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Bromination of Silatranyl-, Germatranyl-, Silyl-, and Germyl-phenylacetylenes

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ABSTRACT: *Reactions of element-substituted alkynes $R_3MC{\equiv}CPh$ ($R_3M = Me_3Si$, Et_3Si, Ph_3Si, Et_3Ge, $n\text{-}Bu_3Sn$, $N(CH_2CH_2O)_3Si$, $N(CH_2CH_2O)_3Ge$, $N(CH_2CHMeO)_3Ge$, and $N(CH_2CH_2O)_2(CH_2CHPhO)Ge)$ with bromine, tetra-n-butylammonium tribromide (TBAT), and N-bromosuccinimide (NBS)/DMSO were investigated. The Z,E-ratio of isomeric dibromoalkenes formed in bromination reaction with Br_2 and TBAT are discussed. The crystal structures of $N(CH_2CH_2O)_3SiC{\equiv}CPh$ and $N(CH_2CHMeO)_3GeX$ ($X = C{\equiv}CPh$, $C(Br){=}C(Br)Ph$, $C(Br_2)C(O)Ph$), and $Ph_3SiC(Br){=}C(Br)Ph$ are reported.* Heteroatom Chem 15:43–56, 2004; DOI 10.1002/hc.10211

INTRODUCTION

The chemistry of metallatranes has attracted considerable interest in recent years [1]. Among them metallatranes of the group 14 elements have been investigated rather in detail by the present time [1–5].

Hypercoordination in these compounds arises from the existence of a transannular interaction between nitrogen and the element atoms. This results in approximately trigonal bipyramidal coordination of the element and also in formal quarternization of nitrogen. Extended coordination explains specificity of metallatrane properties that differ in many respects from the characteristics of tetracoordinated derivatives with the similar structure. Investigation of metallatranes by using different spectroscopic and other physical methods permits to form a general idea about their electronic nature and bonding [1]. It should be noted that the observed changes in physical properties and reactivity successfully correlate with those in the transannular M ← N bond length [2,6]. The latter and a number of other reasons cause metallatranes to make a significant contribution to the theoretic organometallic chemistry.

However, the main efforts in the area discussed were directed toward development of synthetic routes for the preparation of metallatranes with various structures. The chemistry of functionally substituted metallatranes is practically undeveloped. Studies concerning transformations of substituent at the element atom have so far been very limited.

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Earlier we reported that the treatment of $N(CH_2CH_2O)_3GeC{\equiv}CPh$ (**1**) with NBS/DMSO system affords $N(CH_2CH_2O)_3GeCBr_2C(O)Ph$ and the reaction with bromine leads to the formation of *cis*-$N(CH_2CH_2O)_3GeC(Br){=}C(Br)Ph$ [7]. In contrast to this most of alkylatylacetylenes react with bromine in chloroalkanes under conditions of kinetic control to give a mixture of *cis*- and *trans*-dibromoalkenes, the latter considerably prevailing [8,9]. The addition of bromine to alkylphenylacetylenes containing strong electron-withdrawing para-substituents in the phenyl group is stereoselective and yields only the *trans*-dibromo adducts. As an exception, stereoselective cis-addition to *tert*-butylphenylacetylene gives rise to the Z-isomer as the main or single reaction product. Such stereochemical outcome of the reaction may likely be attributed to the considerable steric crowding of the *tert*-butyl substituent [10].

Bromination of element-substituted acetylenes has hitherto been explored insufficiently. Thus, it was shown [11] that bromination of bis(trimethylsilyl)-acetylene with bromine in CCl_4 affords the corresponding dibromo derivative in 56% yield. The product is the single one even if an excess of bromine is used with prolonged heating of the reaction mixture. Lower temperature during the transformation and utilization of pentane as a solvent improve appreciably the yield of 1,2-dibromo-1,2-bis(trimethylsilyl)ethene (82%) [12]. The product obtained was assigned a trans-configuration [11,12]; however, the authors have not adduced any data providing the grounds of such attribution.

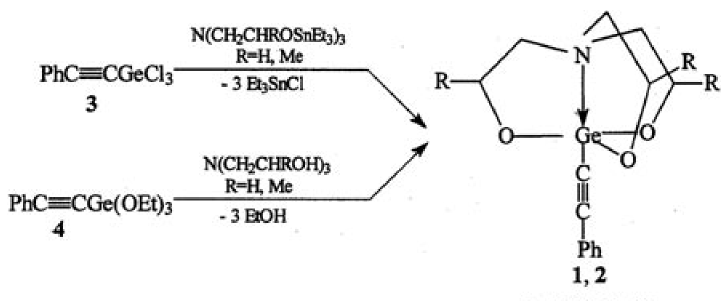
The triple bond of (trialkylsilyl)alkynes $R_3SiC{\equiv}CH$ ($R = Me, Et$) vigorously adds Br_2 without solvent, one molecule of bromine adding at 20–50°C and two molecules at 70–90°C [13]. The reaction was found to proceed somewhat slower and with less heat efficiency in the dark and in the presence of inhibitor (hydroquinone), although the yield of the products does not change considerably. Evidently, free-radical addition of bromine takes place along with the electrophilic process of bromination. The presence of alkoxy groups at the silicon atom was determined to reduce the activity of the triple bond in the bromination reaction [14]. As to stereochemistry of the products, it has not been discussed in the papers cited above.

In the present study we report the results of our investigation concerning the bromination of silatranyl- and germatranylphenylacetylenes as well as tetracoordinate silicon-, germanium-, and tin-substituted phenylacetylenes with Br_2, n-Bu_4NBr_3 (TBAT), and NBS/DMSO.

RESULTS AND DISCUSSION

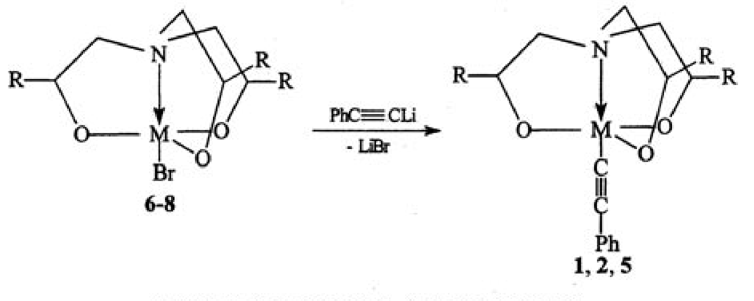
Synthesis of 1-(Phenylethynyl)metallatranes

In the present study synthesis of 1-(phenylethynyl)-germatrane (**1**) as well as 1-(phenylethynyl)-3,7,10-trimethylgermatrane (**2**) required for the further investigation of bromination reactions as more sterically hindered substance was carried out by three ways (Eqs. 1 and 2) [7,15,16].



R = H (**1**), Me (**2**)

(1)

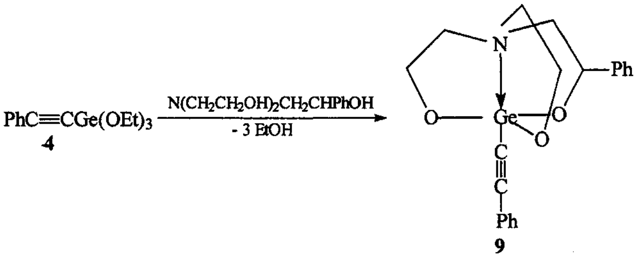


(2)

R=H, M=Ge (**1, 6**); R=Me, M=Ge (**2, 7**); R=H, M=Si (**5, 8**)

1-(Phenylethynyl)silatrane (**5**) has been prepared with 44% yield when lithium phenylacetylide was employed (Eq. 2). Thus, we have found the first example of synthesis of functionally substituted silatrane with use of an organolithium reagent. In the reaction of 1-bromosilatrane (**8**) with *n*-BuLi only substitution, including cleavage of equatorial Si—O bonds, was observed [17].

To obtain 1-(phenylethynyl)-3-phenylgermatrane (**9**) we used the transalkoxylation reaction (Eq. 3) [18].



(3)

Synthesis of R₃MC≡CPh

To synthesize element-substituted acetylenes **10–13** we used the method based on the reaction between lithium phenylacetylide and corresponding trialkylhalosilanes and -germanes as well as triphenylchlorosilane. We chose this way as the most suitable one according to the literature data (Eq. 4 also see the Experimental section).

$$\mathrm{PhC{\equiv}CH} \xrightarrow[\mathrm{-\,BuH}]{n\text{-}\mathrm{BuLi/Et_2O}} \mathrm{PhC{\equiv}CLi} \longrightarrow$$

$$\xrightarrow[\mathrm{-\,LiX}]{\mathrm{R_3MX/Et_2O}} \underset{\textbf{10-13}}{\mathrm{R_3MC{\equiv}CPh}} \qquad (4)$$

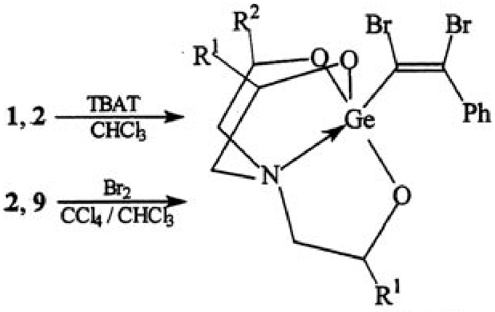
M = Si, R = Me (**10**); M = Si, R = Et (**11**);
M = Si, R = Ph (**12**); M = Ge, R = Et (**13**)

Compounds **10–13** were prepared in 64–95% yields; their structures were confirmed by IR, ^{1}H, and ^{13}C NMR data.

Bromination of Element-Substituted Phenylacetylenes

As mentioned above bromination of **1** with bromine proceeds smoothly and leads to *Z*-isomer as the only product. It seemed to be interesting for us to examine tetra-*n*-butylammonium tribromide (TBAT) as a brominating reagent. Literature data review reveals wide range of acetylenes being treated with this reagent give *trans*-1,2-dibromalkenes as the only products, result of the reaction being independent of its conditions and ratio of reagents [9].

It was found, however, that the reaction between **1** and TBAT affords only *cis*-dibromide **14** in 58% yield (Eq. 5). The behavior of the more bulky 3,7,10-trimethyl-substituted germatrane **2** and 3-phenyl-subsituted germatrane **9** is analogous to that of **1**. Bromination with Br_2 leads to the formation of *cis*-dibromalkenes **15** and **16** as the only reaction products. Similar product was obtained from reaction of **2** with TBAT (Eq. 5).

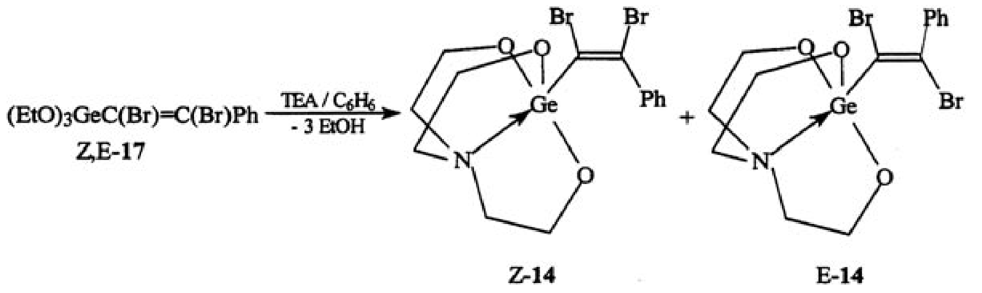


(5)

14, 15, 16

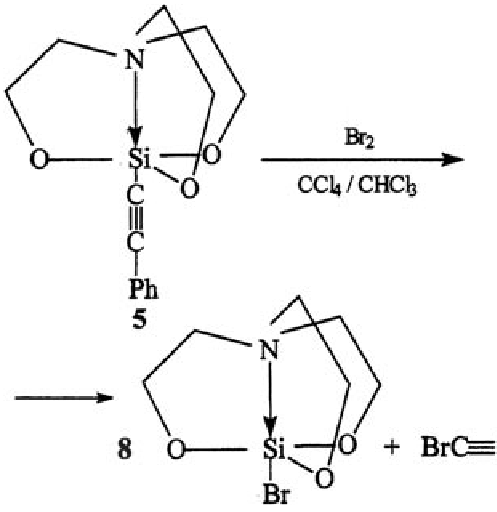
R^1 = R^2 = H (**14**);
R^1 = R^2 = Me (**15**);
R^1 = H, R^2 = Ph (**16**)

The absence of *trans*-$N(CH_2CH_2O)_3GeC(Br){=}C(Br)Ph$ (*E*-**14**) in the reaction between **1** and TBAT was established by NMR spectroscopy. Very recently this *trans*-dibromide was obtained from reaction mixture yielded by the treatment of a mixture *Z*- and *E*-$(EtO)_3GeC(Br){=}C(Br)Ph$ (**17**) with $N(CH_2CH_2OH)_3$ (TEA) (Eq. 6) [19].



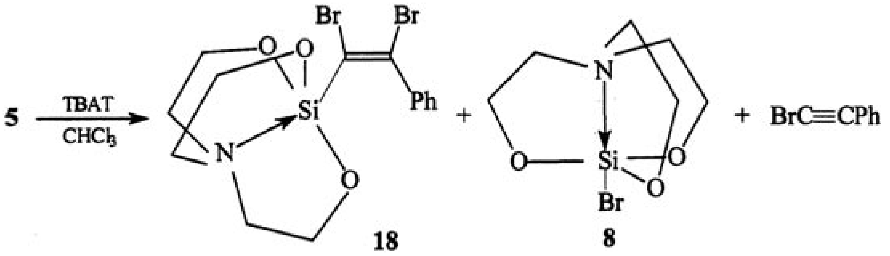
(6)

Essentially different results have been obtained in the bromination of **5** with Br_2. The main course of this reaction is the cleavage of the Si—C bond (Eq. 7).



(7)

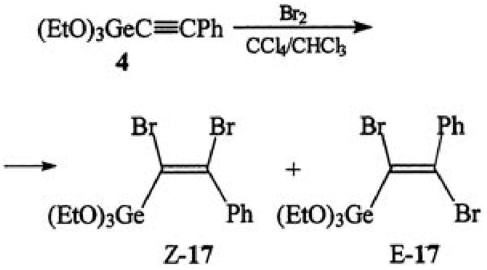
It should be noted, however, that the dibromoderivative *cis*-$N(CH_2CH_2O)_3Si—C(Br){=}C(Br)Ph$ (**18**) is also formed in small amounts. Analogously, silatrane **8** was obtained from reaction of **5** with TBAT (Eq. 8). However, *cis*-adduct **18** is the concomitant product in this case. The yield of *Z*-**18** is about 30% (^1H NMR data). Unfortunately, *Z*-**18** was not isolated from the reaction mixture as a pure substance because of the presence of starting silatrane **5**.



(8)

Perhaps, the more electrophilic nature of bromine in comparison with TBAT leads to the difference of the compound **5** bromination pathways. Thus, the electophilic-substitution reaction is more preferable when **5** was treated with bromine. The easy cleavage of Si—R bond (R = Alk, Ar) in 1-organylsilatranes has been described earlier [20].

Compound **4** is a close tetracoordinated counterpart of germatrane **1**. Recently we have showed that when affected by bromine this compound yields a mixture of *Z*- and *E*-isomers of dibromoalkene **17** in the ratio $Z/E = 3/1$ (NMR data) (Eq. 9) [19].



(9)

The presence of both isomers in this reaction can be attributed to less steric hindrances in the case of triethoxy derivative **4** in comparison with germatrane **1**. No reaction of **4** with TBAT was observed. The reactions of **13** with bromine and TBAT are more complicated. The reaction mixtures contained dibromo adduct *Z*-**19** as well as the Ge—C bond cleavage products. In contrast to the above, **10** and **11** react with bromine and TBAT smoothly giving mixtures of *Z,E*-**20** and *Z,E*-**21**, respectively. The ratios of *cis*-, *trans*-dibromides **20** and **21** from the reaction of **10** and **11** with bromine are $Z/E = 9/1$ in both cases (Eq. 10).

$$\underset{\mathbf{10,11}}{\mathrm{R_3SiC{\equiv}CPh}} \xrightarrow[\mathrm{CCl_4/CHCl_3}]{\mathrm{Br_2}}$$

$$\longrightarrow \underset{\mathbf{20,21}}{Z,E\text{-}\mathrm{R_3SiC(Br){=}C(Br)Ph}}\ (9:1) \qquad (10)$$

R=Me (10, 20); R = Et (11, 21)

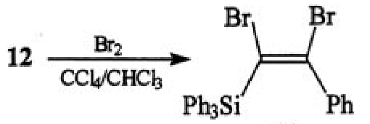
An opposite ratio of **20** and **21** ($Z/E = 1/9$) was found when **10** and **11** were treated with TBAT (Eq. 11).

$$\underset{\mathbf{10,11}}{\mathrm{R_3SiC{\equiv}CPh}} \xrightarrow[\mathrm{CHCl_3}]{\mathrm{TBAT}}$$

$$\longrightarrow \underset{\mathbf{20,21}}{Z,E\text{-}\mathrm{R_3SiC(Br){=}C(Br)Ph}}\ (1:9) \qquad (11)$$

R = Me (10, 20); R = Et (11, 21)

The treatment of acetylene **12** containing very bulky triphenylsilyl group at triple bond with bromine led to the only stereoisomer **22** (Eq. 12).



22

(12)

According to X-ray diffraction data this derivative possesses cis-structure (see below). The reaction of compound **12** with TBAT was not observed.

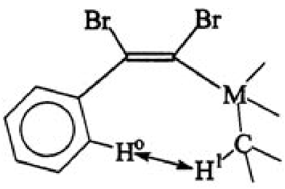
In general, the ^1H NMR spectroscopy data were used for the determination of product steric configuration. Recently we have shown that δ^1H values of R_3M protons in *cis*-$R_3GeC(Br)=C(Br)Ph$ ($R_3Ge = N(CH_2CH_2CO)_3Ge$ (**14**), $(EtO)_3Ge$ (**17**)) shift to high field as compared with ^1H NMR data of related *trans*-dibromoalkene because of the influence of steric proximity of Ph group in *cis*-isomers [19]. So, δ^1H ($CDCl_3$) of CH_2O and NCH_2 protons of atrane skeleton in *Z*-**14** are 3.55 and 2.72 ppm [7], respectively, while "usual" δ^1H for sila- and germatranes are 3.9–4.0 and 2.9–3.0 ppm [2]. Granting this we were able to define the structure of dibromoalkenes **15, 16**, and **18**.

The *Z*/*E* ratios for *cis*-, *trans*-isomer pairs of **19–21** were also found from ^1H NMR data. In present study the assignments of the R_3M protons signals in **19–21** have also been made on the basis of 2D ^1H NOESY correlations. We have confirmed that the signals of Me groups (**20**) and CH_2 groups (**19** and **21**) for *cis*-dibromides can unequivocally be assigned by the strong NOEs from H (Me or CH_2 groups) to the *ortho*-protons of phenyl group (Scheme 1).

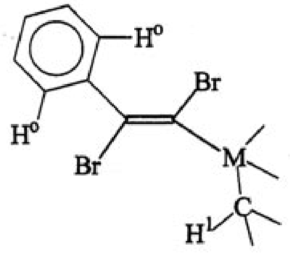
After heating the mixture of *cis*-, *trans*-dibromides **20** ($Z/E = 9/1$) at 180°C for 3 h, the amount of *trans*-isomer has slightly increased ($Z/E = 7/3$). No cleavage products were detected in this reaction. On the contrary, 1-bromogermatrane **6** was the main product of the heating of *cis*-dibromide *Z*-**14** in the same conditions.

It should be noted that the heating of *trans*-dibromide *E*-**14** also led to germatrane **6** but in notably smaller extent. Obviously, only *Z*-isomer (*Z*-**14**) may undergo β-elimination with the formation of germatrane **6**. The presence of compound **6** in heating products of *E*-**14** may be attributed to $E \rightarrow Z$ isomerization with further β-elimination of *Z*-**14**.

To all appearance, the formation of only *cis*-adducts in the reaction of **1, 2, 9** and **12** with bromine as well as in the reaction of **1, 2**, and **5** with TBAT might be attributed to the possible steric hindrances due to the presence of bulky groups at triple bond in these alkynes. This steric crowding is probably less in the case of **4, 10, 11**, and **13** during bromine addition when *E*-adducts are also formed together with *Z*-dibromides. The results of alkyne bromination reactions are summarized in Table 1.



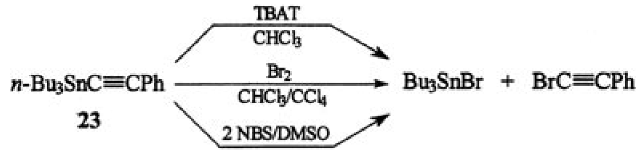
H^o-H^1 NOEs (*Z*-**19-21**)



no H^o-H^1 NOEs (*E*-**19-21**)

SCHEME 1

$Alk_3SnC{\equiv}CPh$ undergoes the bromodestannylation by bromine in DMSO or DMF/CCl_4 [21]. We have shown that the treatment of tin derivative **23** with the softer brominating reagent TBAT, as well as with NBS/DMSO system, and Br_2 in $CHCl_3/CCl_4$ leads to the cleavage of Sn—C bond (Eq. 13).



(13)

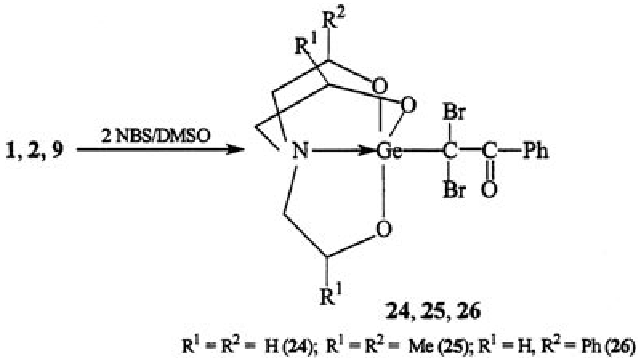
Recently we have shown that the reaction between germatrane **1** and **2** equivalents of NBS in DMSO yielded dibromoketone **24** [7]. Analogous behavior was observed for 3,7,10-trimethyl- and 3-phenyl-substituted germatranes **2** and **9**. It should be noted that we have not detected either diketo-derivatives ($R_3GeC(O)C(O)Ph$) or dibromo adducts ($R_3GeC(Br)=C(Br)Ph$) among the products of the reaction (14), whereas they are formed under the same

TABLE 1 Yields and Product Distribution (Ratio of *E*- and *Z*-Isomers) of $R_3MC(Br)=C(Br)Ph$ for the Reaction of Alkynes With Br_2 and TBAT

		Yield (%)[a]	
	R_3M	*Br_2*	*TBAT*
14	$N(CH_2CH_2O)_3Ge$	55 (100/0) [7]	58 (100/0)
15	$N(CH_2CHMeO)_3Ge$	73 (100/0)	52 (100/0)
16	$N(CH_2CH_2O)_2(CH_2CHPhO)_2Ge$	43 (100/0)	–
17	$(EtO)_3Ge$	72 (75/25) [19]	No reaction
18	$N(CH_2CH_2O)_3Si$	17 (100/0)	30 (100/0)
19	Et_3Ge	38 (100/0)	Trace
20	Me_3Si	95 (90/10)	59 (10/90)
21	Et_3Si	92 (90/10)	39(10/90)
22	Ph_3Si	83 (100/0)	No reaction

[a] Values given in parentheses indicate *Z*/*E* ratio.

conditions in the case of alkylphenylacetylenes [22].



(14)

The treatment of tetracoordinated Si- and Ge-substituted alkynes **10–13** with NBS/DMSO resulted in complicated mixtures of unidentifiable products (see the Experimental section).

Crystal Structures of **2**, **5**, *Z*-**15**, *Z*-**22**, *and* **25**

The molecular structures of **2, 5**, *Z*-**15**, *Z*-**22**, and **25** are shown in Figs. 1–5. The coordination polyhedron of the silicon atom in **5** is the common one for silatrane derivatives [23–25] and represents a distorted trigonal bipyramid with N and C(1) atoms in the apical positions and the three oxygen atoms in equatorial positions. The silicon atom is displaced by 0.14 Å toward the phenylethynyl substituent from the equatorial plane defined by three oxygen atoms. The N—Si—C(1) fragment is almost linear (178.0(1)°). All five-membered rings of the silatrane skeleton in **5** adopt an envelope-like conformation. The carbon atoms in the α-positions to the N atom occupy flap sites, while the C-β atoms are part of the base of the envelope planes. No disordered atoms in the atrane cage were found in the structure of **5**.

The N—Si distance in compound **5** is one of the shortest (2.094(2) Å) among those observed in the structures of silatranes with Si—C bond (2.02–2.23 Å) [25,26]. It should be noted that the N—Si distance in compound **5** is shorter than the N—Ge distance found previously in closely related $N(CH_2CH_2O)_3Ge—C\equiv C—Ph$ (2.178(6) Å) [7]. This fact is in accordance with data reported for absolute majority of sila- and germatrane pairs studied earlier (Table 2). However, there is a study giving the structure of $N(CH_2CH_2O)_3Ge—F$ where the Ge—N distance (2.011(9) Å [46]) is shorter than the Si—N distance in corresponding silatrane. At the same time Eujen et al. [30] have prejudiced the results of mentioned X-ray analysis [46].

The coordination polyhedron of the germanium atoms in 3,7,10-trimethyl-substituted germatranes **2**, *Z*-**15**, and **25** represents a distorted trigonal bipyramid with N and C atoms in the apical positions and the three oxygen atoms in equatorial sites. The

TABLE 2 Transannular N → M Distances in Closely Related Sila- and Germatrances, $N(CH_2CH_2O)_3M–X$

	N → M Distance (Å)	
X	*M = Si*	*M = Ge*
NCS	2.007(3) [27]	2.081(5) [28]
F	2.042(1) [29]	2.104(2) [30]
Cl	2.023 [31]	2.096(3) [30]
$CHCl_2$	2.062 [32]	2.145(5) [33]
2-Furyl	2.112 [34]	2.158(5) [35]
CH_2Cl	2.120 [36]	2.167(2) [37]
2-Pyrrolidonyl-$CH(CH_3)$	2.126(9) [38]	2.223(5) [39]
Ph	2.132(4), 2.156(4), 2.193(5)[a] [41–43]	2.212(5) [40]
4-Me-C_6H_4	2.171(1) [44]	2.217(4) [45]

[a] Different crystalline modifications.

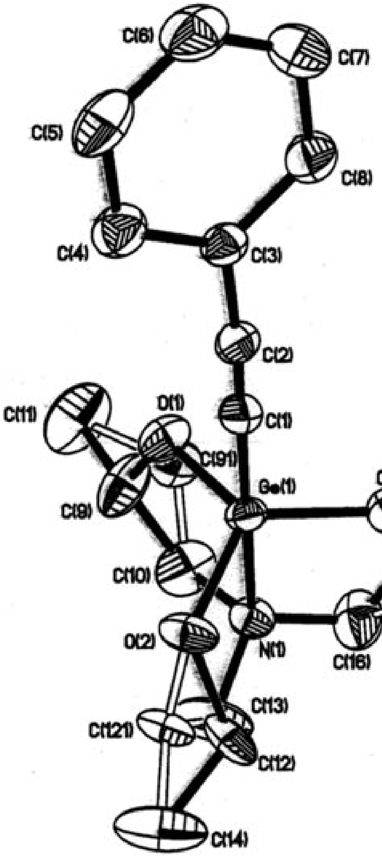


FIGURE 1 Molecular structure of **2**. Displacement ellipsoids are shown at 30% probability level. Hydrogen atoms are omitted for clarity. Minor components of disordered groups are shown using open lines. Selected bond lengths (Å) and angles (°): Ge(1)–N 2.199(4), Ge(1)–C(1) 1.919(6), C(1)–C(2) 1.181(7), N(1)–Ge(1)–C(1) 179.2(2), C(2)–C(1)–Ge(1) 176.2(5).

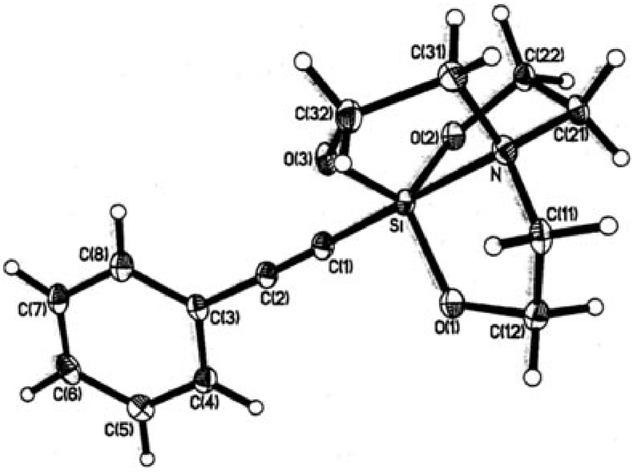


FIGURE 2 Molecular structure of **5**. Displacement ellipsoids are shown at 50% probability level. Selected bond lengths (Å) and angles (°): Si–N 2.094(2), Si–C(1) 1.884(3), C(1)–C(2) 1.211(4), N–Si–C(1) 178.0(1), C(2)–C(1)–Si 171.0(2).

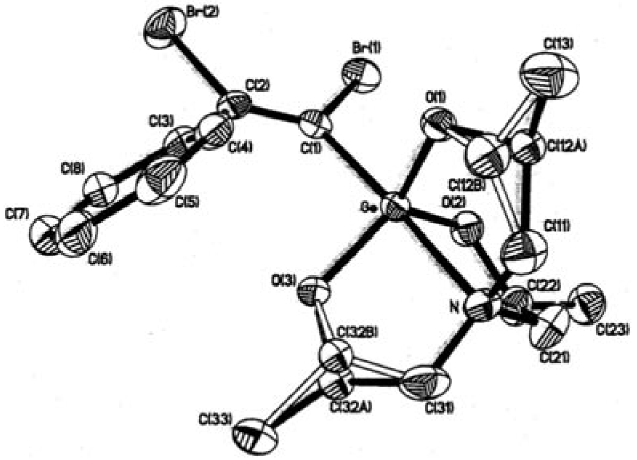


FIGURE 3 Molecular structure of *Z*-**15**. Displacement ellipsoids are shown at 50% probability level. Hydrogen atoms are omitted for clarity. Minor components of disordered groups are shown using open lines. Selected bond lengths (Å) and angles (°): Ge–N 2.196(7), Ge–C(1) 1.977(8), C(1)–C(2) 1.31(1), Br(1)–C(1) 1.898(8), Br(2)–C(2) 1.946(8), N–Ge–C(1) 173.7(3), angles around C(1) and C(2) range within 111.6(6)–126.2(7).

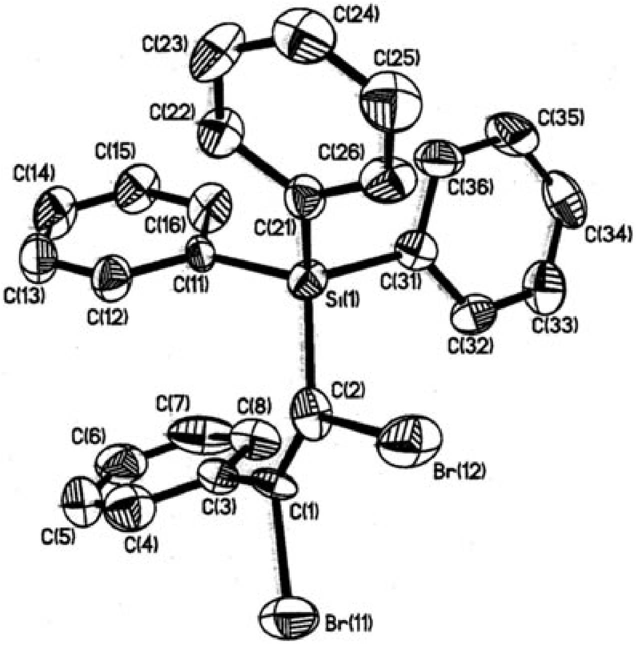


FIGURE 4 Molecular structure of *Z*-**22** (one independent molecule). Displacement ellipsoids are shown at 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Si(1)–C(2) 1.91(1), Br(11)–C(1) 1.933(9), Br(12)–C(2) 1.956(9), C(1)–C(2) 1.27(1), angles around C(1) and C(2) range within 109.1(5)–131.8(8) and angles around Si(1) range within 106.3(5)–112.5(4).

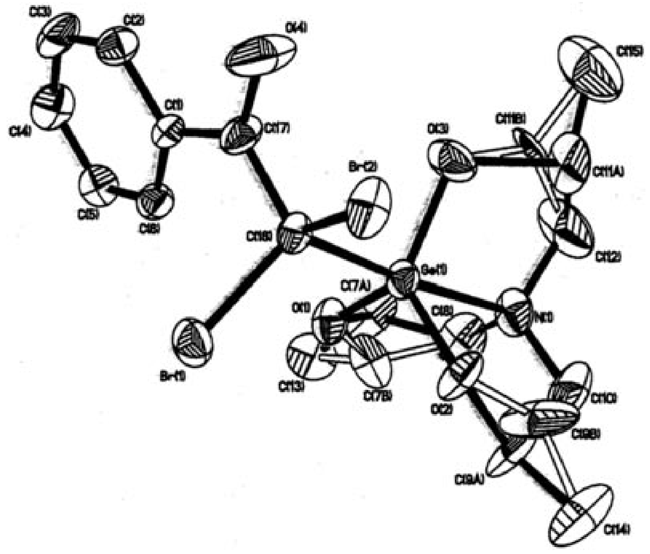


FIGURE 5 Molecular structure of **25**. Displacement ellipsoids are shown at 30% probability level. Hydrogen atoms are omitted for clarity. Minor components of disordered groups are shown using open lines. Selected bond lengths (Å) and angles (°): Ge(1)–N(1) 2.169(6), Ge(1)–C(16) 2.028(7), Br(1)–C(16) 1.952(7), Br(2)–C(16) 1.954(7), O(4)–C(17) 1.193(8), N(1)–Ge(1)–C(16) 174.7(3).

TABLE 3 Transannular N → M Distances in Sila- and Germatranes, $N(CH_2CHRO)_3M–X$

		N→ M Distance (Å)	
M	*X*	*R = H*	*M = Me*
Si	4-Me–C_6H_4,	2.171(1) [44]	2.236(3) [44]
Ge	9-Fluorenyl	2.166(2) [15]	2.194(5) [47]
Ge	9-(9-Me_3Sn)-fluorenyl	2.206(6) [50]	2.247(9) [49]

germanium atom is displaced by 0.21 (for **2**), 0.22 (for *Z*-**15**), and 0.20 Å (for **25**) toward an apical substituent from the equatorial plane defined by three oxygen atoms. The N—Ge—C fragment is almost linear (173.7(3)–179.2(2)°) in all these compounds.

All five-membered rings of the germatrane skeleton in **2**, *Z*-**15**, and **25** adopt an envelope-like conformation. In contrast to compound **5**, the carbon atoms lying in the β-positions to the N atom occupy flap sites, while the C-α atoms are part of the base of the envelope planes. This seems to be characteristic for the structures of 3,7,10-trimethyl-substituted atranes [44,45,47–49]. The carbon atoms of atrane cage in the β-positions to the N atom are disordered between two opposite flap sites in the structures of **2**, *Z*-**15**, and **25**. It should be noted that the bromine atoms in compound *Z*-**15** occupy cis-positions at double carbon–carbon bond as they do in germatrane *Z*-**14** [7].

The N—Ge distance in compound **2** (2.199(4) Å) is slightly longer than that observed in the structure of germatrane **1** (2.178(6) Å) [7]. The same lengthening of the N—M distance has been found previously in three pairs (Table 3).

However, the N—Ge distance in compound *Z*-**15** (2.196(7) Å) is slightly shorter than that observed in the structure of *Z*-**14** (2.23(1) Å) [7]. According to our knowledge this is the first case of shortening of transannular distance N—Ge in germatranes by the formal substitution of hydrogen atoms by methyl groups at positions 3,7,10 of atrane framework. Only one analogous example was previously found among silatranes: $N(CH_2CHRO)_3Si–Ph$, 2.193(5) Å for R = H (α-modification) [41] and 2.175(6) Å for R = Me [45].

On the contrary the Ge—C$_{\text{apical}}$ bond lengths (1.919(6) Å in **2** and 1.977(8) Å in *Z*-**15**) are similar to that observed in the structures of corresponding germatranes $N(CH_2CH_2O)_3Ge–X$ (1.920(8) and 1.98(2) Å, respectively [7]). Of interest, the Ge—C distance in **2** is the shortest one among the previously found in germatranes containing N—Ge—C moiety (1.92–2.01 Å) [7,51,52].

The N—Ge distance in compound **25** (2.169(6) Å) is the shortest among those known by the present time in 3,7,10-trimethyl-substituted germatranes. At the same time the Ge—C$_{\text{apical}}$ distance in compound **25** is the longest one among the previously found in germatranes containing N—Ge—C fragment (1.92–2.01 Å). This may be due to the electronegative character of the $PhC(O)CBr_2$ substituent.

The asymmetric unit of *Z*-**22** contains two independent molecules with very close geometric parameters. Unfortunately, the structure of *Z*-**22** is not of satisfactory quality because of poor crystallinity. Thus, although the atom connectivity is undoubtedly correct, the metrical parameters for *Z*-**22** (Fig. 4, Table 4) should be viewed with due caution. Nevertheless, it is clear that bromine atoms occupy cis-positions such as that found in *Z*-**14** [7] and *Z*-**15**.

In conclusion, we have found that the addition of bromine to triple bond of studied element-substituted acetylenes in $CHCl_3/CCl_4$ leads to forming of *cis*-dibromo adducts as a preferred or single isomer. Obviously, this fact may be attributed to the presence of steric hindrances for *E*-isomer formation. Trialkylsilyl-substituted phenylacetylenes reacting with TBAT preferably gave *trans*-dibromide as a major product of addition reaction. The inclination of the M—C bond in phenylacetylenyl derivatives of the tetracoordinated group 14 elements to

TABLE 4 Crystal Data, Data Collection, Structure Solution, and Refinement Parameters for Compounds **5, 2,** *Z*-**15, 25**, and *Z*-**22**

	5	**2**	*Z*-**15**	**25**	*Z*-**22**
Empirical formula	$C_{14}H_{17}N_1O_3Si_1$	$C_{17}H_{23}N_1O_3Ge_1$	$C_{17}H_{23}N_1O_3Ge_1Br_2$	$C_{17}H_{23}N_1O_4Ge_1Br_2$	$C_{26}H_{20}Br_2Si_1$
Formula weight	275.38	361.95	521.77	537.77	520.33
Color, habit	Colorless plate	Colorless prism	Colorless block	Colorless prism	Colorless block
Crystal size (mm)	0.20 × 0.10 × 0.05	0.30 × 0.20 × 0.10	0.50 × 0.40 × 0.40	0.10 × 0.10 × 0.10	0.20 × 0.10 × 0.10
Crystal system	Monoclinic	Orthorhombic	Monoclinic	Orthorhombic	Triclinic
Space group	$P2_1$	*Pbca*	$P2_1/n$	*Pbca*	$P1$
Unit cell dimensions					
a (Å)	6.4506(2)	12.764(4)	9.739(9)	13.784(2)	9.968(6)
b (Å)	11.2365(4)	17.962(5)	15.352(9)	16.301(3)	11.029(6)
c (Å)	9.5951(3)	15.130(5)	13.841(6)	17.900(3)	21.242(13)
α (°)					95.42(5)
β (°)	107.351(2)		103.78(8)		98.18(5)
γ (°)					96.91(5)
Volume (Å^3)	663.83(4)	3469(2)	2010(2)	4022(1)	2280(2)
Z	2	8	4	8	4
D_{calc} (g cm^{-3})	1.378	1.386	1.724	1.776	1.516
μ (mm^{-}1)	0.180	1.777	5.514	5.518	3.618
F (000)	292	1504	1032	2128	1040
Diffractometer	Bruker SMART	Enraf-Nonius CAD4	Enraf-Nonius CAD4	Enraf-Nonius CAD4	Enraf-Nonius CAD4
Temperature (K)	105.0(2)	293	293	293	293
Radiation (λ/Å)	Graphite-monochromated Mo Kα (0.71073)	Graphite-monochromated Mo Kα (0.71073)	Graphite-monochromated Mo Kα (0.71073)	Graphite-monochromated Mo Kα (0.71073)	Graphite-monochromated Mo Kα (0.71073)
θ Range (°)	2.22–26.99	2.27–25.08	2.01–24.97	2.24–25.07	2.01–25.00
Index ranges	$-7 \le h \le 8$ $-13 \le k \le 14$ $-12 \le l \le 12$	$0 \le h \le 15$ $0 \le k \le 21$ $0 \le l \le 18$	$-11 \le h \le 11$ $-3 \le k \le 18$ $-3 \le 1 \le 16$	$0 \le h \le 16$ $0 \le k \le 19$ $0 \le l \le 21$	$-11 \le h \le 11$ $-3 \le k \le 13$ $-2 \le l \le 25$
Reflections collected	4735	3075	5733	3571	9154
Independent reflections	2602 [$R_{int} = 0.0370$]	3075 [$R_{int} = 0.0000$]	3536 [$R_{int} = 0.0450$]	3571 [$R_{int} = 0.0000$]	7981 [$R_{int} = 0.1388$]
Absorbtion correction	Multiscan	–	Empirical	–	Empirical
Min/max transmission	0.6963/1.0000	–	0.0718/0.1321	–	0.524/0.722
Solution method	Direct methods (SHELXS-86) [53]	Direct methods (SHELXS-86) [53]	Direct methods (SHELXS-86) [53]	Direct methods (SHELXS-86) [53]	Direct methods (SHELXS-86) [53]
Refinement method	Full-matrix least-squares on F^2 (SHELXL-97) [54]	Full-matrix least-squares on F^2 (SHELXL-97) [54]	Full-matrix least-squares on F^2 (SHELXL-97) [54]	Full-matrix least-squares on F^2 (SHELXL-97) [54]	Full-matrix least-squares on F^2 (SHELXL-97) [54]
Data/restraints/params	2602/1/240	3075/0/226	3053/0/216	3571/0/254	5339/0/523
Goodness-of-fit on F^2	1.003	1.071	1.060	0.968	0.888
R indices	$R_1 = 0.0383$ $wR_2 = 0.0860$	$R_1 = 0.0532$ $wR_2 = 0.0922$	$R_1 = 0.0539$ $wR_2 = 0.1450$	$R_1 = 0.0571$ $wR_2 = 0.0909$	$R_1 = 0.0504$ $wR_2 = 0.0934$
Extinction coefficient	–	–	–	0.00023(5)	–
Flack parameter	0.08(14)	–	–	–	–
Largest diff. peak/hole (e Å^{-3})	0.288/−0.221	0.423/−0.334	0.799/−0.724	0.525/−0.471	0.547/−0.594

be broken under the influence of bromine increases in Si < Ge < Sn series. Opposite order is observed for derivatives of pentacoordinated Si (silatrane **5**) and Ge (germatranes **1**, **2**, and **9**), namely, the cleavage of Si—C bond proceeds much easier than that of Ge—C bond.

EXPERIMENTAL

General Comments

Trimethylsilyl-, triethylsilyl-, triphenylsilyl-, and triethylgermyl-phenylacetylenes **10–13** were prepared by literature methods [55,56]. Triethylbromogermane was synthesized according to the literature [57]. NMR spectra of these compounds are given below.

10: ^{1}H NMR ($CDCl_3$) $\delta = -0.25$ (s, 9H, $SiMe_3$); 7.26–7.33 (m, 3H, C_6H_5); 7.44–7.49 (m, 2H, C_6H_5). ^{13}C NMR ($CDCl_3$) $\delta = -0.03$ ($SiMe_3$); 94.02 ($\equiv$CSi); 105.13 (PhC$\equiv$); 123.11, 128.16, 128.44, 131.92 (aromatic C).

11: ^{1}H NMR ($CDCl_3$) $\delta = 0.62$ (q, 6H, $SiCH_2$); 0.99 (t, 9H, CH_3); 7.20–7.24 (m, 3H, C_6H_5); 7.38–7.42 (m, 2H, C_6H_5). ^{13}C NMR ($CDCl_3$) $\delta = 4.42$ ($SiCH_2$); 7.47 (CH_3); 91.45 ($\equiv$CSi); 106.37 (PhC$\equiv$); 123.33, 128.13, 128.33, 132.00 (aromatic C).

12: ^{1}H NMR ($CDCl_3$) $\delta = 7.29$–7.74 (m, 20H, C_6H_5). ^{13}C NMR ($CDCl_3$) $\delta = 89.00$ ($\equiv$CSi); 109.56 (PhC$\equiv$); 122.70, 127.98, 128.27, 129.03, 129.92, 132.23, 133.55, 135.59 (aromatic C).

13: ^{1}H NMR ($CDCl_3$) $\delta = 0.91$ (q, 6H, $GeCH_2$); 1.13 (t, 9H, CH_3); 7.23–7.27 (m, 3H, C_6H_5); 7.42–7.45 (m, 2H, C_6H_5). ^{13}C NMR ($CDCl_3$) $\delta = 5.77$ ($GeCH_2$); 9.00 (CH_3); 91.94 ($\equiv$CGe); 105.96 (PhC$\equiv$); 123.70, 127.96, 128.08, 131.91 (aromatic C).

Et_3GeBr: ^{1}H NMR ($CDCl_3$) $\delta = 1.12$ (t, 9H, CH_3); 1.21 (q, 6H, $GeCH_2$). ^{13}C NMR ($CDCl_3$) $\delta = 8.51$ (CH_3); 10.76 ($GeCH_2$).

1, **2**, and **4** were prepared as previously described [7,19]. Tributylstannyl-phenylacetylene, bromine, TBAT, and NBS were commercial products and were used without further purification. All solvents were dried by standard procedures and distilled before use. NMR spectra were recorded at 25°C on Bruker AC 300 and Varian VXR 400 spectrometers; $CDCl_3$ was used as the solvent and for internal deuterium lock. The chemical shifts in the ^{1}H and ^{13}C NMR spectra are given in ppm relative to internal TMS. The IR spectra were recorded on Zeiss UR-20. Elemental analyses were carried out by the Microanalytical Laboratory of the Chemistry Department of the Moscow State University. Mass spectra (EI-MS) were obtained on a VARIAN CH-7a device using electron impact ionization at 70 eV; all assignments were made with reference to the most abundant isotopes.

*Synthesis of 1-(Phenylethynyl)silatrane (**5**)*

The reaction was carried out under an argon atmosphere. A 1.6 M solution of *n*-BuLi in hexane (5.1 ml, 8.1 mmol) was added dropwise to a stirred solution of phenylacetylene (0.86 ml, 7.9 mmol) in Et_2O (30 ml). The reaction mixture was refluxed for 15 min. The solution of PhC$\equiv$CLi in Et_2O thus obtained was then added with stirring to a suspension of 1-bromosilatrane (2.0 g, 7.9 mmol) in Et_2O (15 ml). After refluxing for 8 h the volatiles were removed entirely and chloroform (30 ml) was added to the residue. The undissolved precipitate was filtered off and the filtrate was evaporated in vacuo. Recrystallization of a solid residue from chloroforom/hexane gave 0.96 g (44%) of **5**, m.p. 259–261°C; [58]: m.p. 275°C (from chloroform).

IR (Nujol): ν(C$\equiv$C) 2165 cm^{-1}. ^{1}H NMR data in $CDCl_3$ are consistent with those reported in literature [53]. ^{13}C NMR ($CDCl_3$) $\delta = 50.87$ (NCH_2); 57.44 (OCH_2); 96.86 ($\equiv$CSi); 101.62 (PhC$\equiv$); 124.03, 127.48, 127.60, 132.32 (aromatic C).

Reactions of Studied Phenylacetylenes With Bromine

A solution of bromine (0.05 mol) in 30 ml of CCl_4 was added dropwise to a solution of phenylacetylene (0.05 mol) in 30 ml of chloroform. Stirring of the reaction mixture for 3–6 h at room temperature was accompanied with gradual disappearance of the red color of bromine. The solvents then were removed in vacuo. Resulting product was isolated by further distillation or recrystallization of the residue.

10: Fractionation of the liquid residue yielded l,2-dibromo-l-(trimethylsilyl)-2-phenylethene (**20**) as a mixture of *Z*- and *E*-isomers. b.p. 102–103°C (2 Torr). Calcd. for $C_{11}H_{14}Br_2Si$ (334.13): C, 39.54; H, 4.22. Found: C, 39.13; H, 4.17%. IR (thin film): ν(C=C) 1553 cm^{-1}. ^{1}H NMR ($CDCl_3$) $\delta = -0.05$ (s, 9H, $SiMe_3$, *Z*-isomer); 0.44 (s, 9H, $SiMe_3$, *E*-isomer); 7.28–7.36 (m, 5H, C_6H_5). ^{13}C NMR ($CDCl_3$) for *Z*-isomer $\delta = 0.11$ ($SiMe_3$); 128.20, 128.81, 129.14, 141.32 (aromatic C); 131.27, 133.52 (C=C). ^{13}C NMR ($CDCl_3$) for *E*-isomer $\delta = 0.49$ ($SiMe_3$); 128.14, 128.25, 128.51, 142.12 (aromatic C), 131.92, 133.52 (C=C). EI MS (70 eV): $m/z = 334$ (M^+, 12%), 319 ($M^+ - Me$, 7%), 253 ($M^+ - Br$, 20%), 73 ($SiMe_3{}^+$, 100%).

11: Fractionation of the liquid residue gave 1,2-dibromo-1-(triethylsilyl)-2-phenylethene (**21**) as a mixture of *Z*- and *E*-isomers. b.p. 118–120°C (1 Torr).

Calcd. for $C_{14}H_{20}Br_2Si$ (376.21): C, 44.70; H, 5.36. Found: C, 44.26; H, 5.58%. IR (thin film): ν(C=C) 1556 cm^{-1}. ^{1}H NMR ($CDCl_3$) $\delta = 0.39$ (q, 6H, $SiCH_2$, *Z*-isomer); 0.68 (q, 6H, $SiCH_2$, *E*-isomer); 0.82 (t, 9H, CH_3, *Z*-isomer); 1.06 (t, 9H, CH_3, *E*-isomer); 7.26–7.36 (m, C_6H_5, 5H). ^{13}C NMR ($CDCl_3$) for *Z*-isomer $\delta = 4.11$ ($SiCH_2$); 7.28 (CH_3); 128.07, 128.86, 129.10, 141.28 (aromatic C); 129.37, 134.34 (C=C). ^{13}C NMR ($CDCl_3$) for *E*-isomer: δ 4.58 ($SiCH_2$); 7.45 (CH_3); 121.68, 128.19, 128.46, 142.48 (aromatic C); signals of double bond carbons were not found due to the small concentration of *E*-**21**. EI MS (70 eV): m/z = 376 (M^+, 6%), 347 (M^+ – Et, 16%), 319 (M^+ – 2Et, 9%), 291 (M^+ – 3Et, 53%).

12: Removal of the solvents afforded a brown oil. Addition of hexane (20 ml) precipitated a beige solid, which was collected by filtration, washed with hexane, and dried in vacuo. The solid was found to be *Z*-1,2-dibromo-1-(triphenylsilyl)-2-phenylethene (*Z*-**22**). m.p. 125–126°C. Calcd. for $C_{26}H_{20}Br_2Si$ (520.34): C, 60.62; H, 3.87. Found: C, 60.15; H, 3.79%. IR (Nujol): ν(C=C) 1550 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 6.73–6.77, 6.85–6.88, 6.99–7.01, 7.22–7.26, 7.30–7.34, 7.47–7.50 (6m, aromatic H). ^{13}C NMR ($CDCl_3$): δ 127.61, 127.69, 128.89, 128.53, 132.86, 135.96, 136.23, 140.04 (aromatic C); 137.34, 139.74 (C=C). EI MS (70 eV): m/z = 520 (M^+, 1%), 441 (M^+ – Br, 21%), 361 (M^+ – 2Br, 44%), 259 ($Si(C_6H_5)_3^+$, 100%).

13: ^{1}H and ^{13}C NMR spectra of the liquid residue revealed the presence of bromophenylacetylene, triethylbromogermane, and dibromoalkene *Z*-**19**. Distillation of the mixture gave two fractions with b.p. 35–40°C and 135–136°C (~1 Torr). According to NMR spectra the former contains bromophenylacetylene and triethylbromogermane. ^{13}C NMR ($CDCl_3$) for PhC≡CBr $\delta = 49.69$ (≡CBr); 79.99 (PhC≡); 122.64, 128.28, 128.63, 131.92 (aromatic C).

The second fraction was *Z*-1,2-dibromo-1-(triethylgermyl)-2-phenylethene (*Z*-**19**). Calcd. for $C_{14}H_{20}Br_2Ge$ (420.71): C, 39.97; H, 4.79. Found: C, 39.63; H, 4.57%. ^{1}H NMR ($CDCl_3$) $\delta = 0.62$ (q, 6H, $GeCH_2$); 0.91 (t, 9H, CH_3); 7.25–7.28, 7.31–7.33 (m, 5H, C_6H_5). ^{13}C NMR ($CDCl_3$) $\delta = 6.28$ ($GeCH_2$); 8.69 (CH_3); 128.16, 128.98, 129.01, 141.28 (aromatic C); 129.39, 131.07 (C=C).

23: In the course of the reaction, immediate decoloration of bromine drops and warming-up of a reaction mixture was observed. Evaporation of the solvents left yellow oil, which contained only bromophenylacetylene and tributylbromostannane (by ^{13}C NMR). Bu_3SnBr: ^{1}H NMR ($CDCl_3$) $\delta = 0.90$ (t, 9H, CH_3); 1.28, 1.33 (m, 12H, $SnC\underline{H}_2CH_2$, $C\underline{H}_2CH_3$); 1.62 (m, 6H, $SnCH_2C\underline{H}_2$). ^{13}C NMR ($CDCl_3$) δ = 14.01 (CH_3); 17.92 ($SnCH_2$); 27.24 ($\underline{C}H_2CH_3$), 28.27 ($SnCH_2\underline{C}H_2$).

2: Removal of the solvent left very viscous brown oil. NMR spectra analysis showed this oil to be practically pure *Z*-1,2-dibromo-1-[1-(3,7,10-trimethyl)germatranyl]-2-phenylethene (**15**) (chemical shifts are consisted with those described below in the reaction with TBAT). The crude product was dissolved in minimum quantity of $CHCl_3$, then 10 ml of hexane was added, and the resulting mixture was stored at −10°C. The compound turned into a crystalline material only after 3 months at this temperature. It was collected by filtration, washed with hexane, and dried in vacuo to yield 0.79 g (73%) of *Z*-**15**.

9: Removal of the solvent left a yellow solid. Crude product was recrystallized from $CHCl_3$/ hexane gave 0.34 g (43%) of *Z*-**22**. Calcd. for $C_{20}H_{21}Br_2GeNO_3$ (555.78): C, 43.22; H, 3.81; N, 2.52. Found: C, 43.32; H, 3.81; N, 2.52%.

IR (Nujol): ν(C=C) 1533 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ = 2.32, 2.81, 3.38, 3.52, 3.82, 4.42 [6 m, 11H, $(AA'XX')_2$ and ABX systems of NCH_2CH_2O and NCH_2CHPhO groups protons], 7.09–7.51 (m, 10H, aromatic protons). ^{13}C NMR ($CDCl_3$) δ (atrane C) 52.80, 53.33, 56.90, 57.08, 59.32, 68.66 (CH—Ph); 126.51 (GeCBr); 134.75 (BrCPh); δ (aromatic C) 125.58, 127.19, 127.72, 128.21, 128.27, 129.21, 140.83, 142.73. EI MS (70 eV): m/z = 555 (M^+, 0.5%), 449 ($M^+ - C_6H_5CHO$, 22%), 296 ($M^+ - CBr{=}CBrC_6H_5$, 10%), 266 ($M^+ - CBr{=}CBrC_6H_5{-}CH_2O$, 10%), 190 ($M^+ - CBr{=}CBrC_6H_5{-}C_6H_5CHO$, 40%): 146 ($M^+ - CBr{=}CBrC_6H_5{-}C_6H_5CHO{-}CH_2CH_2O$, 63%).

5: The solid residue obtained after the removal of the solvents contained 1-bromosilatrane **8** as well as the trace amounts of **5** and *Z*-1,2-dibromo-1-(1-silatranyl)-2-phenylethene *Z*-**18** (according to ^{1}H NMR). ^{1}H NMR ($CDCl_3$) for *Z*-**18**: δ 2.71 (t, NCH_2, 6H); 3.54 (t, OCH_2, 6H); signals of the phenyl group are in the standard area.

Reactions of Studied Phenylacetylenes With TBAT

Under an argon atmosphere [8], solid TBAT (0.01 mol) was added in small portions to a solution of phenylacetylene (0.01 mol) in 45 ml of chloroform. When the addition was complete, the resulting bright orange solution was stirred at room temperature for 7 days; the color of the solution slowly faded during this period. The reaction mixture was then washed with 5% aqueous $Na_2S_2O_3$ (2 × 50 ml) and water (7 × 50 ml), dried (Na_2SO_4), and evaporated. Further distillation or recrystallization of a residue yielded final reaction product.

10: Distillation of a pale yellow liquid afforded a mixture of *Z*- and *E*-isomers of **20**. ^{1}H and ^{13}C NMR spectra for *Z*- and *E*-isomers are identical to those described with Br_2.

11: A liquid residue was distilled in vacuo to give **21** as a mixture of *Z*- and *E*-isomers. ^{1}H and ^{13}C NMR data are consistent with those depicted with Br_2.

12: After 7 days at room temperature no change in color of the reaction mixture was detected. Usual work-up of the solution and removal of the solvent led to a solid material that was found to be unreacted **12** (according to ^{13}C NMR spectrum).

13: Evaporation of the solvent left an oil composition of which was established without further isolation. According to ^{1}H and ^{13}C NMR spectra bromophenylacetylene, triethylbromogermane, and C—Br bond hydrolysis products of the latter are the greater part of the mixture. Besides this, the residue contains small amount of 1,2-dibromo-1-(triethylgermyl)-2-phenylethene (**19**).

23: ^{1}H and ^{13}C NMR spectra of a dark yellow liquid residue revealed the presence of two compounds: bromophenylacetylene and tributylbromostannane.

4: No exterior changes of the reaction mixture have been observed. The course of the reaction was monitored by means of ^{13}C NMR. Analysis of spectra obtained after stirring the reaction mixture for 7 and 20 days showed the presence of only starting phenylacetylene **4** and ammonium salt in the solution.

1: Removing the solvent afforded a foam looking solid. It was recrystallized from hexane/CH_2Cl_2 mixture to give 0.82 g (58%) of *Z*-1,2-dibromo-1-(1-germatranyl)-2-phenylethene (**14**). ^{1}H and ^{13}C NMR data are consistent with those already published [7].

2: After the solvent was removed under reduced pressure, hexane (5 ml) was added to the oily residue. The solid precipitated after a while was filtered off, washed with hexane, and dried in vacuo. As a result, 0.57 g (52%) of *Z*-**15** was obtained as a yellowish solid. m.p. 123–125°C. Calcd. for $C_{17}H_{23}Br_2GeNO_3$ (521.77): C, 39.13; H, 4.44. Found: C, 38.87; H, 4.28%. IR (Nujol): ν(C=C) 1533 cm^{-1}. ^{1}H NMR ($CDCl_3$) $\delta = 0.93$–3.94 (18 H, $ABXM_3$ system of NCH_2CHMeO group protons); 7.23–7.25, 7.48–7.51 (2m, 5H, C_6H_5). ^{13}C NMR ($CDCl_3$): δ 20.06, 20.27, 20.51, 22.93 (CH_3); 59.79, 62.31, 62.68, 62.81, 63.75, 64.13, 65.68, 66.17 (OCH_2, NCH_2); 121.64, 127.08, 128.05, 129.37, 129.77, 130.07, 132.51, 133.96, 134.23, 135.37, 139.16, 142.95 (C=C, aromatic C). EI MS (70 eV); $m/z = 477$ ($M^+ - CH_3CHO$, 3%), 442 ($M^+ - Br$, 9%); 262 ($M^+ - C_6H_5CBr{=}CBr$, 27%).

5: After the standard work-up the reaction mixture contained starting **5**, 1-bromosilatrane (**8**), bromophenylacetylene, and *Z*-1,2-dibromo-1(1-silatranyl)-2-phenylethene (*Z*-**18**) in ca. ratio 1:2:1 (according to ^{1}H NMR).

Reactions of Studied Phenylacetylenes With NBS in DMSO Solution

Under an argon atmosphere [22], NBS (0.02 mol) was added in one portion with stirring to a solution of phenylacetylene (0.01 mol) in DMSO (30 ml). As a result, a transparent bright orange solution was obtained and in general noticeable amount of heat was produced. The reaction mixture was stirred at ambient temperature for 48 h, the color intensity gradually diminishing during this period. The reaction mixture was then diluted with water (240 ml). Yellowish solid precipitated immediately. The resulting mixture was extracted with chloroform (120 ml). Combined chloroform extracts were washed successively with water (3 × 40 ml) and brine (2 × 40 ml). After drying over $MgSO_4$, the solvent was removed under reduced pressure, and the residue was analyzed by ^{1}H and ^{13}C NMR spectroscopy.

10: NMR spectra revealed the presence of complicated mixture of compounds. The major part of this mixture is unreacted **10**. Besides, we could establish the presence of small amounts of bromophenylacetyelene and *Z*-**20**, as well as trace amounts of *E*-**20**. Other components of the resulting mixture were not identified.

11: The main reaction products are bromophenylacetylene and hexaethyldisiloxane; and latter results from the treatment of the reaction mixture with water.

12: The solid residue contains complicated mixture of compounds, which are difficult to be identified.

13: The dominant reaction pathway is the cleavage of the Ge—C bond with the formation of bromophenylacetylene, triethylhydroxygermane, and hexaethyldisiloxane. Et_3GeOH and $(Et_3Ge)_2O$ arise from the treatment of the reaction mixture with water and are evidently products of Ge—Br linkage hydrolysis in triethylbromogermane.

23: The reaction results in the formation of a mixture of bromophenylacetylene and tributylbromostannane (according NMR and mass spectra).

5: A mixture of compounds difficult to be identified was obtained. ^{1}H NMR spectrum showed the absence of compounds containing atrane fragment among the reaction products.

2: Removal of the solvent gave 1.74 g (59%) of 2,2-dibromo-2-[1-(3,7,10-trimethyl)germatranyl]-1-phenyl-1-ethanone (**25**) as a yellow oil. It solidified from $CHCl_3$/hexane mixture when left to stand at −10°C for 1 month. Calcd. for $C_{17}H_{23}Br_2GeNO_4$ (537.77): C, 37.97; H, 4.31. Found: C, 37.62: H, 4.20%. ^{1}H NMR ($CDCl_3$) $\delta = 1.15$–4.21 (18H, $ABXM_3$

system of NCH_2CHMeO group protons); 7.33–7.47, 8.29–8.34 (2m, 5H, C_6H_5). ^{13}C NMR ($CDCl_3$) $\delta =$ 20.18, 20.57, 20.62, 22.82, (CH_3); 40.94, 41.00 (CBr_2); 59.35, 60.34, 62.87, 63.31, 64.33, 64.53, 65.77, 66.47 (OCH_2, NCH_2); 127.28, 127.37, 130.91, 131.01, 131.95, 132.17, 133.85, 134.26 (aromatic C); 190.91, 191.23 (C=O). EI MS (70 eV); $m/z = 537$ (M^+, 5%), 262 ($M^+ - C_6H_5COCBr_2$, 100%).

9: After removal of the solvent, the solid residue was washed with hexane (2 × 5 ml) to yield 1.5 g (52%) of 2,2-dibromo-2-[1-(3-phenyl)-germatranyl]-1-phenyl-1-ethanone (**26**). Calcd. for $C_{20}H_{21}Br_2GeNO_4$ (571.70): C, 42.02; H, 3.70; N, 2.45. Found: C, 42.45; H, 3.54; N, 2.31%. IR (Nujol): ν(C=O) 1661 cm^{-1}. ^{1}H NMR ($CDCl_3$) $\delta = 2.85$–3.18, 3.76–4.18, 4.88–4.91) (3 m, 11H, $(AA'XX')_2$ and ABX systems of NCH_2CH_2O and NCH_2CHPhO groups protons); 7.20–7.52, 8.36–8.37 (2 m, 10H, C_6H_5). ^{13}C-NMR ($CDCl_3$) δ (atrane C) 52.98, 53.41, 57.37, 57.46, 59.57, 68.52 (CH—Ph); 41.09 ($GeCBr_2$); δ (aromatic C) 125.35, 127.55, 127.77, 128.42, 131.06, 132.32, 132.59, 141.54; 190.14 (C=O). EI MS (70 eV): $m/z = 571$ (M^+, 0.8%), 296 ($M^+ - C_6H_5COCBr_2$, 13%), 190 ($M^+ - C_6H_5COCBr_2$—C_6H_5CHO, 33%), 146 ($M^+ - C_6H_5COCBr_2$—C_6H_5CHO—CH_2CH_2O, 33%), 105 ($C_6H_5CO^+$, 100%).

X-Ray Crystallography Study of **2**, **5**, *Z*-**15**, *Z*-**22**, *and* **25**

Table 4 summarizes the crystal data as well as details of data collection and structure determination. For all compounds non-hydrogen atoms (including disorder components) were refined with anisotropic thermal parameters. In the structure of **5**, all hydrogen atoms were found from difference Fourier map and refined isotropically. As for the structures of **2**, *Z*-**15**, *Z*-**22**, and **25**, all hydrogen atoms were placed in calculated positions and refined using a riding model. Atrane frameworks in the structures of **2**, *Z*-**15**, and **25** were found to be disordered with approximate occupancies ratios 0.5/0.5.

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publications no. CCD-191695 for **5**, 191696 for **2**, 191697 for *Z*-**15**, 191698 for **25**, and 191699 for *Z*-**22**. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44(1223)336-033; e-mail: deposit@ccdc.cam.ac.uk).

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