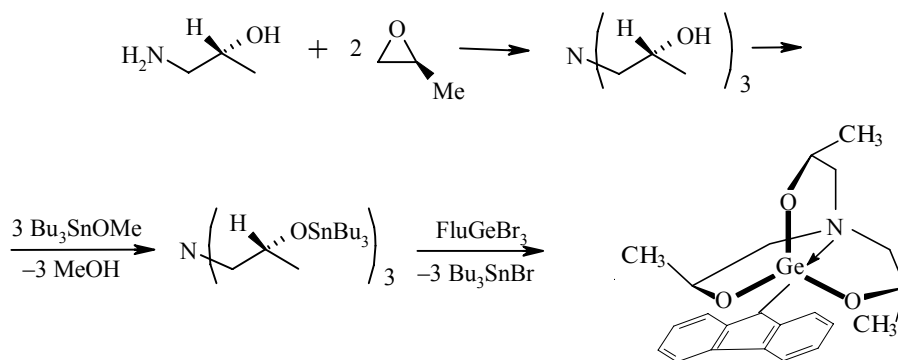


Hal = Cl, Br; Alk = Et, *n*-Bu; R' = H, Me; R = H, All, $\text{Ph}(\text{Me}_3\text{Si})\text{CH}$, Ph_2CH , $\text{MeO}_2\text{C}(\text{Me}_2)\text{C}$, $\text{MeO}_2\text{C}(\text{Me}_3\text{Si})\text{CH}$, $\text{MeO}_2\text{C}(\text{Ph})\text{CH}$, $\text{EtO}_2\text{C}(\text{Ph})\text{CH}$, $(\text{EtO}_2\text{C})_2\text{CH}$, 



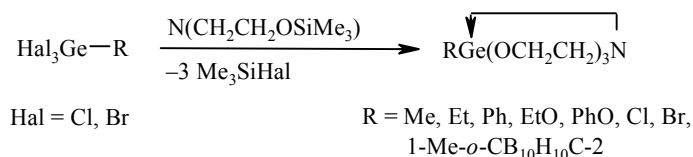
R'' = H, Me_3Si , Me_3Ge

The symmetrical diastereomer of 3,7,10-trimethyl-substituted germatrane was first obtained according to the scheme presented below [77].



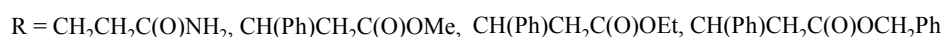
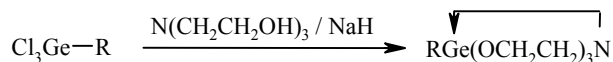
There are data on the possibility of using mercapto and acyloxy derivatives as well as trihalogenogermans in this reaction [80].

In addition to the stannyl ethers of trialkanolamines, their silyl analogs have also been applied for the synthesis of germatranes [81, 82].

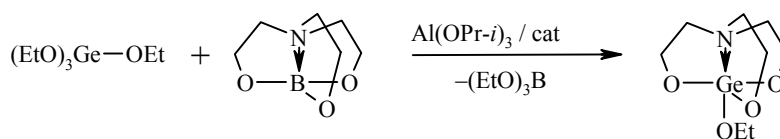


The silyl ethers of triethanolamine give possibility to avoid the relatively toxic organotin derivatives. It should be noted, however, that the method is greatly restricted by the fairly low yields of the germatranes obtained in this case (37-85%) and also by the need to boil the reagents at high temperature. The silyl version was used for the synthesis of furyl- and thienylgermatranes [29], but unfortunately the authors did not describe the reaction conditions.

In 1985 a method was proposed for the creation of the germatrane fragment using the trisodium salt of triethanolamine $\text{N}(\text{CH}_2\text{CH}_2\text{ONa})_3$ which was generated *in situ* in solution of DMF by the action of sodium hydride on triethanolamine [34, 83]. On account of the comparatively low yields (40-60%) and also the complexity of the separation of the final products from sodium chloride this method has not been widely used for the synthesis of germatranes.



Recently Lukevics and co-workers reported on the synthesis of 1-ethoxygermatrane with a yield of 87% by the reaction of tetraethoxygermane and boratrane.



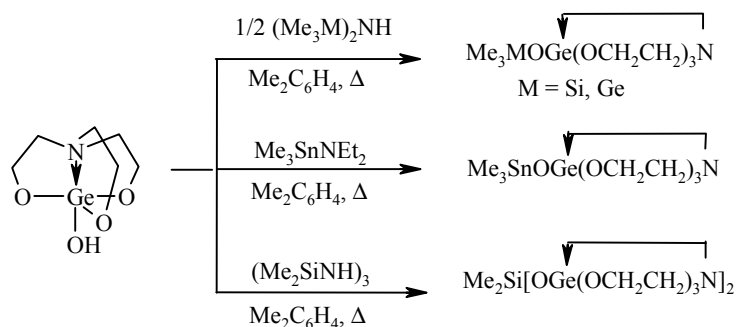
The authors note that tetraethoxygermane is significantly more active in this reaction than the corresponding silane [84]. (In the latter case the reaction under the same conditions takes 3 h and gives an 80% yield of the corresponding silatrane.)

2. THE CHEMICAL PROPERTIES OF GERMATRANES

2.1. Reactions Taking Place with Retention of the Germatrane Fragment

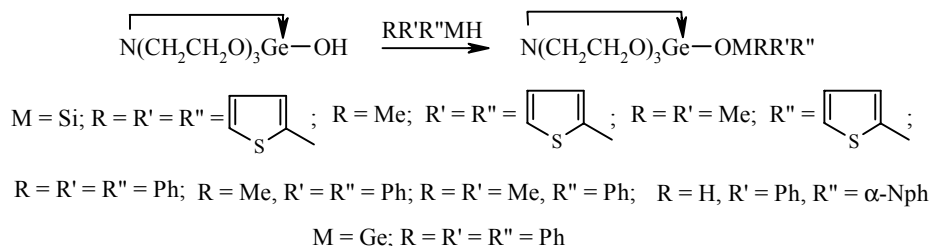
The chemical properties of germatranes has been insufficiently investigated. This is probably due to the specific behavior of the atrane fragment under the influence of the various reagents. The most studied compound among the germatranes is 1-hydroxygermatrane.

Heating of 1-hydroxygermatrane with silicon, germanium, and tin amides in xylene leads to quantitative cleavage of the M–N bond [9, 33, 61] with the formation of the corresponding siloxy-, germyoxy-, and stannoxygermatranes with yields of about 90%.

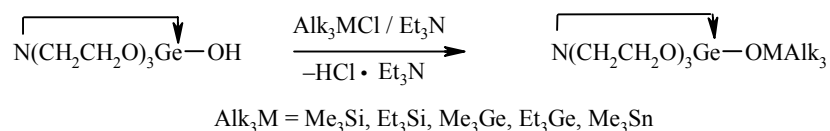


The treatment of the product from the reaction of germanium dioxide, triisopropanolamine, and water by hexamethylsilazane without isolation of the 1-hydroxy-3,7,10-trimethylgermatrane an 87% yield of 1-trimethylsiloxy-3,7,10-trimethylgermatrane was obtained [85].

In boiling xylene the reaction of 1-hydroxygermatrane with hydrosilanes and hydrogermanes proceeds with cleavage of the element(Si,Ge)–hydrogen bond. The reaction takes place without a catalyst, when there is a 2-thienyl substituent at the silicon atom. In other cases the presence of a catalyst (H_2PtCl_6 or Amberlyst 15) is necessary [86]. However, the yields of the 1- R_3MO -germatranes differ greatly (2-80%), and depend on the catalyst.

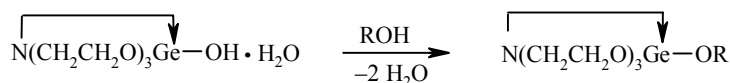


1-Trialkylsiloxy, 1-trialkylgermyoxy-, and 1-trialkylstannoxygermatranes can also be obtained by the condensation of 1-hydroxygermatrane with Alk_3MCl ($\text{M} = \text{Si}, \text{Ge}, \text{Sn}$) in the presence of triethylamine at room temperature. However, the yields in this case are significantly lower (30-40%) [9, 33].

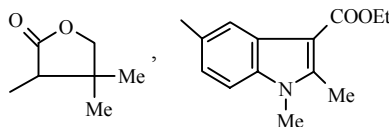


An attempt to prepare $\text{N}(\text{CH}_2\text{CH}_2\text{O})_3\text{GeOGe}(\text{OCH}_2\text{CH}_2)_3\text{N}$ by the condensation of 1-hydroxygermatrane and 1-chlorogeratrane in boiling xylene was unsuccessful. Only the initial substances were isolated from the reaction mixture [9, 33]. Bis(germatranyl)oxide was subsequently obtained by Mironov by heating (160°C) 1-hydroxygermatrane monohydrate under vacuum [87].

The condensation of 1-hydroxygermatrane with alcohols, phenols, and naphthols is a convenient preparative method for the synthesis of 1-organooxygermatranes [88, 89].



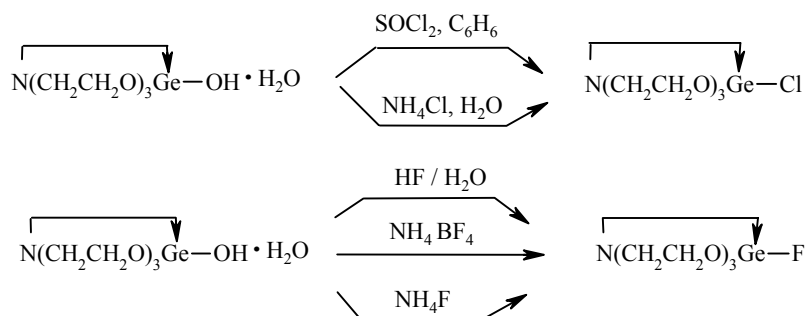
$\text{R} = \text{CHMe}_2, \text{CH}_2\text{CHMe}_2, \text{CH}_2\text{CH}_2\text{CHMe}_2, \text{cyclohexyl}, \text{CH}_2\text{Ph}, 4\text{-MeC}_6\text{H}_4, \text{C}_6\text{Cl}_5, \alpha\text{-Nph}, \beta\text{-Nph},$



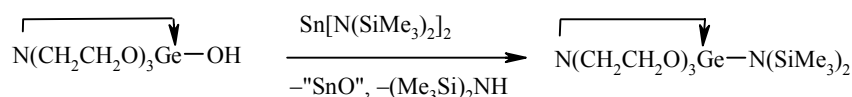
In the case of aliphatic alcohols 1-hydroxygermatrane is boiled in an excess of the corresponding alcohol, while in other cases the reaction is carried out in boiling xylene. The yields of 1-organooxygermatranes in this reaction are about 90%. When the reaction was carried out in boiling benzene ($\text{R} = 2\text{-H}_2\text{NC}_6\text{H}_4$), the yield of the respective germatrane amounted to 56% [60].

1-Hydroxygermatrane is a convenient starting compound for the synthesis of 1-halogenogeratranes. 1-Fluorogeratrane can be obtained with a yield of 87% by the action of HF on 1-hydroxygermatrane in water [33], with yields of about 90% by the action of NH_4F or NH_4BF_4 in water [90], or with a yield of 82% by the action of $\text{BF}_3 \cdot \text{Et}_2\text{O}$ in acetonitrile [91]. 3,7,10-Trimethyl-1-fluorogeratrane was obtained with yields of about 90% by the action of NH_4F or NH_4BF_4 on the corresponding germatrane in water.

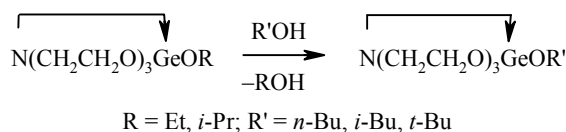
1-Chlorogeratrane is formed with a yield of 62% by the action of SOCl_2 on 1-hydroxygermatrane in boiling benzene [33] and with yields of about 90% by the action of ammonium chloride in water [90]. 1-Chloro-3,7,10-trimethylgermatrane was also obtained by the last method.



An interesting replacement of the hydroxy group at the germanium atom by $\text{N}(\text{SiMe}_3)_2$ was discovered during the treatment of 1-hydroxygermatrane with bis[bis(trimethylsilyl)amino]stannylene. 1-[Bis(trimethylsilyl)amino]germatrane, isolated with a yield of 77%, is the first example of a germatrane containing a $\text{N}-\text{GeO}_3-\text{N}$ group [92]. The mechanism proposed by the authors includes a stage with the formation of $(\text{Me}_3\text{Si})_2\text{N}-\text{Sn}-\text{O}-\text{GeAtr}$.

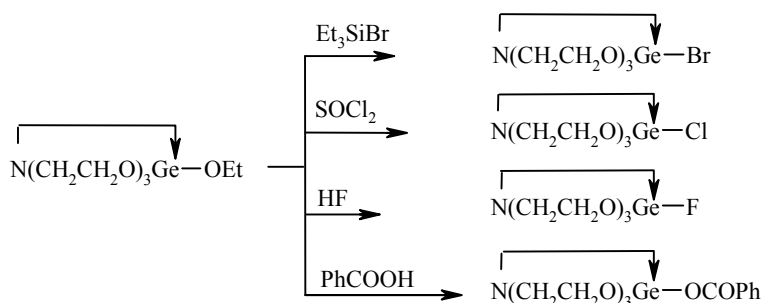


1-Organooxygermatranes and 1-trimethylsiloxygermatranes have properties similar to the properties of 1-hydroxygermatrane. The first paper devoted to germatranes [6] describes the transalkoxylation of alkoxygermatranes by higher alcohols.



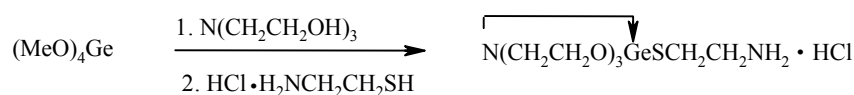
The authors of [9] obtained 1-triphenylsiloxygermatrane with a yield of 95% by boiling a mixture of triphenylsilanol and 1-methoxygermatrane in dichlorobenzene and also obtained 1-acetoxygermatrane with a yield of 91% by boiling a mixture of acetic anhydride, acetic acid, and 1-methoxygermatrane in dichlorobenzene.

The properties of 1-ethoxygermatrane were investigated in detail by Mironov and co-workers [33].



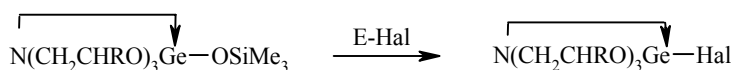
Fluorination and chlorination take place at room temperature in isopropyl alcohol and chloroform respectively. The yield of 1-fluorogermatrane amounts to 71%, and that of 1-chlorogermatrane to 73%. To obtain 1-bromogermatrane (86%) and 1-benzoyloxygermatrane (85%) the reaction was carried out by boiling in *o*-dichlorobenzene and *o*-xylene respectively.

The Ge–O bond in 1-methoxygermatrane is cleaved smoothly by the action of sulfur derivatives [93].



In [94, 95] the reaction of 1-ethoxy- and 1-methoxygermatranes with diphenylketene and bis(trifluoromethyl)ketene, leading to the formation of the derivatives of carboxylic esters, was studied.

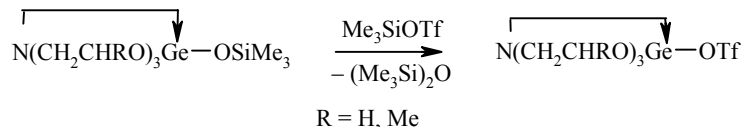
Some halogenating reagents cleave the apical Ge–O bond in 1-trimethylsiloxygermatrane to form 1-halogenogermatranes [85, 89].



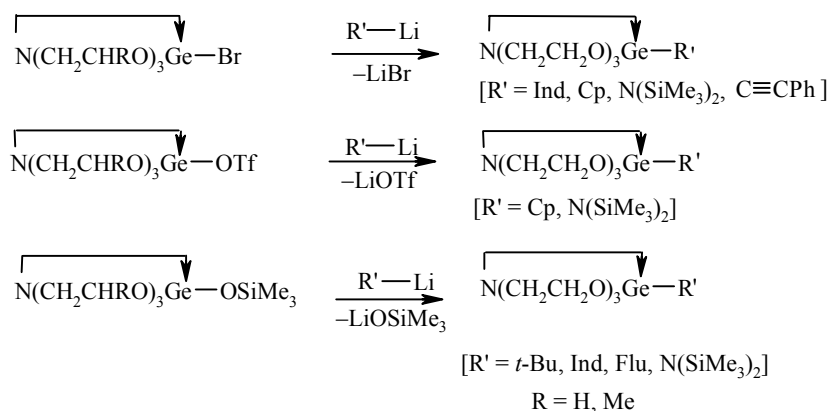
R = H; E-Hal = SOCl₂, Me₃SiBr; R = Me; E-Hal = HF, SOCl₂, Me₃SiBr, Me₃SiI

In all cases except trimethylbromosilane (boiling in xylene) the reaction is carried out at room temperature. The yields of the 1-halogenogermetranes amount to 60-85%.

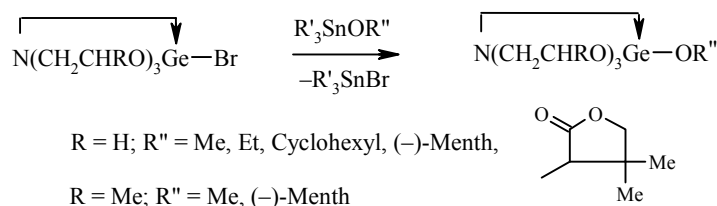
Treatment of 1-trimethylsiloxygermatrane and its 3,7,10-trimethyl-substituted analog with trimethylsilyl triflate Me_3SiOTf ($\text{Tf} = \text{SO}_2\text{CF}_3$) at room temperature leads to a quantitative yield of 1-germatranyl triflates [96].



Unlike tetracoordinated trialkoxygermanes, the simplest germatranes (1-bromo-, 1-trimethylsiloxygermatranes, and 1-germatranyl triflates) react with lithium derivatives in THF, giving high yields of functionally substituted germatranes [96, 97].

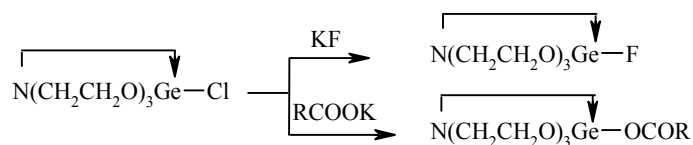


The Ge-Hal bond in 1-halogenogermetranes is more inert than in the tetracoordinated germanium derivatives. However, Nasim, Zaitseva, and others found [89, 98] that the treatment of 1-bromogermatrane or 1-bromo-3,7,10-trimethylgermatrane with trialkylalkoxystannanes led to high yields of 1-organooxygermatranes (85-95%).



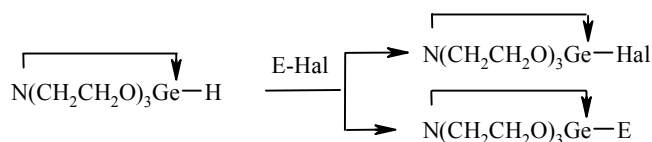
Treatment of 1-chlorogermatrane with 1-triphenylsilanol in the presence of triethylamine gave 1-triphenylsiloxygermatrane with a yield of 51% [9].

1-Chlorogermatrane can be converted into 1-fluoro- and 1-acyloxygermatranes by the action of potassium fluoride and KOC(O)R respectively [66, 99].



Unlike 1-hydrosilatane, which reacts with alcohols and phenols in the presence of bases to form 1-organooxysilatrane [100], 1-hydrogermatrane does not react with *n*-butanol even in the presence of a catalyst, but with phenol in the presence of sodium phenolate or colloidal nickel it gives 1-phenoxygermatrane with yields of 10 and 14% respectively. It should be noted that triethylgermane does not react with phenol under these conditions. 1-Hydrogermatrane does not form identifiable products in reaction with ethyl acrylate and acetonitrile in the presence of azodiisobutyronitrile.

The reactions of 1-hydrogermatrane with various halogenating agents have been studied well [33]. The treatment of 1-hydrogermatrane with N-bromosuccinimide and bromoform under mild conditions gives 1-bromogermatrane with yields of 60 and 98% respectively. The reaction with other halogen-containing compounds takes place in a more complicated manner.



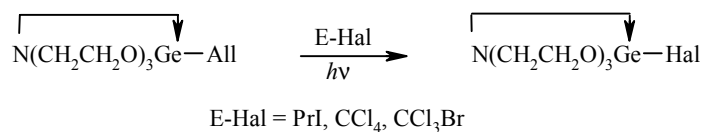
Halogenating agent	Solvent	Yield, %	
		AtrGe-Hal	AtrGe-E
CH ₂ =CHCH ₂ Br	Acetonitrile	45	—
CH ₂ =CHCH ₂ Br*	Benzene	—	21
CH ₂ =CHCH ₂ I		—	13
Ph ₃ CCl	Acetonitrile	42	43
Ph ₃ CCl	Benzene	6	8
CDCl ₃ **		—	45.5

* Catalyst benzoyl peroxide.

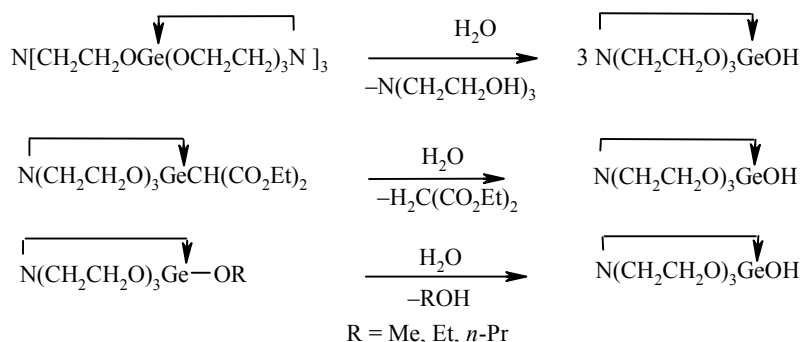
** Catalyst hydroquinone.

A detailed investigation of the reaction of 1-hydrogermatrane with chloroform showed that the yield of 1-chlorogermatrane is significantly affected by the type of catalyst, but the amount of 1-dichloromethylgermatrane formed does not depend on the reaction conditions (about 30%) [33].

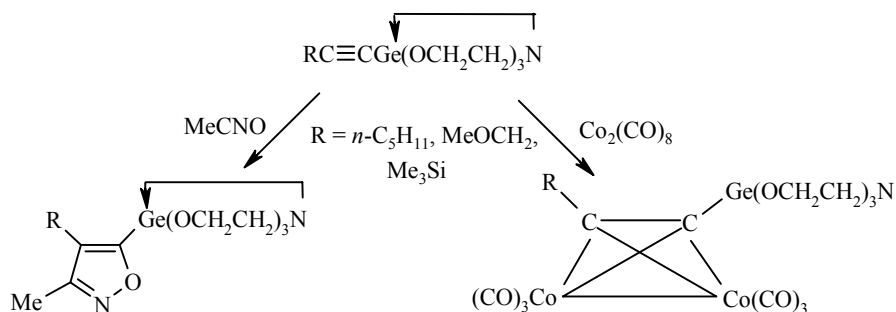
The reaction of 1-allylgermatrane with polyhalogenoalkanes leads to cleavage of the Ge–C bond and the formation of 1-halogenogermatranes with high yields [101].



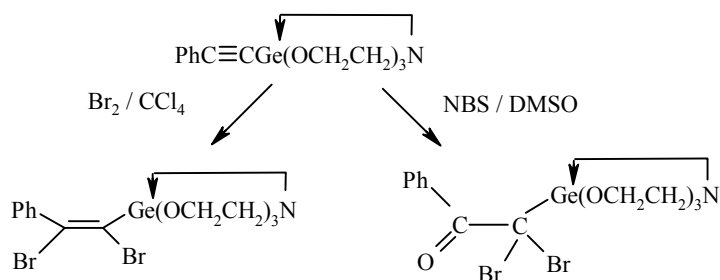
There are no papers specially devoted to the hydrolysis of germatranes in the literature. However, some data suggest that in the overwhelming majority of cases hydrolysis leads to the smooth formation of 1-hydroxygermatrane [9, 74, 87].



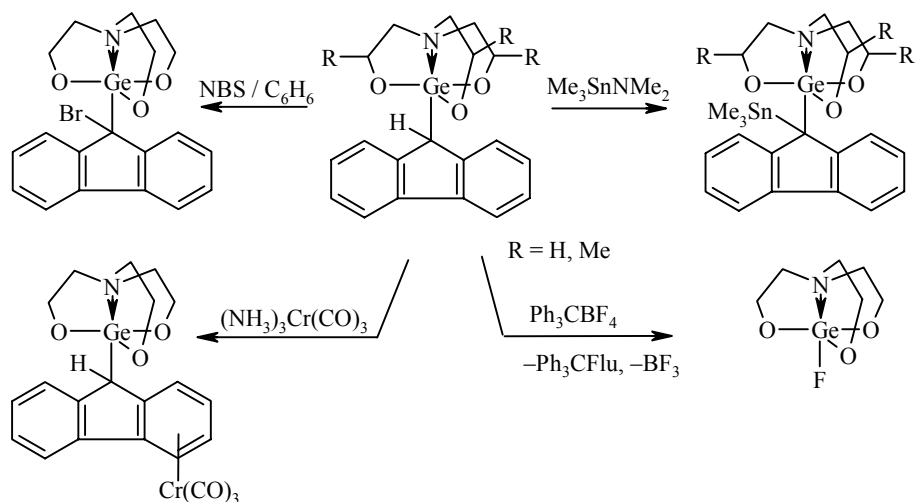
Recently the attention of researchers has been attracted to the chemical transformations taking place in the substituent at the germanium atom. The most widely studied at the present time are 1-ethynylgermatranes and 1-fluorenylgermatranes. Lukevics and co-workers investigated the reaction of ethynyl derivatives with acetonitrile oxide and $\text{Co}_2(\text{CO})_8$ [44].



The reaction of 1-phenylethynylgermatrane with N-bromosuccinimide in DMSO or in water leads to the formation of an α,α -dibromo ketone, while treatment with a solution of bromine in carbon tetrachloride gives a *cis*-addition product [97].

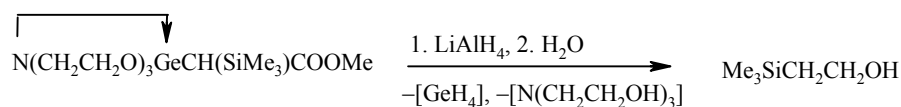


For 1-(9-fluorenyl)germatrane, which contains several reaction centers (the apical Ge–C bond, the equatorial Ge–O bonds, the mobile hydrogen atom at position 9, the fluorenyl group, and the aromatic rings), the reactions with reagents that could affect each of these centers were studied [76, 77, 102].

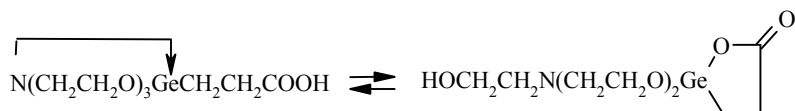


2.2. Reactions Leading to Destruction of the Atrane Fragment

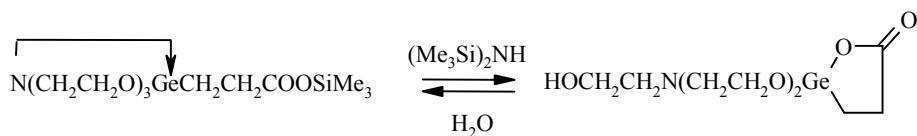
There is little information in the literature on reactions of germatranes leading to destruction of the atrane fragment. During the treatment of 1-hydrogermatrane with iodoform, diiodomethane, or bromine the atrane fragment is cleaved. The reaction of 1-allylgermatrane with I_2 leads to the same result [33]. Reduction of methyl germatranyl(trimethylsilyl)acetate with lithium aluminum hydride [74] leads to the formation of the respective organosilicon β -alcohol.



Treatment of 1-bromogermatrane and 1-trimethylsiloxy-3,7,10-trimethylgermatrane with n -BuLi and LiNMe_2 leads to $(n\text{-Bu})_4\text{Ge}$ and $(\text{Me}_2\text{N})_4\text{Ge}$, and an excess of t -BuLi also cleaves the germatrane skeleton [96]. A germocine–germatrane rearrangement takes place with cleavage of the germatrane fragment.

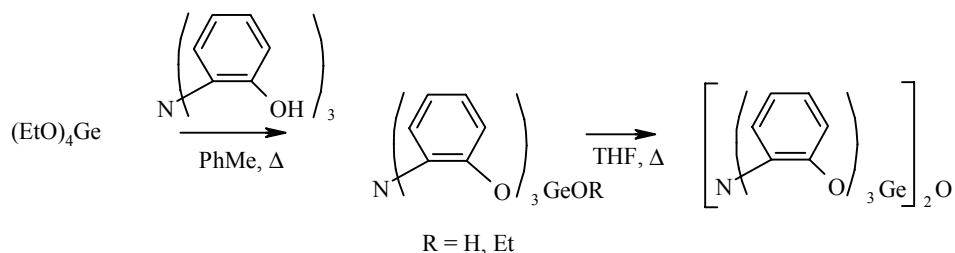


In solution of DMSO at room temperature both forms exist. Increase of temperature shifts the equilibrium toward the germatrane. The data from the mass spectra indicate that only the germatrane form exists in the gas phase. The germocine can be converted into the germatrane by chemically bonding the proton of the carboxyl group [12, 55, 103].

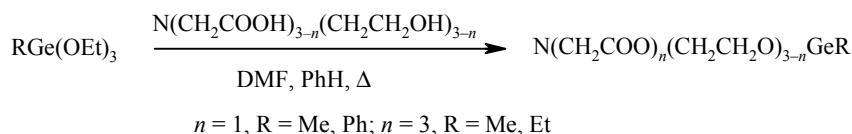


3. SYNTHESIS AND CHEMICAL PROPERTIES OF THE GERMATRANE ANALOGS

In addition to germatranes with classical structure, a series of their analogs are known. In 2001 a series of compounds belonging to a previously unknown type of germatranes containing the tris(2-hydroxyphenyl)amine residue as ligand were obtained [104]. Transalkoxylation led to a mixture of compounds, in which ethoxygermatrane predominated (^1H , ^{13}C NMR and mass spectra). After dissolution in boiling THF and removal of the THF for several weeks it was possible to isolate crystals of germoxane suitable for X-ray crystallographic analysis. However, according to ^1H NMR data the whole sample also contained ethoxygermatrane. The authors suggest that hydroxygermatrane was also present in both mixtures.



In 1980 Mironov and co-workers obtained germatranones – carbonyl-containing germatranes [105].



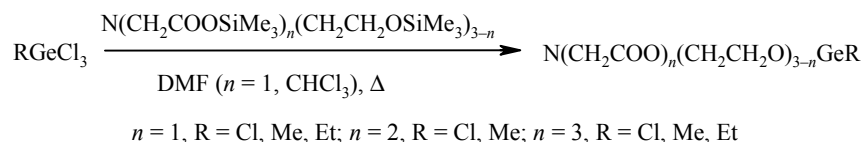
1-Organylgermatrane-3,7,10-triones were isolated in the form of complexes with one molecule of DMF. The yields in this reaction amounted to 60-87%. Subsequently, a series of other germatranones were obtained by transalkoxylation [106]. In the case of nitrilotriacetic acid in a DMSO–benzene mixture 1:1 adducts with DMSO are formed.

n	R	Ligand	Yield, %
1	Et	—	69
2	Me	—	54
2	Et	—	70
3	Me	DMSO	82
3	Ph	DMSO	97

When heated under vacuum the complex $\text{N}(\text{CH}_2\text{COO})_3\text{GeMe} \cdot \text{DMSO}$ loses the DMSO, quantitatively forming 1-methylgermatrane-3,7,10-trione.

Polyorganogermosquisulfides can also be used as organogermanium starting compounds in the reaction with nitrilotriacetic acid [59].

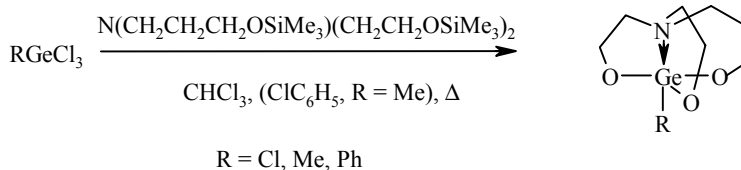
The reaction of the silyl esters of aminoacetic acids and trichlorogermans also leads to the formation of germatranones (1:1 adducts with DMF in the case of the 3,7,10-triones) [107]. The yields of the germatranones amount to 50-85%.



1-Hydroxygermatrane-3,7,10-trione was obtained in the form of the trihydrate by the treatment of GeCl_4 with a hot saturated solution of nitrilotriacetic acid [108]. (The yield was not determined.)

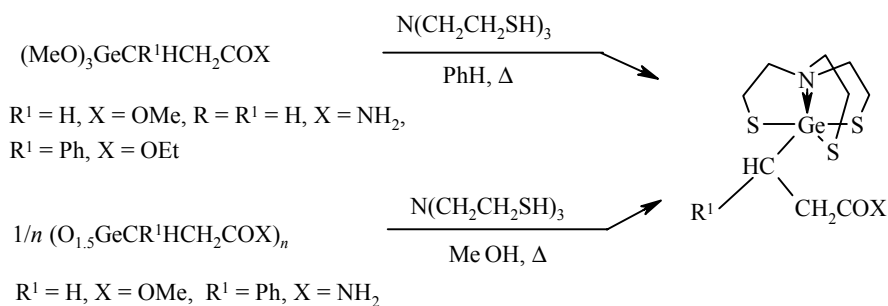
All the germatranones known at the present time are white high-melting substances poorly soluble in organic solvents.

In 1982 Lukevics and co-workers described the synthesis of 1-substituted 3-homogermatranes [81].

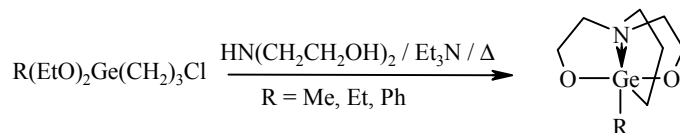


1-Methyl-3-homogermatrane was also obtained in the transalkoxylation of methyltriethoxygermane with 3-hydroxypropylbis(2-hydroxyethyl)amine by boiling in xylene solution in the presence of potassium hydroxide. 1-Phenyl-3-homogermatrane and α -naphthyl-3-homogermatrane were obtained by treating the corresponding organogermasesquioxanes with 3-hydroxypropylbis(2-hydroxyethyl)amine under the same conditions.

Akiba and co-workers described the synthesis of another type of germatrane analogs – 2,8,9-trithiagermatranes [109, 110] and noted high resistance to hydrolysis of $\text{N}(\text{CH}_2\text{CH}_2\text{S})_3\text{GeCH}_2\text{CH}_2\text{COOH}$.

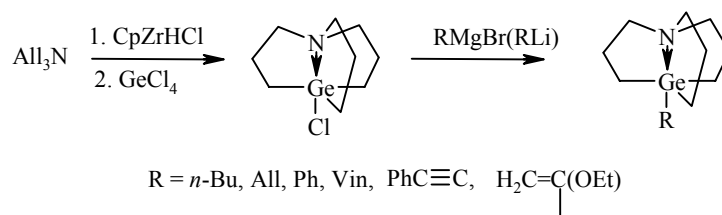


Carbon analogs of germatranes – carbagermatranes – are also known. Mironov and co-workers obtained 2-carbagermatranes – germatranes in which one oxygen atom in the atrane skeleton is replaced by a CH_2 group [111, 112]. They are low-melting solids (1-ethyl-2-carbagermatrane is a viscous liquid), more susceptible to hydrolysis than the corresponding germatranes.

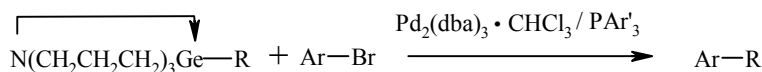


The yields of the 2-carbagermatranes are low (20-50%), and the reaction is complicated by the formation of a large amount of polymer. An attempt to obtain 1-ethoxy-2-carbagermatrane led to the formation of only $(\text{EtO})_3\text{Ge}(\text{CH}_2)_3\text{OEt}$.

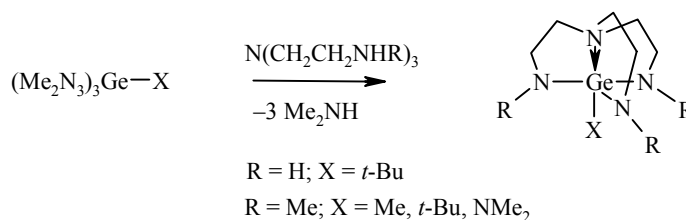
2,8,9-Tricarbagermatranes were obtained by transmetalation [113]. The yield of 1-chloro-2,8,9-carbagermatrane amounted to 89%. Its treatment with organomagnesium or organolithium compounds led to the formation of 1-organyl-2,8,9-tricarbagermatranes with high yields (74-98%). (The yield of 1-phenylethynyl-2,8,9-tricarbagermatrane amounted to 11%.)



The authors [113] studied the cross coupling of the obtained germatranes with aryl halides. It was noticed that the carbagermatranes had higher reactivity than the corresponding tributylgermanes, and the authors explained this by the presence of the transannular Ge←N bond in the molecules of the carbagermatranes.



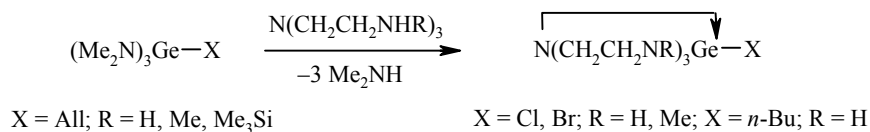
In 1993 Verkade and co-workers first synthesized the nitrogen analogs of germatranes – azagermatranes [68]. They were synthesized by the transamination of the corresponding tris(dimethylamino)germanes and also tetrakis(dimethylamino)germane with tris(2-aminoethyl)amines.



The product yields amounted to 60-70%, except for the case where R = Me, X = NMe₂. The azagermatrane N(CH₂CH₂NH)₃GeNMe₂ could not be isolated at all. The authors explained this by the formation of oligomers as a result of further substitution at the N–H bond of the azagermatrane. During the reaction of 1-alkylazagermatranes with triethanolamine quantitative substitution of the azaatrane fragment by the oxygen-containing analog occurs.

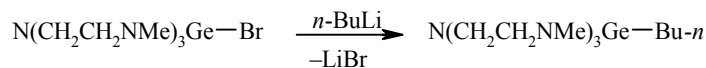
The number of papers on the synthesis and properties of azametallatranes of the 14 group has recently increased greatly. Unfortunately, azagermatranes are the least investigated among these compounds, which are extremely attractive both from the standpoint of fundamental investigations and at the applied level [68].

In 1998 Zaitseva and co-workers obtained a number of 1-allylazagermatranes using the transamination reaction [75]. It is interesting to note that 1-chloro- and 1-bromoazagermatranes, unlike their silicon analogs [114, 115], can also be obtained by transamination [116].

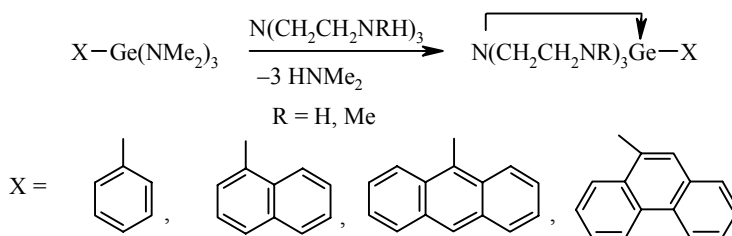


Other azagermatranes were obtained similarly with high yields [116]. 1-Halogenoazagermatranes containing hydrogens at the equatorial nitrogen atoms were isolated in the form of adducts with dimethylamine. An attempt to remove the Me₂NH led to the formation of unidentifiable products.

1-*n*-Butyl-N,N',N''-trimethylazagermatrane was obtained in the reaction of 1-bromo-N,N',N''-trimethylazagermatrane with *n*-butyllithium. The authors noted that the derivative of pentacoordinated germanium was less active than its analog containing tetracoordinated germanium [116].

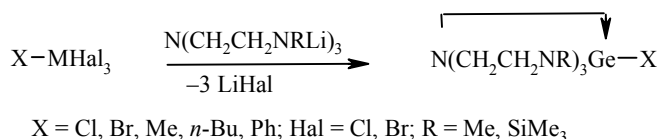


In 2001 1-arylazagermatranes – a previously unknown type of compound – were obtained also by transamination [45].



In all cases the yields were higher than 50%. 1-Anthracenyl-N,N',N''-trimethylazagermatrane was investigated in reaction with triethanolamine. As in the case of 1-alkylazagermatranes [68], the corresponding germatrane was obtained with a high yield. By treating 1-phenylazagermatrane with three equivalents of *n*-butyllithium and trimethylsilyl chloride it was possible to obtain (with a low yield) the corresponding tris(trimethylsilyl)-substituted azagermatrane [45].

Thus, more than 20 azagermatranes have been obtained using transamination. However, the method has a substantial disadvantage in the instability of the initial tris(dimethylamino)germanes. A more promising approach to azagermatranes is the alternative method of generating the azagermatrane fragment by the reaction of trihalogenogermanes with $\text{N}(\text{CH}_2\text{CH}_2\text{NRLi})_3$ [117].

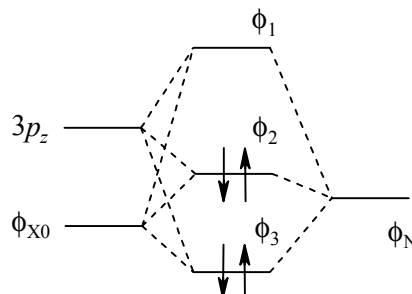


4. INTRAMOLECULAR Ge←N INTERACTION IN GERMATRANES AND THEIR ANALOGS

The suggestion about the existence of an intramolecular coordinated Si←N bond in silatranes was put forward immediately after the appearance of the data on their synthesis [118]. It was based on the discovered inertness of the nitrogen atom in these compounds toward methyl iodide and also on the greater stability to hydrolysis compared with the respective triethoxysilanes. Later, after a series of theoretical and experimental investigations Voronkov and co-workers demonstrated convincingly that the plano-concave structure with a pentacoordinated silicon atom and a tetracoordinated nitrogen atom is the energetically most favorable for silatranes [119]. This agrees with data obtained during the investigation of silatranes by X-ray crystallographic analysis. A similar structure is realized in the germatranes [4].

The first idea about the nature of this interaction was the hypothesis about partial transfer of the unshared electron pair of the nitrogen atom to the unoccupied 3*d*-orbital of the silicon atom [120]. More recently, however, it became clear that the 3*d*-orbitals of silicon are less energetically favorable and significantly more diffuse than the 4*s*- and 4*p*-orbitals [121].

In 1977 a report was published in which the model of "hypervalent bonds" was proposed to explain the structure of silatranes. In terms of this model the interaction of the silicon atom with the three equatorial oxygen atoms takes place through the three sp^2 -hybridized orbitals, while the p_z -electron forms a three-center three-orbital four-electron hypervalent bond jointly with the unpaired electron of the nitrogen and the valence electron of the substituent [122].



This model explains the inverse relationship in the variation of the lengths of the Si–X and Si–N bonds. It also applies to the germanium analogs of silatranes – germatranes. In terms of the hypervalent germanium–nitrogen interaction it was shown for the case of six germatranes that the sum of the orders of the Ge–X and Ge–N bonds is constant and also that the inequality $E_{\text{Ge-N}} > E_{\text{Si-N}}$ is preferred over the inequality $E_{\text{Ge-N}} < E_{\text{Si-N}}$ [123].

At the present time the structure of metallatranes is usually discussed in terms of this theory. However, it is necessary to mention the paper [124], devoted to quantum-chemical investigation of the structure of germatranes. The authors calculated the electronic structure of five compounds $\text{N}(\text{CH}_2\text{CH}_2\text{O})_3\text{GeX}$ ($\text{X} = \text{F}, \text{Cl}, \text{Br}, \text{I}, \text{Me}$) by the SCC-DV- X_α method. The bond lengths and angles obtained for 1-bromogermatrane by X-ray diffraction were used as the necessary structural parameters, and the known values for the tetracoordinated derivatives were used for the Ge–X bond lengths ($\text{X} \neq \text{Br}$). It was concluded that the coordinated $\text{Ge} \leftarrow \text{N}$ bond is formed by coupling between the $4s$ -orbital and the $2s$ -orbital of the nitrogen. The authors estimated the strength of this bond as 50% of a normal covalent Ge–N bond. The three-center N–Ge–X bond mainly has the characteristics of a σ -bond, but π -interaction, in which the $4d$ -orbitals of the germanium atom participate, also makes a small contribution to the bonding. The mechanism of the N–M–X interaction ($\text{M} = \text{Si}, \text{Ge}$) is similar for silatranes and germatranes. The orbitals that participate in bonding are presented below. σ -Interaction in silatranes, (Si) $3sp$ – (N) $2sp$; in germatranes, (Ge) $4s$ – (N) $2s$; π -interaction, (R) np_x – (M) np_x + (M) nd_z – (N) $2p_x$. Variation of the substituent X at the germanium atom affects not only the characteristics of the N–Ge–X bond but also the characteristics of the molecule as a whole. However, these ideas are to some extent uncertain, since a large part of the structural parameters used by the authors is incorrect. However, the general conclusion about the effect of the nature of the substituent on the strength of the N–Ge–X bond does not differ from that discussed above.

4.1. Investigation of the Structure of Germatranes by X-ray Crystallography and Quantum Chemistry

The existence of intramolecular coordination $\text{Ge} \leftarrow \text{N}$ interaction in germatranes is demonstrated most convincingly by investigation of these compounds by X-ray crystallography. At present about 60 germatranes and their analogs have been studied by this method. The principal structural characteristics of these compounds are presented in Tables 1 and 2.

TABLE 1. The Principal Structural Characteristics of Germatranes

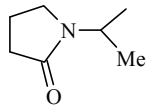
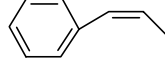
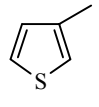
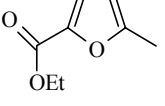
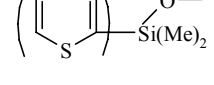
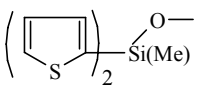
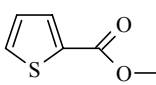
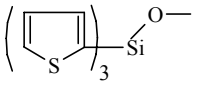
Apical substituent at germanium atom	$d(\text{Ge-N}),$ Å	$d(\text{Ge-X}),$ Å	$\angle(\text{X-Ge-N}),$ °	$\Delta \text{Ge},$ Å	References
1	2	3	4	5	6
$\text{N}(\text{CH}_2\text{CH}_2\text{O})_3\text{GeCH}_2$	2.29	1.95	175.5	0.29	[128]
$(\text{Me}_3\text{Si})_2\text{N}$	2.242	1.845	179.6	—	[92]
Et	2.24	1.97	177.0	0.23	[168]
$\alpha\text{-Nph}$	2.24	1.94	179.0	0.25	[169]
CMe_3	2.238	1.971	180.0	0.27	[171]
$\text{H}_2\text{NCOCH}_2\text{CH}_2$	2.231	1.97	177.0	0.25	[170]
2- MeC_6H_4	2.230	1.94	144.2	0.263	[27, 133]
$\text{C}(\text{Br})=\text{C}(\text{Br})\text{Ph}$	2.228	1.981	178.0	0.24	[97]
	2.223	1.980	177.1	0.24	[172]
$\text{C}(\text{Me}_2)\text{COOMe}$	2.222	2.006	179.0	0.24	[74]
4- MeC_6H_4	2.217	1.946	179.0	0.245	[27, 133]
	2.215	1.939	178.6	0.239	[37]
3- MeC_6H_4	2.214	1.947	176.3	0.253	[133]
Ph	2.212	1.947	177.5	0.238	[27, 133]
$\text{MeOOCCH}(\text{Me})\text{CH}_2$	2.210	—	—	—	[173]
	2.210	—	—	0.23	[174]
$\text{CH}(\text{SiMe}_3)\text{COOMe}$	2.209	1.975	175.72	0.23	[74]
$\text{CH}_2\text{CH}=\text{CH}_2$	2.208	1.956	179.4	0.25	[72]
$\text{C}_{13}\text{H}_8(\text{SnMe}_3)$	2.206	1.964	176.6	0.24	[76]
$\text{C}_{13}\text{H}_8(\text{SiMe}_3)$	2.202	1.987	178.0	0.22	[76]
$\text{MeOOCCH}_2\text{CH}_2$	2.192	—	—	—	[175]
ICH_2	2.190	1.940	175.6	0.21	[176]
4- $\text{Cl-C}_6\text{H}_4\text{C}(\text{O})\text{NHCH}_2$	2.185	1.959	178.2	0.22	[177]
$\text{C}\equiv\text{CPh}$	2.178	1.920	179.4	—	[97]
1- $\text{Me-}o\text{-CB}_{10}\text{H}_{10}\text{C-2}$	2.171	2.004	177.7	—	[82]
ClCH_2	2.167	1.951	176.7	0.21	[17, 136]
$\text{C}_{13}\text{H}_8(\text{H})$	2.166	1.991	177.1	0.21	[73]
2.165	1.937	177.6	0.196	[135]	
					
$\text{C}\equiv\text{CPh} \cdot \text{CHCl}_3$	2.160	1.924	179.1	0.19	[73]
$\text{CH}(\text{Ph})\text{COOMe}$	2.158	1.999	175.0	0.19	[74]
2.156	1.774	—	—	—	[131]
					
(-)-1-MenthO	2.150	1.767	174.5	0.18	[98]
Cl_2CH	2.146	—	—	—	[178]
HO	2.146	1.778	178.7	0.16	[134]

TABLE 1 (continued)

1	2	3	4	5	6
	2.144	1.776	—	—	[131]
Me ₃ SiO	2.128	1.810	—	—	[131]
Ph ₃ SiO	2.126	—	—	—	[86]
	2.12	—	—	—	[99]
F ₃ C	2.108	2.006	179.18	—	[38]
	2.105	1.757	—	—	[131]
Cl	2.096	2.209	179.44	—	[66]
Br	2.09	2.36	179.8	0.11	[132]
SCN	2.081	1.917	179.4	—	[22]
F*	2.011	1.781	179.1	—	[91]
F*	2.104	1.751	179.28	—	[66]

* Two different investigations.

TABLE 2. The Principal Structural Characteristics of the Germatrane Analogs

Compound	$d(\text{Ge-N})$, Å	$d(\text{Ge-X})$, Å	$\angle(\text{X-Ge-N})$, ^o	ΔGe , Å	Reference
Ph-Ge[Me ₃ SiNCH ₂ CH ₂] ₃ N	2.766	1.985	176.4	0.54	[45]
HO ₂ CCH ₂ CH ₂ -Ge(SCH ₂ CH ₂) ₃ N	2.63	—	—	—	[109]
Me-Ge(OCH ₂ CH ₂) ₂ (CH ₂ CH ₂ CH ₂) ₃ N	2.436	1.957	174.5	0.37	[129]
Ph-Ge(CH ₃ NCH ₂ CH ₂) ₃ N	2.307	1.984	176.15	0.32	[45]
Cl-Ge[Me ₃ SiNCH ₂ CH ₂] ₃ N	2.278	2.273	179.5	0.25	[117]
C ₁₃ H ₈ (GeMe ₃)-Ge(OCHMeCH ₂) ₃ N	2.268	1.974	177.6	0.27	[179]
C ₁₃ H ₈ (SnMe ₃)-Ge(OCHMeCH ₂) ₃ N	2.247	1.97	175.5	0.25	[179]
[N(<i>o</i> -C ₆ H ₄ O) ₃ Ge] ₂ O	2.247	1.743	—	—	[104]
	2.235	1.750			
C ₆ H ₅ -Ge(OCH ₂ CH ₂) ₂ [OC(O)CH ₂] ₃ N	2.203	1.952	175.0	0.25	[130]
C ₁₃ H ₈ (H)-Ge(OCHMeCH ₂) ₃ N	2.194	1.999	173.6	0.22	[77]
Cl-Ge(MeNCH ₂ CH ₂) ₃ N	2.167	2.2968	180.0	0.22	[117]
HO-Ge(OCH ₂ CH ₂) ₂ [OCH ₂ CHEt] ₃ N	2.166	1.767	178.8	—	[63]
HO-Ge[OC(O)CH ₂] ₃ N·H ₂ O	2.084	1.762	174.4	0.17	[108]

The investigation of a series of thienylgermatranes by X-ray crystallographic analysis was mentioned in [125], but the authors did not give the structural parameters. Seven structures of thienylgermatranes (Ge←N in the range of 2.155-2.190 Å) and benzylgermatranes (Ge←N 2.184-2.208 Å) are given in Ignatovich's dissertation [125].

The coordination environment of the germanium atom in the investigated compounds represents a distorted trigonal bipyramid with the atoms of the nitrogen and the substituent in the apical positions. The germanium atom is displaced from the plane formed by the three equatorial oxygen atoms toward the apical

substituent. The coordination environment of the nitrogen atom is a distorted trigonal pyramid, and the nitrogen atom is displaced from the plane formed by the three carbon atoms toward the germanium [126, 127]. The Ge←N distance in the germatranes lies within the limits of 2.011(9) Å (for 1-fluorogermatrane [91]) and 2.32(1) Å (for bis-1-germatranylmethane [128]). This distance lies between the values of the sums of the covalent radii of germanium and nitrogen (1.92 Å) and the van der Waals radii of these elements (3.5 Å). With the introduction of a more electronegative substituent at the germanium atom the Ge←N distance is shortened. It is interesting that if germanium is replaced by silicon in metallatranes with an identical apical substituent the metal–nitrogen distance is reduced by 0.03–0.08 Å; the exceptions are 1-fluorometallatranes, where the length of the Ge←N bond is 0.03 Å [91] shorter than the Si←N distance.

Replacement of the oxygen atoms in the atrane skeleton by sulfur atoms or a CH₂ group greatly increases the length of the Ge←N bond, due to the decrease in electron density at the germanium atom with the introduction of the less electronegative CH₂ groups or sulfur atoms [109, 129]. Replacement of one OCH₂ group in the germatrane skeleton by an OC=O group or of an NCH₂ group by an NCH–Et group has practically no effect on the Ge←N distance [63, 130]. With the accumulation of OC(O) groups [compound N(CH₂COO)₃GeO·H₂O] the Ge←N bond is appreciably shortened [108].

An important characteristic of the geometry of the germatrane fragment is the distance by which the germanium atom is displaced toward the apical substituent from the plane formed by the three equatorial oxygen atoms [Δ(Ge)]. It was suggested that the change of this structural parameter is a reflection of the change in the strength of Ge←N interaction, since the Δ(Ge) value lies within the limits between ~0 Å (for 1-fluorogermatrane [91]) and 0.52 Å (for 1-phenyl-N,N',N''-trimethylazagermatrane [45], in the molecule of which Ge←N is the longest distance), while the distance between the nitrogen atom and the equatorial plane is practically unchanged and amounts to ~2.0 Å [4].

The Ge–X distance [minimum 1.757(4) Å for 1-tri(2-thienyl)siloxygermatrane [131]; maximum 2.360(4) Å for 1-bromogermatrane [132]] depends on the nature of the substituent and its variation is the inverse to the variation of the Ge←N distance. The introduction of a sterically hindered substituent in the apical position to the germanium atom considerably reduces the X–Ge–N angle, which is usually equal to 175–180°. Thus, the C–Ge–N angle in 1-(*o*-tolyl)germatrane amounts to 144.2(8)° [133].

The other fragments of the atrane skeleton remain practically unchanged with change of the substituent at the germanium atom. The Ge–O bond lengths lie in the range of 1.74–1.81 Å. It should be noted that the GeO–O_{ax} and Ge–O_{eq} bonds in 1-organylgermatranes are practically identical, although according to the theory of the hypervalent bond Ge–O_{eq} must be shorter than the Ge–O_{ax} bond [63]. It is quite difficult to establish the effect of the substituent at the germanium atom on the C–C, C–O, and C–N bonds of the germatrane skeleton, since their values change slightly from molecule to molecule, although it was noticed that a more electronegative substituent leads to some increase in the length of the C–C bond [134].

All the five-membered rings of the atrane skeleton, including the transannular bond Ge←N (GeOCH₂CH₂N), have the envelope conformation. The substituents at the nitrogen and germanium atoms are in the screened positions while the flaps of the envelope are formed by the carbon atoms at positions 4, 6, and 11 [127]. With the introduction of methyl substituents at positions 3, 7, and 10 of the germatrane fragment the flaps of the envelope are formed by the carbons at positions 3, 7, and 10 [102].

It is necessary to mention the correlations that exist for the structural characteristics of the germatrane skeleton. In 1984 Lukevics and co-workers showed (for the eight germatranes investigated at that time by X-ray crystallographic analysis) that there is a relation between the germanium–nitrogen distance [*d*(Ge←N)] and the deviation of the germanium atom from the plane formed by the three equatorial oxygen atoms Δ(Ge), described by the equation below [135]:

$$\Delta(\text{Ge}) = 0.71d(\text{Ge}\leftarrow\text{N}) - 1.36; \quad r = 0.97 (n = 8).$$

This equation was later refined for 14 compounds [136]:

$$\Delta(\text{Ge}) = 0.72d(\text{Ge}\leftarrow\text{N}) - 1.37; \quad r = 0.960 (n = 14).$$

A similar correlation exists in the molecules of silatranes. On the basis of the analysis of 32 structures Greenberg and Wu [137] found that

$$\Delta(\text{Si}) = 0.61d(\text{Si}\leftarrow\text{N}) - 1.24; \quad r = 0.970 (n = 32).$$

It was also found that the size of the angle (N–Ge–O) in germatranes depends linearly on the Ge←N distance [136].

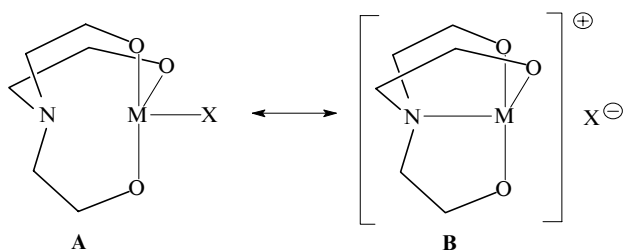
$$\alpha(\text{NGeO}) = -21.1d(\text{Ge}\leftarrow\text{N}) + 129.3; \quad r = 0.926 (n = 13).$$

Systemic disorder of the atoms in the atrane skeleton is often observed in the structures of germatranes. Usually the carbon atoms at positions 3, 7, and 10 are disordered [131], but there are exceptions. Thus, disorder of the thienyl groups at the silicon among two positions was observed in the molecule of 1-[methyldi(2-thienyl)siloxy]germatrane. Calculation of this molecule by the CNDO SCF method in the free state showed the presence of two global energy minima, which correlate with the location of the thienyl radicals in the crystal [131].

Lukevics and co-workers found that the best of the semiempirical methods for calculation of the parameters of the metallatrane structures (M = Si, Ge) was the MNDO method [138]. For 1-hydrogermatrane a curve was obtained for the dependence of the energy of intramolecular interaction on the Ge←N distance. This relationship hardly differs at all from the analogous relationship for 1-hydrosilatrane. The main structural parameters (Ge←N, Ge–O, Ge–R) were calculated for N(CH₂CH₂O)₃GeX (X = H, F, Cl, Br, I, Me, Ph). As for the silatranes, the calculated Ge←N distance for the free molecule was ~0.5-0.6 Å larger than the value obtained experimentally in the crystal by X-ray crystallography; the other structural parameters were comparable with the values found in the crystals. In the opinion of the authors this indicated a significant contribution from crystal field forces to the intramolecular interaction in metallatranes. There is a linear correlation between the calculated Ge←N distance and the effective charge at the N atom (q_N).

$$d(\text{Ge}\leftarrow\text{N}) = 13.589|q_{\text{N}}| - 3.322; \quad r = 0.994 (n = 7).$$

During the investigation of metallatranes by the MNDO method an extremely satisfactory explanation was given for the proximity of the Ge–N and Si–N distances (in germatranes and silatranes respectively) both in the free molecules and in the crystal [138]. The authors proposed to treat the molecules of the metallatranes schematically in the form of two limiting structures **A** and **B**.



Calculation of the ionic and covalent components of the M–N and M–H bonds for 1-hydrometallatrane showed that the part of form **B** was larger for germatranes than for silatranes. The $d(\text{Ge}\leftarrow\text{N})$ values obtained for a wide range of germatranes by X-ray crystallography were closer to the $d(\text{Ge}\leftarrow\text{N})$ value calculated for the germatranyl cation (1.959 Å) than to the $d(\text{Ge}\leftarrow\text{N})$ value calculated for the free molecules. This indicates that the specific gravity of form **B** in the crystal is higher than in the free molecule.

In a continuation of this work the authors [133] made a comparison of the structural and energy parameters of 1-phenyl- and 1-tolylgermatranes in the crystal and in the isolated state (calculated by the MNDO SCF method). It was shown that the order of the $\text{Ge}\leftarrow\text{N}$ in the crystal was higher than for the free molecule, which correlates with the results obtained earlier [138]. All the bond lengths (except $\text{Ge}\leftarrow\text{N}$ and $\text{Ge}\text{--}\text{C}$) for the isolated molecule are comparable with those for the crystalline phase, i.e., the decrease of the $\text{Ge}\leftarrow\text{N}$ distance in the crystal is due to change of the torsion angles in the molecules in the crystalline phase and leads to a change of the angles in the atrane skeleton (e.g., $\text{C}\text{--}\text{Ge}\text{--}\text{O}$). This is confirmed by the fact that the molecules of germatranes in the isolated form and in the crystal exist in different conformations. The authors explain the inverse variation of the $\text{Ge}\leftarrow\text{N}$ distance in the crystal and in the free state by the different stacking coefficients for these compounds.

At the same time calculation of the geometric parameters for the germatrane molecules by the DFT method gives more satisfactory results. Zaitseva and co-workers made an analysis of more than 40 different metallatranes, including more than 20 germatranes [102, 139]. The calculated lengths of the transannular $\text{Ge}\leftarrow\text{N}$ bond differ from the values found in the solid phase by X-ray crystallography by 0.25–0.35 Å, corresponding to the change in the length of the transannular bond in the transition from the solid phase to the gas (data from gas electron diffraction for silatranes [140, 141]). Analysis of the electron density at the critical points of the transannular bond in the metallatranes of the 14 group elements showed that the strength of $\text{M}\leftarrow\text{N}$ interaction increases in the order: $\text{Si}\leftarrow\text{N} < \text{Ge}\leftarrow\text{N} < \text{Sn}\leftarrow\text{N} < \text{Pb}\leftarrow\text{N}$.

An extremely interesting special case in the effect of crystal forces on the structure of germatranes is the change of the $\text{N}\text{--}\text{Ge}\text{--}\text{C}$ angle in 1-(*o*-tolyl)germatrane [133]. In the crystal, as mentioned above, it is $144.2(8)^\circ$, although the standard value of this angle lies in the range of $175\text{--}180^\circ$. The calculated value of this angle (the MNDO method) amounts to 178.4 . The authors explain this by the fact that due to the decrease of the $\text{C}\text{--}\text{Ge}\text{--}\text{O}$ angles and $\Delta(\text{Ge})$ in the crystal the distances between the hydrogen atoms of the methyl group and the atrane oxygen atom decrease, leading to a decrease in the $\text{N}\text{--}\text{Ge}\text{--}\text{C}$ angle.

4.2. Investigation of Germatranes by Other Physicochemical Methods

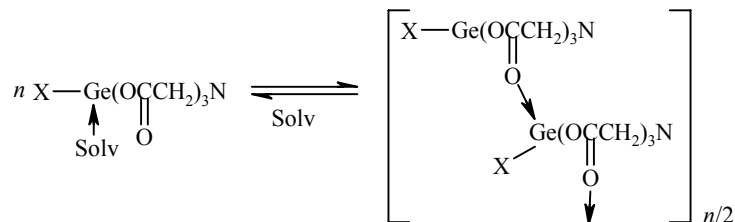
4.2.1. Dipole Moments. In 1983 the dipole moments of eight germatranes and three 2-carbagermatranes were determined using a vectorial scheme [10]. The authors estimated the dipole moment of the $\text{Ge}\leftarrow\text{N}$ bond (directed from the nitrogen atom toward the germanium atom) in 1-substituted germatranes as 2.6 ± 0.1 D and in 1-substituted 2-carbagermatranes as 1.8 ± 0.1 D, which is equivalent to the transfer of 0.24 and 0.18 electron respectively. In this way it was shown that if the oxygen atom in the equatorial position at the germanium atom is replaced by a CH_2 group the $\text{Ge}\leftarrow\text{N}$ interaction in the germatranes is weakened.

The value of the dipole moment for the $\text{Si}\text{--}\text{N}$ bond in silatranes is 2.2 D [142, 143]. The difference between the dipole moments of the $\text{Ge}\leftarrow\text{N}$ and $\text{Si}\text{--}\text{N}$ bonds was explained by the tentative nature of both values [10]. Moreover, in the opinion of the authors, the increase in the dipole moment of the transannular bond in metallatranes in the transition from silicon to germanium is normal, since germanium comes below silicon in the Periodic System of elements.

4.2.2. IR and UV Spectroscopy. The IR spectra of 1-substituted germatranes were first recorded in 1979 [9]. Vibrations in the region of $515\text{--}1280\text{ cm}^{-1}$ were assigned to the vibrations of the germatrane fragment, but the authors did not indicate the absorption band that could be assigned to the $\text{Ge}\text{--}\text{N}$ bond.

During investigation of 1-fluoro-, 1-chloro-, and trifluoromethylgermatranes by Raman spectroscopy it was suggested that the weak band in the region of 260-270 cm^{-1} corresponds to the vibrations of the Ge–N bond, although this band may at the same time belong to the deformation vibrations of the GeO_3 fragment [38, 66].

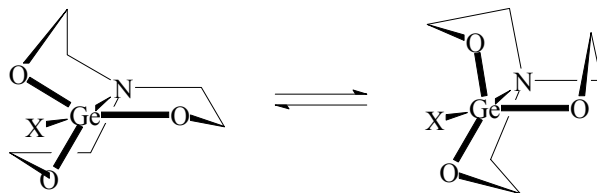
It was established by IR spectroscopy that an equilibrium exists for the 1-substituted 3,7,10-germatranones, i.e., the germanium atom in these compounds is hexacoordinated [106].



During investigation of the dependence of the IR spectrum for 1-hydrogermatrane on the temperature and the solvent it was shown that these relationships are less clearly defined than the corresponding relationships for 1-hydrosilatrane [144]. The authors suppose that this may indicate an increase in the strength of the M←N interaction in the metallatranes during the transition from silicon to germanium.

It should be noted that this conclusion is contradicted by data obtained from the UV spectra of 1-alkyl-substituted metallatranes [145]. The authors explained the short-wave shift of the absorption bands of the metallatranes (in water) compared with the model compound (triethylamine) by the formation of a transannular M←N bond; since the shift was larger for silatranes than for germatranes, it was suggested that the Si←N interaction was stronger. (although this may also be explained by the fact that the bands of the group of the germanium atom lie in a more longwave region compared with the group of the silicon atom).

4.2.3. ^1H NMR Spectroscopy. The ^1H NMR spectra of germatranes were first investigated systematically in 1979 by Voronkov and co-workers [146]. The general form of the ^1H NMR spectrum of the atrane skeleton, $\text{N}(\text{CH}_2\text{CH}_2\text{O})_3\text{Ge}$, represents a (AA'XX')₃ system, appearing in the form of two broad triplets. As shown by two-dimensional ^1H NMR spectroscopy (NOESY), conformational transitions, occurring not by a synchronous mechanism but by a multistage mechanism, are possible in the molecules of germatranes [147].



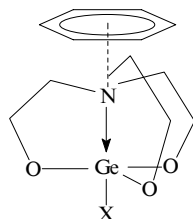
In deuteriochloroform the center of the multiplet for the OCH_2 group lies in the region of 3.76-3.97 ppm, while the NCH_2 group is at 2.76-2.98 ppm. The difference in the chemical shifts of the two multiplets is constant and amounts to ~ 1 ppm. This indicates transmission of the electronic effect of the substituent not only through the system of σ bonds of the atrane skeleton but also through the Ge←N bond. It should be noted that although, according to data from X-ray crystallography, the Ge←N bond becomes longer during substitution of one equatorial oxygen atom by a CH_2 group this does not affect the transmission of the electronic effect of the substituent through the transannular bond [111]. The introduction of substituents at positions 3, 7, and 10 of the atrane skeleton greatly complicates the form of the PMR spectrum. Such systems were analyzed in [13, 148].

Correlations between the chemical shifts of the protons in the atrane skeleton and the electronic constants of the substituent at the germanium atom were calculated in [148] and had the general form

$$\delta \text{ } ^1\text{H} = \delta_0 + a\sigma_i + b\sigma_j \text{ (where } \sigma_i = \sigma^*, \sigma_j = 0; \sigma_i = \sigma_I, \sigma_j = \sigma_R^0 \text{ and } \sigma_i = \text{F}, \sigma_j = \text{R}).$$

It is seen that a more electronegative substituent at the germanium atom intensifies the Ge←N interaction [149] and the centers of the multiplets are shifted downfield. A series in which the Z←N bond in metallatranes $N(\text{CH}_2\text{CH}_2\text{O})_3\text{Z}$ is weakened was proposed on the basis of data from ^1H NMR spectroscopy: $\text{Z: O}=\text{V} > \text{O}=\text{Mo}(\text{OH}) > \text{B} \gg \text{CH}_3\text{Ge} \sim \text{CH}_3\text{Si}$ [149].

The signals of the NCH_2 group protons in the ^1H NMR spectrum, recorded in C_6D_6 , are shifted substantially upfield; the signals of the OCH_2 group protons are also shifted upfield but to a lesser degree. It was suggested that this effect is due to the formation of a charge-transfer complex on account of the positive charge on the germanium atom in germatranes resulting from the transannular Ge←N interaction [150].



In the transition from germatranes, $\text{N}(\text{CH}_2\text{CH}_2\text{O})_3\text{GeX}$, to germatranones, $\text{N}(\text{CH}_2\text{COO})_{3-n}(\text{CH}_2\text{CH}_2\text{O})_n\text{GeX}$, replacement of a CH_2 group at positions 3, 7, 10 by a $\text{C}=\text{O}$ group strengthens the germanium–nitrogen bond [107], as demonstrated (according to [151]) by the downfield shift of the multiplets for $\text{N}(\text{CH}_2\text{CH}_2\text{O})$ groups (for $n = 1, 2$) compared with unsubstituted germatranes.

In 1-substituted homogermatranes the Ge–N bond is also stronger (according to data from ^1H NMR spectroscopy) than in the corresponding germatranes [81], although the inverse relationship is observed for the silicon derivatives.

4.2.4. ^{13}C and ^{17}O NMR Spectroscopy. For the case of silatranes it was shown that the chemical shifts of the carbon atoms in the atrane skeleton hardly depend at all on the nature of the apical substituent at the metal atom. It was not therefore possible to reach a conclusion about the degree of silicon–nitrogen interaction [119, 152]. However, the groups of Lukevics and Mironov suppose on the basis of the ^{13}C NMR data for atranes that the degree of $\text{M}\leftarrow\text{N}$ coordination interaction for the 1-substituted derivatives decreases in the order [81, 111]: silatranes > homosilatranes > homogermatranes > germatranes > 2-carbagermatranes.

The values of the induction (σ_I) and resonance (σ_R^0) parameters of the substituents $(\text{RO})_3\text{Ge}$ and $\text{N}(\text{CH}_2\text{CH}_2\text{O})_3\text{Ge}$ in the corresponding phenyl derivatives were estimated. In the opinion of the authors [153] the obtained data indicate a stronger donor capacity for the germatranyl group than for the trialkoxygermyl group.

The formation of the atrane ring has practically no effect on the chemical shifts of the ^{17}O atoms of the germatrane skeleton [154].

4.2.5. ^{15}N and ^{73}Ge NMR Spectroscopy. The NMR spectra at nuclei directly participating in the formation of the Ge–N bond can inevitably provide useful information on the nature of this bond. Unfortunately, the ^{73}Ge NMR spectra are difficult to record, and there is therefore little experimental information on the chemical shifts of the germanium atom in germatranes [81, 86, 155]. By heteronuclear INDOR $^1\text{H}\text{-}\{^{73}\text{Ge}\}$ NMR spectroscopy on seven germatranes with the general formula $\text{N}(\text{CH}_2\text{CH}_2\text{O})_3\text{GeOR}$ it was shown that the screening constant of the germanium atom was higher for germatranes than for tetraalkoxygermanes. This may indicate an increase in the coordination of the germanium atom in the germatranes [81, 155].

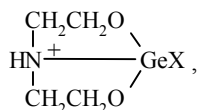
Data interpreted in different ways were obtained during investigation of the ^{15}N NMR spectra. Since the signal of the nitrogen atom is shifted downfield compared with the model compound (triethylamine), this indicates the existence of the $\text{N}\rightarrow\text{Ge}$ bond [81, 156-158], and besides in germatranones the bond becomes stronger with the introduction of each following $\text{C}=\text{O}$ group [156]. The chemical shifts of the ^{15}N atom depend linearly on the electronic constant of the substituent σ_X^* . On the basis of data from the ^{15}N NMR spectra Voronkov and co-workers [157] suppose that the $\text{M}\text{-N}$ bond in metallatranes $\text{N}(\text{CH}_2\text{CH}_2\text{O})_3\text{Z}$ becomes stronger

in the series: $Z = RGe \sim RSn < RSi < O=V \leq B \sim O_2Mo$. On the basis of the smaller effect of the solvent on the chemical shift of the ^{15}N atom in germatranes compared with silatranes Lukevits and co-workers put forward the view that the $Ge \leftarrow N$ bond may be stronger than the $Si \leftarrow N$ bond [158], but later, having obtained more data, they came to the conclusion that there was less transfer of charge from the nitrogen atom to the germanium atom [81].

4.2.6. Mass Spectrometry and Other Physicochemical Methods. The structure of germatranes in the crystalline and liquid phases was investigated by the methods described above. It is clear that the structure of a substance in the gas phase can differ fundamentally from its structure in the condensed phase. For silatranes the structure of the 1-methyl and 1-fluoro derivatives has been investigated by gas electron diffraction [140, 141]. The length of the silicon–nitrogen bond in these compounds is $\sim 0.2\text{--}0.3 \text{ \AA}$ greater than in the solid phase. Germatranes have not been investigated by gas electron diffraction, but indirect data on the characteristics of the germanium–nitrogen bond in the gas phase can be obtained from electron impact mass spectrometry [29, 56, 71, 159-161].

The dissociation of germatranes $N(CH_2CH_2O)_3GeX$ under electron impact can be realized in two ways. The first type of dissociation is the successive ejection of CH_2O molecules and CH_2CH_2O particles from the germatrane skeleton with retention of the $Ge-X$ bond; the second is removal of the substituent X with the formation of the germatranyl cation, which then dissociates with the ejection of neutral CH_2O molecules and CH_2CH_2O particles. The introduction of alkyl or aryl substituents into the germatrane skeleton also does not change the dissociation paths [39]. Germatranones are less stable under these conditions, since there is no molecular ion signal in the spectra; under electron impact they dissociate with the ejection of CH_2O or CO_2 [106].

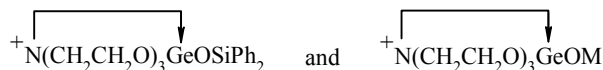
Analysis of a fairly large amount of experimental data [162] made it possible to propose the absence of a germanium–nitrogen bond in the gas phase. This conclusion was reached on the basis of the fact that, in contrast to silatranes [163], in the mass spectra of germatranes: 1) The contribution of the amine dissociation path (the formation of the $[M^+ - CH_2O]$ ion) is large; 2) the rearrangement ion



is practically absent; 3) there is no anomalous relation between the intensity of the $[M^+ - X]$ ion and the nature of X (i.e., the calculated intensity corresponds to the experimental value).

A systematic investigation of dissociation under electron impact for germatranes containing a heteroaryl substituent at position 1 also showed a preference for the amine dissociation path [29, 160].

An interesting case of the dissociation of germatranes $N(CH_2CH_2O)_3GeOSiPh_3$, $[N(CH_2CH_2O)_3Ge]_2CH_2$ and $N(CH_2CH_2O)_3GeCH_2Si(OCH_2CH_2)_3N$ was noted by the authors in [164]. Dissociation takes place with the ejection of one phenyl group in the case of 1-triphenylsiloxygermatrane and a triethanolamine residue in the case of bis(metallatranyl)methanes and with the formation of the most intense ions with the possible structure.



During investigation of the CI (chemical ionization) mass spectra [165] and FAB (fast atom bombardment) mass spectra [166], recorded in the liquid phase, the amine dissociation path was absent, which once again confirms the presence of the $Ge \leftarrow N$ bond in germatranes in the liquid phase.

Further elegant proof of the existence of this bond in the liquid phase is provided by data obtained during the investigation of the behavior of germatranes under the conditions of HPLC. The authors [167] explain the difference between the experimental and calculated values of the retention time ($\delta I_{N \rightarrow Ge}$), related linearly to $\Delta\mu$ (the difference between the experimental and calculated dipole moments) $\delta I = -500 + 231 \Delta\mu$ ($r = 0.93$, $n = 11$), by the existence of the Ge←N bond under the investigated conditions.

Thus, according to the published data, the existence of the Ge←N bond in germatranes in the solid phase and in solution can be considered reliably proved. In the gas phase this interaction (if it exists, and this was demonstrated by the calculation procedures) is extremely insignificant. The question of the comparative strength of the Ge←N bond (M = Ge, Si) remains open, since the published data are conflicting.

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