Synthesis of Germatranyl Derivatives of Esters of Carboxylic Acids via Organometallic (Si, Ge, Sn) Reagents

Galina S. Zaitseva*[a], Ljudmila I. Livantsova[a], Mohammed Nasim[a], Sergei S. Karlov[a], Andrei V. Churakov[b], Judith A. K. Howard[b], Evgeni V. Avtomonov[c], and Jörg Lorberth*[c]

Chemistry Department, Moscow State University[a],
B-234 Vorob'evy Gory, 119899 Moscow, Russia

Department of Chemistry, University of Durham, Science Laboratories[b],
South Road, Durham, DH1 3LE, England

Fachbereich Chemie, Philipps-Universität Marburg[c],
Hans-Meerwein-Straße, D-35032 Marburg/Lahn, Germany

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Trialkylstannyl esters of tris(2-hydroxyalkyl)amines, $N(CH_2CHROSnAlk_3)_3$ (**9**–**11**) (R = H, Me; Alk = Et, Bu), react with $X_3GeC(R^1)(R^2)COOR^3$ (**12**–**17**) (X = Cl or Br; R^1, R^2 = H, Me, Ph, $SiMe_3$, COOEt; R^3 = Me, Et) to give esters of α-germatranylcarboxylic acids, $N(CH_2CHRO)_3GeC(R^1)(R^2)$-$COOR^3$ (**1**–**8**), in high yields. The synthesis of esters **12**–**17** is reported. Esters of α-germatranyldiphenylacetic acid **24** and **25** can be obtained by treatment of diphenylketene with Et_3SnOMe to give in situ $Et_3SnC(Ph_2)COOMe$ (**23**), followed by reaction with $GeCl_4$ to give in situ $Cl_3GeC(Ph_2)COOMe$ (**22**) and further reactions with **9** or **11**, respectively. Reduction of germatrane **6** with $LiAlH_4$ in diethyl ether leads to cleavage of the germanium–carbon bond with subsequent formation of (2-hydroxyethyl)trimethylsilane. The crystal structures of **3**, **6**, and **7** are reported. 1-Acyloxygermatranes **26** and **27** are obtained by treatment of 1-methoxygermatrane (**28**) with diphenyl- and dichloroacetic acid, respectively.

Interest continues in metallatranes $N(CH_2CHAlk)_3M-Y$ (M = Si, Ge), having been reported some years ago for the first time; the main focus has been the nature of the transannular M–N bond[1]. However, theoretical aspects of the research on metallatranes did not render synthetic approaches to a second-order problem. Moreover, many silatranes and germatranes show biological activity, which makes them interesting for medicinal chemistry and pharmacology[2–4].

So far, functionalized silatranes and germatranes[5–11], e.g. metallatranes with a functional group (e.g. C=O, C=C) in the β position to the metal atom, have not been studied in detail. Similar compounds belong to a more general class of σ,π-conjugated systems, with characteristic features of the relatively labile metal–carbon bond and (e.g. in the case of β-oxo derivatives) with the ability to undergo isomeric transformations under catalytic conditions or on heating[12–14]. Whereas the synthesis and reactivity of 1-allylsilatranes were subject of numerous investigations, there is almost no information available on the chemistry of 1-allylgermatrane: only cleavage reactions of the Ge–C bond in 1-allylgermatrane were reported[11]. Our investigations included reactions at the C=C bond of 1-allylmetallatranes which occur with retention of the "atrane" skeleton and the metal–carbon bond, e.g. the cyclopropanation of 1-allylmetallatranes (M = Si, Ge)[10,11].

In this paper we report on the synthesis and properties of the series of esters of α-germatranylcarboxylic acids **1**–**8**, starting from trihalogenogermanium derivatives **12**–**17**, and tris(2-trialkylstannoxyalkyl)amines **9**–**11**. Other organotin reagents, e.g. Et_3SnOMe, were also used in the synthesis of 1-acyloxygermatranes **26** and **27**. In addition, the crystal structures of compounds **3**, **6**, and **7** are discussed in comparison.

We have recently described the synthesis of the first of β-oxo derivatives of metallatranes: silatranylacetaldehyde and 3,7,10-trimethylsilatranylacetaldehyde, $N(CH_2CHRO)_3Si-CH_2CHO$ (R = H, Me)[6]. The compounds are air-stable and undergo no rearrangement (as a result of migration of the silatranyl group) to the corresponding *O*-silyl enols[9].

This has provided a basis for extended studies which are presented here. Derivatives of carboxylic acid esters seem to be easily available among β-oxogermatranes. We were interested in developing synthetic routes to α-germatranylcarboxylic acid esters which have not been reported previously. It was essential that those systems had to be synthesized, which comprise substituents with different steric and electronic properties at the α position to the carbonyl group (as well as to the metallatrane fragment), thus influencing the stability, reactivity, and ability to undergo isomeric transformations.

Results and Discussion

Esters of α-Germatranylcarboxylic Acids 1–8

A general synthetic route to metallatranes (Si, Ge) is the transesterification reaction, i.e. the interaction of or-

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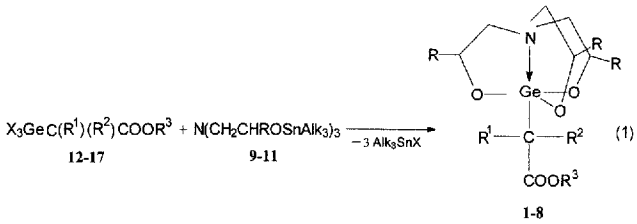
ganometal (Si, Ge) triesters with trialkanolamines[2]. The reaction of organotrihalogenosilanes and -germanes with organotin derivatives of tris(2-hydroxyalkyl)amines ("organotin route") has been used less frequently[15,16].

At the same time, the use of the readily available and very reactive organotin reagents often facilitates the synthesis of complex structures, since these reagents are "soft" and effective for the transfer of functionalized organic fragments. In our opinion, this method will become more important in cases when the starting materials and the final products contain bonds and groups which are sensitive towards reactions with nucleophilic or electrophilic reagents and towards heating[17].

This method is used in the present work for the synthesis of esters of α-germatranylcarboxylic acids **1**–**8** (Equation 1).

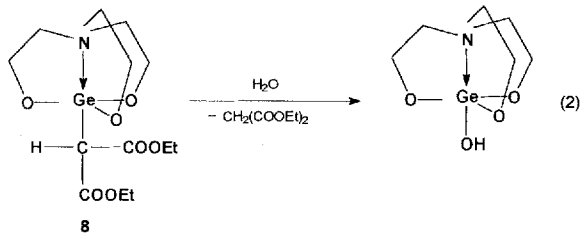


	R	R^1	R^2	R^3	Alk	X
1	H	H	H	Me		
2	Me	Me	H	Me		
3	H	H	Ph	Me		
4	Me	H	Ph	Me		
5	H	H	Ph	Et		
6	H	H	$SiMe_3$	Me		
7	H	Me	Me	Me		
8	H	H	COOEt	Et		
9	H				Et	
10	H				*n*Bu	
11	Me				Et	
12		H	H	Me		Cl
13		H	Ph	Me		Cl
14		H	$SiMe_3$	Me		Cl
15		H	Ph	Et		Br
16		Me	Me	Me		Br
17		H	COOEt	Et		Br

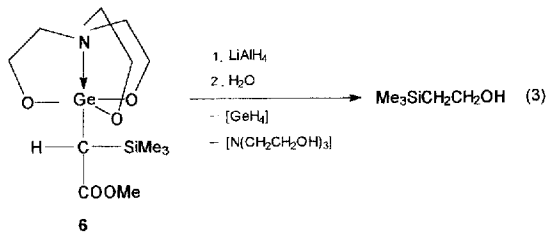
These reactions proceed smoothly after mixing the reagents under mild conditions, followed by keeping the reaction mixture for several hours at room temperature. After addition of *n*-pentane or *n*-hexane the resulting germatranes precipitate and can easily be separated by filtration. Analytically pure samples are obtained by washing the precipitates with *n*-pentane or *n*-hexane, recrystallization from benzene or toluene, followed by drying in vacuo at 1–3 Torr: compounds **1**–**8** are thus obtained in excellent yields (90–95%).

Trialkyltin halides are formed as by-products of the transmetallation reaction and can be recovered almost quantitatively and further used for the preparation of trialkyltin methoxides. The latter are useful for the preparation of trialkylstannyl esters of trialkanolamines **9**–**11** as well as (vide infra) for the synthesis of esters of α-trichlorogermylcarboxylic acids **12**–**14**.

Diethyl germatranylmalonate (**8**) reacts with traces of water upon cleavage of the Ge–C bond, forming 1-hydroxygermatrane and diethyl malonate (Equation 2) and has not been isolated so far in an analytically pure form. Nonetheless, ^{1}H- and ^{13}C-NMR and EI-MS studies of **8** unambiguously confirm its structure. Equation 2 shows that the polar Ge–C bond in **8** is essentially labile.



In contrast, esters **1**–**7** are more stable towards hydrolysis. It should also be noted that only the corresponding organosilicon β-alcohol is obtained by reduction of ester **6** with $LiAlH_4$ (Equation 3).



This observation contrasts with that reported for the tetracoordinated analogues, viz. $Alk_3GeCH_2COOAlk$, which are smoothly converted to the corresponding β-alcohols, $Alk_3GeCH_2CH_2OH$, by reduction with $LiAlH_4$[18].

In the course of this study the choice of appropriate synthetic methods of esters of α-trihalogenogermylcarboxylic acids **12**–**17** was very important. Some optimized methods were found in which ketene, trimethylsilylketene, phenylketene trimethylsilyl methyl acetal (**21**) and $GeBr_2$ · dioxane are used as key starting reagents. The syntheses of esters **12**–**17** are summarized in Equations 4–7; Equations 4–6 show that organotin reagents were successfully used for the preparation of esters of α-trichlorogermylcarboxylic acids **12**–**14**.

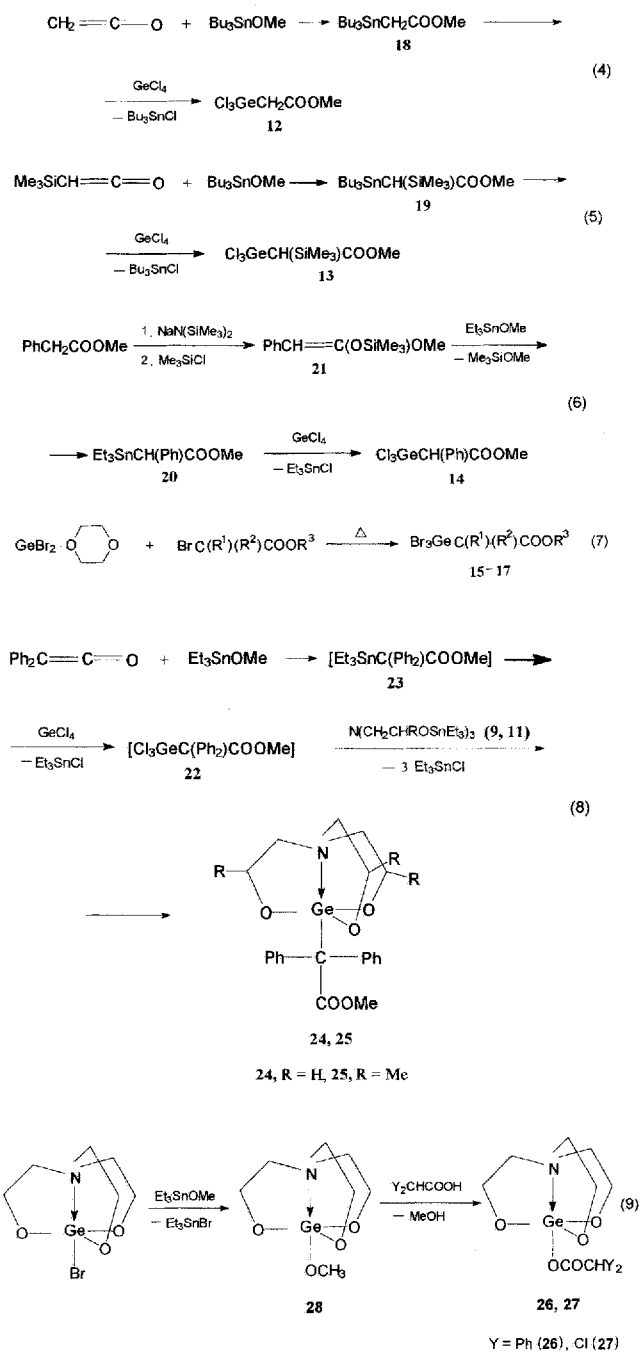
Although syntheses of **12**–**14** and **17** were described earlier (see Experimental Section), their detailed ^{1}H- and ^{13}C-NMR data are presented in this work for the first time.

An effective route to the esters of α-germatranyldiphenylacetic acid **24** and **25**, excluding isolation of the intermediate esters of trialkylstannyl- and trichlorogermyldiphenylacetic acid **23** and **22** is shown in Equation 8.

1-Acyloxygermatranes 26 and 27

For a comparative study we synthesized and characterized *O*-substituted esters, 1-acyloxygermatranes **26** and **27**. These compounds were prepared by the reaction of 1-methoxygermatrane (**28**), which can be synthesized by treatment of 1-bromogermatrane with triethylmethoxystannane[7], with diphenyl- and dichloroacetic acids under reflux in *o*-xylene according to Equation 9.

The new compounds **1**–**8**, **15**, **16**, **24**–**27** were characterized by elemental analyses and by IR, ^{1}H-, ^{13}C- and ^{29}Si-



(6)-NMR spectroscopy. Compounds **1**, **3**, **5**–**8**, **25**–**27** were also characterized by mass spectrometry.

^{1}H- and ^{13}C-NMR spectra are in accord with the suggested structures. In the ^{1}H-NMR spectra of **1**, **3**, **7**, **8**, **24**, **26**, and **27** the signals of the methylene protons of the germatrane skeleton appear as a set of two pseudo-triplets at δ = 2.72–2.98 (NCH_2) and at δ = 3.69–3.97 (OCH_2), forming an AA'XX' spin system (J = 5.5–5.8 Hz). The coupling constants for these triplets are independent of the nature of the apical group. This pattern is a general feature of the "atrane" framework for a variety of germatranes[2,7,11]. In the ^{1}H-NMR spectra of **5** and **6** the signals of the methylene protons of the (OCH_2) groups of the germatrane skeleton appear as doublets of triplets at δ = 3.68, 3.69 (**5**) and at δ = 3.72, 3.74 (**6**). As a consequence of the diastereotopic nature of the methylene protons of the $COOCH_2CH_3$ group two different quadruplets are observed for **5**, **8**, **15**, and **17**. In the ^{13}C-NMR spectra of **1**, **3**, **5**–**8**, **24**, **26**, and **27** the signals of the carbon atoms of the "atrane" skeleton appear at δ = 51.7–52.3 (NCH_2) and δ = 56.8–57.5 (OCH_2)[2]. 3,7,10-Trimethyl-substituted metallatranes **2** and **25** are mixtures of two diastereomers which differ in the orientation of the methyl groups relative to the Ge–N axis. **4** is a mixture of four diastereomers. In the ^{1}H-NMR spectra the signals of the protons of the $OCHCH_2$ groups of the "atrane" framework appear as complex multiplets ($ABMX_3$ spin system)[7,19]. In this case the composition of mixtures can be examined by ^{13}C-NMR spectroscopy as described earlier for other 1-substituted germatranes[7,20].

In the mass spectra of **1**, **3**, **5**–**8**, and **25** the peak of highest intensity corresponds to the germatranyl ion resulting from the loss of the apical substituent from the parent ion. This behavior is analogous to that observed for 1-allylgermatrane[11] and is assumed to be a reflection of the relative bond strength of the Ge–O ring bonds. A cluster of peaks at m/z = 130 has been attributed to the ion $GeN(CH_2)_3^+$, which is consistent with the germatrane structure. The molecular-ion peak carries a relatively small portion of the ion current (4–15%). Only in the case of **1** a peak resulting from the elimination of a CH_2O unit from the parent ion is observed. Apart from the principle peaks, others with intensities >5% of the base peak are given without assignments[19,21–23].

Crystal Structures of 3, 6, and 7

The molecular structures of **3**, **6**, and **7** are shown in Figures 1–4. Table 2 summarizes significant geometrical parameters.

In the structures of **3**, **6**, and **7** the coordination polyhedron of the germanium atom represents a distorted trigonal bipyramid with N and C atoms in the apical positions and the three oxygen atoms in equatorial positions[35–40]. The Ge–N distances are in the normal range for "atranes" containing an N–Ge–C group (2.19–2.32 Å)[35,36]. However, the Ge–C bonds in **3** and **7** are noticeably longer than those previously found in germatranes (1.94–1.97 Å)[37,38].

The "atrane" moiety and the ester group in **3** exhibit positional disorder (see Figure 1). Similar conformational disorder for the germatrane skeleton were observed earlier[11,39,40]. Refinement of the site-occupation factors for both disordered fragments resulted in very close values: 0.79/0.21 ("atrane" fragment) and 0.75/0.25 (ester fragment). That is in full agreement with the fact that the only short intermolecular contacts observed in the crystal structure of **3** were those between the major and minor components of different disordered groups (see Figure 2).

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Figure 1. Molecular structure of **3**; displacement ellipsoids are shown at 50-% probability level; minor components of the disordered groups are drawn by dashed circles, hydrogen atoms are omitted for clarity

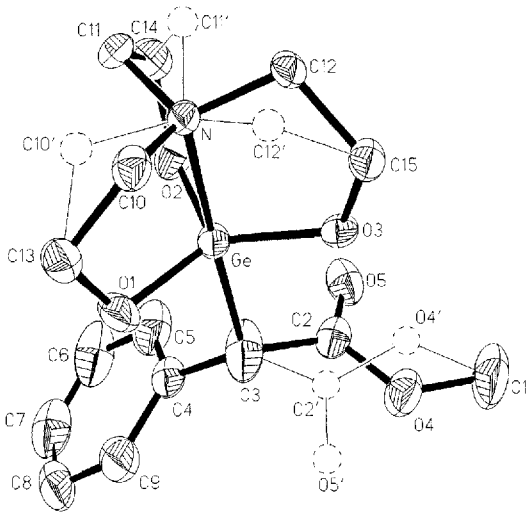
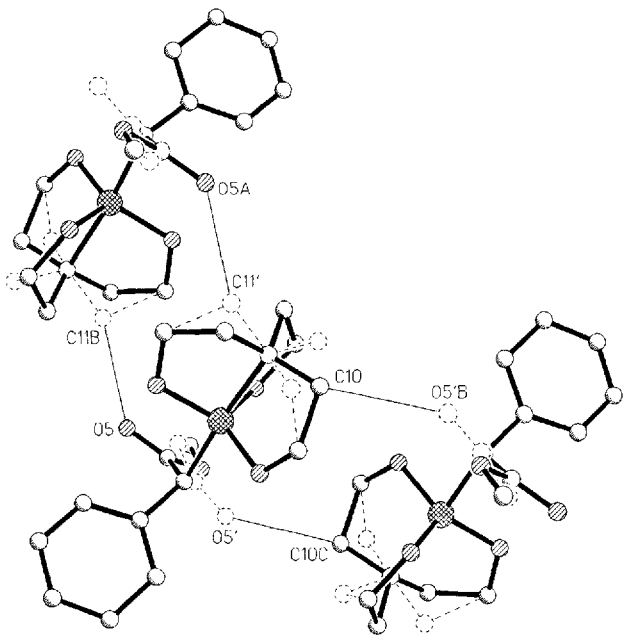


Figure 2. Intermolecular contacts in the crystal structure of **3**; minor components of the disordered groups are drawn by dashed circles; short distances between major and minor components of the disordered groups are shown by thin lines; $d\{O(5)-C(11B)\} = d\{O(5A)-C(11')\} = 2.72$ Å, $d\{C(10)-O(5'B)\} = d\{C(10C)-O(5')\} = 3.02$ Å



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Experimental Section

Solvents were dried by standard methods and distilled prior to use. – All melting points are uncorrected. – IR: Zeiss UR-20. – NMR: Bruker AC 300 (^{1}H: 300 MHz, ^{13}C: 75 MHz), Bruker AM 400 (^{29}Si: 80 MHz), Varian VXR-400 (^{1}H: 400 MHz, ^{13}C: 100 MHz); standard: $SiMe_4$. – MS: Varian CH-7a (EI, 70 eV); all assignments were made with reference to the most abundant isotopes. – Elemental analyses: Microanalytical Laboratory of the Chemistry Department of the Moscow State University and of the Fachbereich Chemie of the Philipps University of Marburg, Heraeus-Rapid Analyzer. – Crystal data, details of data collection and structure determination for **3**, **6**, and **7** are presented in Table 1[41]. All non-hydrogen atoms were refined with anisotropic thermal parameters. In the case of compound **3**, hydrogen atoms were placed in calculated positions [d(C–H) = 0.97 Å] and refined using a riding model (U_{iso} were taken as 1.2 · U_{eq} of the parent C atoms). As to the structures of **6** and **7**, all hydrogen atoms were found from difference Fourier syntheses and refined in an isotropic approximation. SHELXTL-Plus software was used to prepare materials for publication[42].

Figure 3. Molecular structure of **6**; displacement ellipsoids are shown at 50-% probability level

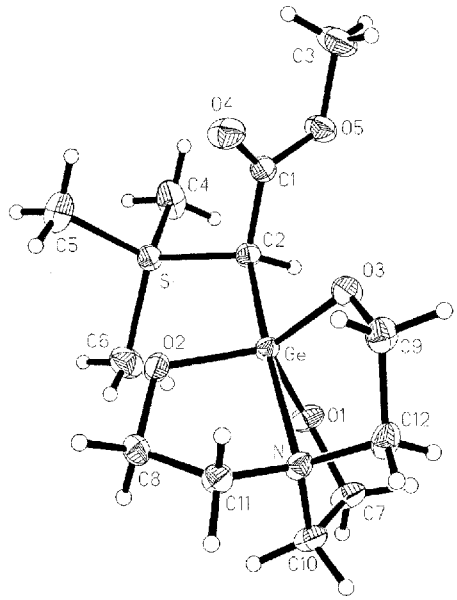
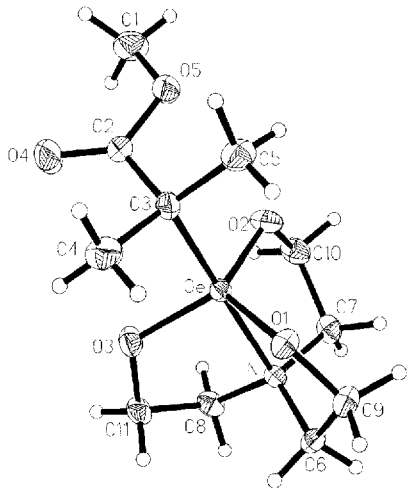


Figure 4. Molecular structure of **7**; displacement ellipsoids are shown at 50-% probability level



Tris(2-trialkylstannoxyalkyl)amines **9**–**11** were prepared according to a modified procedure[16] with use of an excess of trialkyltin methoxides.

Table 1. Crystal data, data collection, and structure determination parameters for **3**, **6**, and **7**

	3	6	7
Empirical formula	$C_{15}H_{21}GeNO_5$	$C_{12}H_{25}GeNO_5Si$	$C_{11}H_{21}GeNO_5$
Formula weight	367.90	364.01	319.88
Color, habit	colorless, block	colorless, block	colorless, block
Crystal size [mm]	0.45 × 0.28 × 0.10	0.40 × 0.18 × 0.12	0.20 × 0.10 × 0.02
Crystal system	triclinic	monoclinic	monoclinic
Space group	$P\bar{1}$	$P2_1/n$	$P2_1/n$
Unit cell dimensions:			
a [Å]	8.1567(2)	10.9515(1)	9.3836(2)
b [Å]	9.2940(2)	9.7080(1)	11.5702(3)
c [Å]	11.5814(2)	15.3539(2)	13.2655(3)
α [°]	71.4420(1)	90	90
β [°]	74.6830(1)	96.672(1)	109.499(1)
γ [°]	74.8360(1)	90	90
V [Å^3]	787.48(3)	1621.33(3)	1357.64(5)
Z	2	4	4
ρ(calcd.) [g/cm^3]	1.543	1.491	1.565
μ [mm^{-1}]	1.967	1.980	2.269
F(000)	380	760	664
Diffractometer	Siemens SMART	Siemens SMART	Siemens SMART
T [K]	150.0(2)	150.0(2)	150.0(2)
Radiation (λ [Å])	graphite-monochromatized Mo-K_α (0.71073)		
Scan mode	ω	ω	ω
Scan step (in ω) [°]	0.3	0.3	0.3
Time per step [s]	10	10	30
θ range [°]	1.89 to 27.49	2.17 to 27.52	2.33 to 27.49
Index ranges	$-10 \le h \le 10$, $-11 \le k \le 12$, $-14 \le l \le 15$	$-14 \le h \le 14$, $-11 \le k \le 12$, $-19 \le l \le 14$	$-12 \le h \le 12$, $-14 \le k \le 14$, $-17 \le l \le 16$
Reflections collected	5804	11415	9733
Independent reflections	3566	3710	3110
R_{int}	0.0405	0.0347	0.0688
Data reduction	Siemens SAINT (Siemens Analytical X-ray Instruments, 1995)		
Absorption correction	empirical (SHELXTL-Plus)	face-indexed (SHELXTL-Plus)	empirical (SHELXTL-Plus)
Min. and max. transmission	0.360 and 0.570	0.517 and 0.808	0.562 and 0.626
Solution method	direct methods (SHELXTL-Plus)		
Refinement method	full-matrix least squares on F^2 (SHELXTL-Plus)		
Data/restraints/parameters	3508/0/255	3449/0/282	2751/0/248
Goodness-of-fit on F^2	1.097	1.040	1.078
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0463$, $wR_2 = 0.1214$	$R_1 = 0.0244$, $wR_2 = 0.0564$	$R_1 = 0.0357$, $wR_2 = 0.0662$
R indices (all data)	$R_1 = 0.0497$, $wR_2 = 0.1279$	$R_1 = 0.0355$, $wR_2 = 0.0697$	$R_1 = 0.0691$, $wR_2 = 0.0871$
Extinction coefficient	0.002(2)	0.0015(3)	0.0022(4)
Largest diff. peak and hole [e·Å^{-3}]	1.162 and −0.615	0.382 and −0.334	0.443 and −0.695

Table 2. Selected geometrical parameters [Å, °] for **3**, **6** and **7**

	3	6	7
Ge–N	2.158(3)	2.2090(14)	2.222(2)
Ge–C	1.999(4)	1.975(2)	2.006(3)
Ge–O(1)	1.803(3)	1.8147(12)	1.809(2)
Ge–O(2)	1.795(3)	1.8047(12)	1.805(2)
Ge–O(3)	1.795(2)	1.8062(12)	1.801(2)
Ge–PL[a]	0.19[b]	0.23[b]	0.24[b]
C–Ge–N	175.0(2)	175.72(6)	179.02(11)
O(1)–Ge–O(2)	118.28(14)	118.04(6)	118.75(10)
O(1)–Ge–O(3)	119.80(13)	118.25(6)	116.50(9)
O(2)–Ge–O(3)	118.54(12)	118.90(6)	119.49(10)
O(1)–Ge–C	94.2(2)	94.05(6)	96.48(11)
O(2)–Ge–C	100.9(2)	100.65(6)	98.37(11)
O(3)–Ge–C	93.3(2)	97.24(6)	98.14(10)
O(1)–Ge–N	84.18(11)	82.36(5)	82.58(9)
O(2)–Ge–N	83.96(12)	83.15(5)	81.87(8)
O(3)–Ge–N	83.45(10)	82.51(5)	82.54(9)

[a] PL means the plane defined by O(1), O(2), and O(3) atoms. – [b] Positive sign indicates that the germanium atom is displaced towards the carbon atom.

Tris(2-tributylstannoxyethyl)amine (**10**): A solution of tributylmethoxystannane (43.2 g, 0.135 mol) and triethanolamine (6.0 g, 0.04 mol) in benzene (50 ml) was refluxed for 4 h. The solvent and the excess of tributylmethoxystannane (4.8 g; b.p. 117–120°C/3.5 Torr) were removed by distillation giving a nonvolatile oil. Yield: 40.6 g (100%); n_D^{20} = 1.4945. – NMR ($CDCl_3$): ^{1}H: δ = 3.70 (m, 6H, OCH_2), 2.61 (m, 6H, NCH_2), 0.8–1.6 (m, 81H, *n*Bu). – ^{13}C: δ = 64.47 (OCH_2), 60.13 (NCH_2), 27.82 (CH_2), 27.01 (CH_2), 14.38 ($SnCH_2$), 13.47 (CH_3). – $C_{42}H_{93}NO_3Sn$ (1016.28): calcd. C 49.64, H 9.22, Sn 35.04; found C 49.45, H 9.35, Sn 35.20.

Tris(2-triethylstannoxyethyl)amine (**9**): Triethylmethoxystannane (50.6 g, 0.214 mol) and triethanolamine (9.7 g, 0.065 mol). Yield: 49.6 g (98%). – NMR ($CDCl_3$): ^{1}H: δ = 3.17 (m, OCH_2, 6H), 2.51 (m, 6H, NCH_2), 0.8–1.3 (m, 45H, CH_3CH_2); ^{13}C: δ = 64.48 (OCH_2), 60.01 (NCH_2), 9.66 ($SnCH_2$), 5.49 (CH_3). The product was used without further purification, but can be purified by distillation; b.p. 210–220°C/1.5 Torr (ref.[16] 1 Torr, bath temp. 210°C).

Tris(2-triethylstannoxypropyl)amine (**11**): Triethylmethoxystannane (47.4 g, 0.20 mol) and triisopropanolamine (11.5 g, 0.06 mol). Yield: 49.2 g (98%). The liquid product was used without further purification.

(Z)-Phenylketene Methyl Trimethylsilyl Acetal (**21**): A solution of methyl phenylacetate (38.8 g, 0.22 mol) in ether (250 ml) was treated with a solution of $NaN(SiMe_3)_2$ (45.2 g, 0.25 mol) in ether (200 ml) at −65°C, and the mixture was stirred for 0.5 h. A solution of 26.0 g (30 ml, 0.245 mol) of Me_3SiCl in 30 ml of ether was added dropwise at −65°C over a period of 0.5 h. The reaction mixture was stirred for 24 h, the precipitate was filtered off, and the product was purified by distillation. Yield: 45 g (82%); b.p. 88–89°C/1.5 Torr (ref.[24] b.p. 88–89°C/1.5 Torr). – NMR ($CDCl_3$): ^{1}H: δ = 7.77–7.05 (m, 5H, aromatic H), 4.67 (s, 1H, CH=), 3.72 (s, 3H, CH_3), 0.36 [s, 9H, $Si(CH_3)_3$]. – ^{13}C: δ = 157.80 (COSi), 137.04, 128.05, 126.31, 123.47 (4 C, aromatic C), 78.70 (CH=), 55.07 (OCH_3), 0.43 [$Si(CH_3)_3$].

The following compounds were prepared according to literature procedures: *methyl (tributylstannyl)acetate* (**18**) by reaction of tributyltin methoxide with ketene[25]; *methyl (trichlorogermyl)acetate* (**12**) by reaction of ester **18** with germanium tetrachloride[26]; *methyl phenyl(triethylstannyl)acetate* (**20**) by reaction of ketene acetal **21** with triethyltin methoxide[24]; *methyl (tributylstannyl)(trimethylsilyl)acetate* (**19**) by reaction of (trimethylsilyl)ketene with tributyltin methoxide[27].

Methyl Phenyl(trichlorogermyl)acetate (**14**): $GeCl_4$ (5.3 g, 25 mmol) was added to methyl phenyl(triethylstannyl)acetate (8.0 g, 23 mmol) dropwise with stirring. The reaction mixture was heated for 1 h at 80°C; **14** was purified by distillation. Yield: 4.5 g (60%) M; b.p. 131–133°C/2.5 Torr, m.p. 72–73°C (ref.[24]: b.p. 115–118°C/1 Torr, m.p. 72–73°C). – IR (benzene solution): $\tilde{\nu}$ = 1740 cm^{-1} (C=O). – NMR ($CDCl_3$): ^{1}H: δ = 7.5–7.3 (m, 5H, aromatic H), 4.48 (s, 1H, GeCH), 3.85 (s, 3H, OCH_3). – ^{13}C: δ = 167.48 (C=O), 129.33, 129.13, 129.09, 128.86 (4 C, aromatic C), 55.78 (GeCH), 53.35 (OCH_3).

Methyl (Trichlorogermyl)(trimethylsilyl)acetate (**13**) was prepared according to the procedure for **14**: 3.8 g (18 mmol) of $GeCl_4$ and 6.8 g (16 mmol) of methyl (tributylstannyl)(trimethylsilyl)acetate. Yield: 1.8 g (60%); b.p. 85–90°C/1.5 Torr (ref.[28]: b.p. 83–85°C/1.5 Torr). – IR (thin film): $\tilde{\nu}$ = 1710 cm^{-1} (C=O). – NMR ($CDCl_3$): ^{1}H: δ = 3.73 (s, 3H, OCH_3), 2.87 (s, 1H, GeCH), 0.29 [s, 9H, $Si(CH_3)_3$]. – ^{13}C: δ = 168.41 (C=O), 52.61 (OCH_3), 44.88 (GeCH), −0.94 [$Si(CH_3)_3$].

Synthesis of Tribromogermyl Derivatives **15**–**17** *and* **26**

Ethyl Phenyl(tribromogermyl)acetate (**15**): A mixture of ethyl 2-bromo-2-phenylacetate (10.7 g, 44 mmol) and $GeBr_2$ · dioxane[29] (9.6 g, 30 mmol) was refluxed for 4 h. The product was purified by distillation. Yield: 1.7 g (12%); b.p. 183–185°C/1 Torr; n_D^{20} = 1.5933. – IR (thin film): [si2]==gν = 1710–1740 cm^{-1} (C=O). – NMR ($CDCl_3$): ^{1}H: δ = 7.50–7.35 (m, 5H, aromatic H), 4.61 (s, 1H, GeCH), 4.29, 4.34 (2 q, J = 7 Hz, 2H, OCH_2), 1.37 (t, J = 7 Hz, 3H, CH_3). – ^{13}C: δ = 167.51 (C=O), 130.18, 129.48, 129.05,

128.81 (4 C, aromatic C), 62.25 (OCH_2), 58.85 (GeCH), 14.18 (CH_3). – $C_{10}H_{11}Br_3GeO_2$ (475.50): calcd. C 25.26, H 2.33; found C 25.21, H 2.18.

Methyl Dimethyl(tribromogermyl)acetate (**16**) was obtained according to the procedure for **15** from methyl 2-bromo-2,2-dimethylacetate (6.3 g, 35 mmol) and $GeBr_2$ · dioxane (7.2 g, 22 mmol). Yield: 4.0 g (45%); b.p. 93–94°C/4 Torr; n_D^{20} = 1.5512. – IR (thin film): $\tilde{\nu}$ = 1715 cm^{-1} (C=O). – NMR ($CDCl_3$): ^1H: δ = 3.76 (s, 3H, OCH_3), 1.49 [s, 6H, $GeC(CH_3)_2$]. – ^{13}C: δ = 172.00 (C=O), 52.94 (OCH_3), 52.48 (GeC), 20.61 (CH_3). – $C_5H_9Br_3GeO_2$ (475.50): calcd. C 14.53, H 2.19; found C 14.01, H 2.18.

Diethyl (Tribromogermyl)malonate (**17**) was obtained according to the procedure for **15**: 14.8 g (61 mmol) of diethyl bromomalonate and $GeBr_2$ · dioxane (11.3 g, 35 mmol). Yield: 3.5 g (21%); b.p. 130–135°C/3 Torr (ref.[30] 105–110°C/1.5 Torr). – NMR ($CDCl_3$): ^1H: δ = 4.34 (s, 1H, GeCH), 4.25, 4.26 (2 q, J = 7 Hz, 4H, OCH_2), 1.29 (t, J = 7 Hz, 6H, CH_3). – ^{13}C: δ = 163.61 (C=O), 63.02 (OCH_2), 57.70 (GeCH), 13.90 (CH_3).

Synthesis of Esters of α-Germatranylcarboxylic Acids **1–8**

Methyl Germatranylphenylacetate (**3**): A solution of methyl (trichlorogermyl)phenylacetate (**14**) (4.7 g, 14 mmol) in 15 ml of $CHCl_3$ was added dropwise to a solution of tris(2-triethylstannoxyethyl)amine (**9**; 12.1 g, 16 mmol) in 6 ml of $CHCl_3$. The reaction mixture was stirred for 4 h, then *n*-pentane (15 ml) was added and the precipitate was filtered off, washed with cold *n*-pentane (5 × 5 ml) and dried in vacuo (1 Torr) for 2 h. Yield: 4.8 g (93%); m.p. 198–200°C (after recrystallization from toluene or benzene). – IR (nujol): $\tilde{\nu}$ = 1705 cm^{-1} (C=O). – NMR ($CDCl_3$): ^1H: δ = 7.5–7.05 (m, 5H, aromatic H), 3.7 (s, 1H, GeCH), 3.69 (t, 6H, OCH_2), 3.62 (s, 3H, OCH_3), 2.72 (t, 6H, NCH_2). – ^{13}C: δ = 173.71 (C=O), 136.83, 129.62, 127.66, 125.52 (4 C, aromatic C), 57.11 (OCH_2), 52.17 (NCH_2), 51.78 (OCH_3), 47.94 (GeCH). – MS (70 eV); *m/z* (%): 369 (15) [M^+], 252 (5), 220 (100) [A, A = M^+ – $C_6H_5CHCOOCH_3$], 190 (3) [A – CH_2O], 160 (13) [A – 2 CH_2O], 146 (7) [A – CH_2O – CH_2CH_2O], 130 (3) [A – 3 CH_2O], 118 (21), 91 (7), 90 (8), 86 (5), 70 (6), 56 (23), 42 (6). – $C_{15}H_{21}GeNO_5$ (367.93): calcd. C 48.97, H 5.75, N 3.81; found C 48.77, H 5.84, N 3.63.

Esters **1**, **2**, **4–8** were obtained according to the procedure for **3**.

Methyl Germatranylacetate (**1**): 1.44 g (5.7 mmol) of methyl (trichlorogermyl)acetate (**12**) and 6.9 g (5.7 mmol) of tris(2-triethylstannoxyethyl)amine (**9**). Yield: 1.6 g (96%); m.p. 163–164°C. – IR (nujol): $\tilde{\nu}$ = 1714 cm^{-1} (C=O). – NMR ($CDCl_3$): ^1H: δ = 3.82 (t, 6H, OCH_2), 3.67 (s, 3H, OCH_3), 2.86 (t, 6H, NCH_2), 2.18 (s, 2H, $GeCH_2$). – ^{13}C: δ = 172.99 (C=O), 56.83 (OCH_2), 51.70 (NCH_2), 51.60 (OCH_3), 26.67 (GeC). – MS (70 eV); *m/z* (%): 293 (7) [M^+], 263 (12) [M^+ – CH_2O], 262 (10) [M^+ – OCH_3], 250 (13) [M^+ – CH_2CHO], 220 (100) [A = M^+ – CH_2COOCH_3], 190 (53) [A – CH_2O], 160 (51) [A – 2 CH_2O], 146 (13) [A – CH_2O – CH_2CH_2O], 130 (8) [A – 3 CH_2O], 91 (7), 89 (7), 86 (21), 70 (9), 56 (41), 44 (8), 43 (8), 42 (19), 41 (5). – $C_9H_{17}GeNO_5$ (291.83): calcd. C 37.04, H 5.87, Ge 24.87; found C 36.91, H 6.16, Ge 24.87.

Methyl (3,7,10-Trimethylgermatranyl)acetate (**2**): 1.2 g (4.75 mmol) of methyl (trichlorogermyl)acetate (**12**) and 3.89 g (4.75 mmol) of tris(2-triethylstannoxypropyl)amine (**11**). Yield: 1.55 g (98%); m.p. 179–180°C. – IR (nujol): $\tilde{\nu}$ = 1720 cm^{-1} (C=O). – NMR ($CDCl_3$): ^1H: δ = 3.62, 3.61 (2 s, 3H, OCH_3), 2.18, 2.16 (2 s, 2H, $GeCH_2$), $ABMX_3$ system of $OCH(CH_3)CH_2$ group protons. – ^{13}C: δ = 173.51, 173.39 (C=O), 65.77, 65.58, 64.11, 63.45, 62.51, 62.45, 62.02, 59.13 (OCH, NCH_2), 51.24, 51.23 (OCH_3), 27.31, 27.12 ($GeCH_2$), 23.43, 20.90, 20.60, 20.52 (CH_3), 2 diastereomers. – $C_{12}H_{23}GeNO_5$ (333.91): calcd. C 43.17, H 6.94, Ge 21.74; found C 43.13, H 7.11, Ge 21.62.

Methyl Phenyl(3,7,10-trimethylgermatranyl)acetate (**4**): 3.6 g (11 mmol) of methyl phenyl(trichlorogermyl)acetate (**14**) and 9.0 g (12 mmol) of tris(2-triethylstannoxypropyl)amine (**11**). Yield: 4.2 g (93%); m.p. 153–156°C. – IR (nujol): $\tilde{\nu}$ = 1720 cm^{-1} (C=O). – NMR ($CDCl_3$): ^1H: δ = 7.6–7.05 (m, 5H, aromatic H), 3.75, 3.76, 3.77, 3.78 (4 s, 1H, GeCH), 3.67, 3.66, 3.65, 3.64 (4 s, 3H, OCH), $ABMX_3$ system of $OCH(CH_3)CH_2$ group protons. – ^{13}C: δ = 173.45, 173.42 (C=O), 136.94, 136.93, 136.93, 136.91, 129.81, 129.77, 129.68, 129.62, 127.20, 127.18, 127.11, 127.09, 125.07, 125.05, 125.03, 125.01 (aromatic C), 65.89, 65.88, 64.15, 64.07, 63.59, 63.57, 62.16, 62.13, (OCH), 65.47, 65.44, 62.64, 62.56, 62.41, 62.26, 59.39, 59.21 (NCH_2), 51.37, 51.35 (OCH_3), 47.96, 47.90, 47.84, 47.70 (GeCH), 23.04, 23.13, 20.66, 20.65, 20.45, 20.44, 20.41, 20.40 (CH_3), 4 diastereomers. – $C_{18}H_{27}GeNO_5$ (410.01): calcd. C 52.73, H 6.64, N 3.42; found C 52.20, H 6.86, N 3.32.

Ethyl Germatranylphenylacetate (**5**): 1.2 g (2.5 mmol) of ethyl phenyl(tribromogermyl)acetate (**15**) and 2.8 g (2.8 mmol) of tris(2-tributylstannoxyethyl)amine (**10**). Yield: 0.9 g (95%); m.p. 194–198°C. – IR (nujol): $\tilde{\nu}$ = 1705 cm^{-1} (C=O). – NMR ($CDCl_3$): ^1H: δ = 7.55–7.05 (m, 5H, aromatic H), 3.7 (s, 1H, GeCH), 3.69 (t, 6H, OCH_2), 4.15, 4.11 (2 q, J = 7 Hz, 2H, OCH_2), 2.76 (t, 6H, NCH_2), 1.23 (t, J = 7 Hz, 3H, CH_3). – ^{13}C: δ = 172.69 (C=O), 136.83, 129.54, 127.57, 125.41 (4 C, aromatic C), 60.15 (OCH_2CH_3), 57.03 (OCH_2), 52.15 (NCH_2), 48.17 (GeCH), 14.27 (CH_3). – MS (70 eV); *m/z* (%): 383 (12) [M^+], 266 (7), 220 (100) [A, A = M^+ – $C_6H_5CHCOOCH_3$], 190 (3) [A – CH_2O], 160 (10) [A – 2 CH_2O], 146 (8) [A – CH_2O – CH_2CH_2O], 130 (3) [A – 3 CH_2O], 118 (17), 91 (6), 90 (5), 70 (6), 56 (23), 42 (5). – $C_{16}H_{23}GeNO_5$ (383.08): calcd. C 50.12, H 6.05, N 3.66; found C 49.85, H 6.06, N 3.66.

Methyl Germatranyl(trimethylsilyl)acetate (**6**): 1.6 g (5 mmol) of methyl (trichlorogermyl)(trimethylsilyl)acetate (**13**) and 4.2 g (6 mmol) of tris(2-triethylstannoxyethyl)amine (**9**). Yield: 1.7 g (93%); m.p. 158–160°C. – IR (nujol): $\tilde{\nu}$ = 1690 cm^{-1} (C=O). – NMR ($CDCl_3$): ^1H: δ = 3.72, 3.74 (2 t, 6H, OCH_2), 3.59 (s, 3H, OCH_3), 2.77 (t, 6H, NCH_2), 1.98 (s, 1H, GeCH), –0.10 [s, 9H, $Si(CH_3)_3$]. – ^{13}C: δ = 174.25 (C=O), 56.89 (OCH_2), 52.11 (NCH_2), 51.27 (OCH_3), 32.98 (GeCH), –0.38 [$Si(CH_3)_3$]. – ^{29}Si: δ = 2.85. – MS (70 eV), *m/z* (%): 365 (4) [M^+], 350 (37) [M^+ – CH_3], 318 (9), 252 (18) [M^+ – C_5H_9SiO], 220 (100) [A, A = M^+ – $(CH_3)_3SiCHCOOCH_3$], 190 (24) [A – CH_2O], 160 (20) [A – 2 CH_2O], 146 (12) [A – CH_2O – CH_2CH_2O], 130 (3) [A – 3 CH_2O], 99 (5), 86 (4), 73 (9) [$Si(CH_3)_3$], 70 (6), 59 (10), 56 (17), 55 (7), 42 (7). – $C_{12}H_{25}GeNO_5Si$ (364.01): calcd. C 39.60, H 6.92, N 3.85; found C 39.42, H 6.99, N 3.62.

Methyl Germatranyldimethylacetate (**7**): 3.4 g (8.2 mmol) of methyl dimethyl(tribromogermyl)acetate (**16**) and 6.9 g (9 mmol) of tris(2-triethylstannoxyethyl)amine (**9**). Yield: 2.5 g (95%); m.p. 161–163°C. – IR (nujol): $\tilde{\nu}$ = 1690 cm^{-1} (C=O). – NMR ($CDCl_3$): ^1H: δ = 3.70 (t, 6H, OCH_2), 3.62 (s, 3H, OCH_3), 2.73 (t, 6H, NCH_2), 1.35 (s, 6H, CH_3). – ^{13}C NMR: δ = 178.26 (C=O), 57.11 (OCH_2), 52.36 (NCH_2), 51.66 (OCH_3), 40.63 (GeC), 22.02 (CH_3). – MS (70 eV); *m/z* (%): 321 (7) [M^+], 252 (8), 220 (100) [A, A = M^+ – $(CH_3)_2CCOOCH_3$], 190 (18) [A – CH_2O], 160 (27) [A – 2 CH_2O], 146 (10) [A – CH_2O – CH_2CH_2O], 130 (4) [A – 3 CH_2O], 118 (6), 86 (5), 70 (9), 56 (29), 42 (14), 41 (8). – $C_{11}H_{21}GeNO_5$ (319.88): calcd. C 41.30, H 6.62, N 4.38; found C 40.82, H 6.49, N 4.34.

Diethyl Germatranylmalonate (**8**): 2.9 g (6.2 mmol) of diethyl tribromogermylmalonate (**17**) and 6.6 g (6.8 mmol) of tris(2-tributyl-

stannoxyethyl)amine (**10**). According to NMR spectra a mixture of diethyl germatranylmalonate (**8**; 90%) and 1-hydroxygermatrane (10%) was obtained.

8: IR (nujol): $\tilde{\nu}$ = 1735 cm^{-1} (C=O). – NMR ($CDCl_3$): ^1H: δ = 4.22, 4.21 (2 q, J = 7 Hz, 4H, OCH_2), 3.82 (t, 6H, OCH_2), 3.53 (s, 1H, GeCH), 2.86 (t, 6H, NCH_2), 1.25 (t, J = 7 Hz, 6H, CH_3). – ^{13}C: δ = 164.10 (C=O), 60.62 (OCH_2CH_3), 57.14 (OCH_2), 52.22 (NCH_2) 48.51 (GeCH), 14.24 (CH_3). – MS (70 eV); *m/z* (%): 379 (0.63) [M^+].

1-Hydroxygermatrane: NMR ($CDCl_3$): ^1H: δ = 3.87 (t, OCH_2, 6H), 2.92 (t, NCH_2, 6H), 1.64 (br. s, OH, 1H) [ref.[31]: ^1H: δ = 3.87 (t, 6H, OCH_2), 2.91 (t, 6H, NCH_2), 1.68 (br. s, 1H, OH)]. – ^{13}C: δ = 56.88 (OCH_2), 52.02 (NCH_2) [ref.[31]: ^{13}C: δ = 57.01 (OCH_2), 52.15 (NCH_2)].

A solution of **8** in $CDCl_3$ (not dried prior to use) was stored in a NMR tube for 2 weeks. The ^1H- and ^{13}C-NMR data showed complete hydrolysis of germatrane **8** resulting in the formation of 1-hydroxygermatrane and diethyl malonate.

Synthesis of Methyl Germatranyldiphenylacetates **24** *and* **25**

Mehyl Germatranyldiphenylacetate (**24**): Triethyltin methoxide (3.35 g, 14.2 mmol) was added dropwise at room temp. to diphenylketene (2.75 g, 14.2 mmol). The reaction mixture was stirred for 18 h and the product, $Et_3SnC(Ph_2)COOMe$ (**23**), was formed [IR (thin film): $\tilde{\nu}$ = 1730 cm^{-1} (C=O)], which was added to $GeCl_4$ (3.2 g, 15 mmol). This mixture was allowed to stir for 1 h. The excess of $GeCl_4$ and formed Et_3SnCl were removed by distillation [Et_3SnCl, 3.42 g, 99%, b.p. 92–93°C/10 Torr, n_D^{20} = 1.5138 (ref.[32]: b.p. 210°C, n_D^{20} = 1.5130)]. A solution of the residue, $Cl_3GeC(Ph_2)COOMe$ (**22**) [IR (thin film): $\tilde{\nu}$ = 1725 cm^{-1} (C=O)], in 4 ml of $CHCl_3$ was added to tris(2-triethylstannoxyethyl)amine (**9**) (10.84 g, 14.2 mmol). After a period of 3 h, $CHCl_3$ was removed in vacuo and *n*-hexane (10 ml) was added. The upper layer (a solution of Et_3SnCl in *n*-hexane) was separated and the oily layer was dried at 1 Torr for 3 h. Yield: 5.86 g (93%). **24** crystallized in 1 month. Recrystallization from $CHCl_3$/*n*-hexane gave a product with m.p. 194–195°C. – IR (nujol): $\tilde{\nu}$ = 1725 cm^{-1} (C=O).– NMR ($CDCl_3$): ^1H: δ = 7.3–7.1 (m, 5H, aromatic H), 3.76 (s, 3H, OCH_3), 3.75 (t, 6H, OCH_2), 2.79 (t, 6H, NCH_2). – ^{13}C: δ = 175.47 (C=O), 142.66, 130.62, 127.55, 125.52 (4 C, aromatic C), 57.63 (OCH_2), 52.21 (NCH_2), 51.56 (OCH_3). – $C_{21}H_{25}GeNO_5$ (444.02): calcd. C 56.62, H 5.66, Ge 16.61; found C 56.56, H 5.72, Ge 16.24.

Methyl Diphenyl(3,7,10-trimethylgermatranyl)acetate (**25**) was obtained according to the procedure as described for **24**: triethylmethoxystannane (2.44 g, 10.3 mmol), diphenylketene (2.0 g, 10.3 mmol), $GeCl_4$ (2.36 g, 11 mmol), and tris(2-triethylstannoxypropyl)amine (**11**, 8.44 g, 10.3 mmol). Yield: 4.8 g (96%); m.p. 188–192°C. – IR (nujol): $\tilde{\nu}$ = 1710 cm^{-1} (C=O). – NMR ($CDCl_3$): ^1H: δ = 7.3–7.1 (m, 5H, aromatic H), 3.7 (s, 3H, OCH_3), ABMX$_3$ system of $OCH(CH_3)CH_2$ group protons. – ^{13}C: 1st (major) diastereomer: δ = 175.58 (C=O), 142.56, 130.46, 127.45, 125.54 (4 C, aromatic C), 66.40, 64.25, 64.24 (OCH), 65.55, 63.34, 62.13 (NCH_2), 51.96 (OCH_3), 22.95, 20.88, 20.78 (CH_3); 2nd (minor) diastereomer: δ = 141.85, 130.33, 127.18, 125.37 (4 C, aromatic C), 62.56 (OCH), 60.06 (NCH_2), 20.47 (CH_3). – MS (70 eV); *m/z* (%): 487 (8) [M^+], 262 (100) [A = M^+ – $(Ph)_2CCOOCH_3$], 194 [$(Ph)_2CCO$] (43), 174 (11) [A – 2 CH_3CHO], 166 (32), 165 (23), 160 (5) [A – CH_3CHO – $CH_2CH(CH_3)O$], 130 (7) [A – 3 CH_3CHO)], 105 (5), 100 (5), 70 (13), 42 (9), 41 (7). – $C_{24}H_{31}GeNO_5$ (486.10): calcd. C 59.30, H 6.43, Ge 14.93; found C 59.14, H 6.52, Ge 14.87.

Reaction of Germatrane **6** *with* $LiAlH_4$: A suspension of $LiAlH_4$ (0.1 g, 2.5 mmol) in Et_2O (15 ml) was refluxed for 0.5 h, then cooled to room temp. and germatrane **6** (0.2 g, 0.55 mmol) was added. The resulting mixture was stirred for 16 h at room temp. After the addition of wet Et_2O and then water, the ethereal layer was separated and dried with anhydrous $MgSO_4$, ether was removed by distillation. Yield of (2-hydroxyethyl)trimethylsilane: 0.05 g (98%); n_D^{20} = 1.4271 (ref.[33]: n_D^{20} = 1.4231). – NMR ($CDCl_3$): ^1H: δ = 3.87 (t, J = 8.1 Hz, 2H, OCH_2), 3.15 (s, 1H, OH), 0.90 (t, J = 8.1 HZ, 2H, $SiCH_2$), –0.05 [s, 9H, $Si(CH_3)_3$] {ref.[33]: ^1H: δ = 3.65 (t, J = 8.2 Hz, 2H, OCH_2), 3.12 (s, 1H, OH), 0.90 (t, J = 8.2 Hz, 2H, $SiCH_2$), 0.01 [s, 9H, $Si(CH_3)_3$]}. – ^{13}C: δ = 60.08 (OCH_2), 22.19 ($SiCH_2$), –1.42 [$Si(CH_3)_3$] {ref.[34]: ^{13}C: δ = 59.40 (OCH_2), 21.90 ($SiCH_2$), –1.50 [$Si(CH_3)_3$]}.

Synthesis of 1-Acyloxygermatranes **26** *and* **27**

1-(Diphenylacetoxy)germatrane (**26**): A mixture of 1-methoxygermatrane (**28**; 0.5 g, 2 mmol) and diphenylacetic acid (0.42 g, 2 mmol) in *o*-xylene (20 ml) was refluxed for 4 h. Methanol formed and *o*-xylene were removed in vacuo. The residual solid was recrystallized from $CHCl_3$/*n*-pentane and dried in vacuo. Yield: 0.8 g (93%); m.p. 202°C. – NMR ($CDCl_3$): ^1H: δ = 7.3–7.1 (m, 10H, aromatic H), 5.0 (s, 1H, CH), 3.88 (t, 6H, OCH), 2.82 (t, 6H, NCH_2). – ^{13}C: δ = 173.25 (C=O), 140.24, 129.00, 218.19, 126.54 (4 C, aromatic C), 58.38 (CH), 57.33 (OCH_2, 52.16 (NCH_2). – $C_{20}H_{23}GeNO_5$ (430.0): calcd. C 55.87, H 5.39, N 3.26; found C 55.98, H 5.06, N 3.17.

1-(Dichloroacetoxy)germatrane (**27**) was prepared analogously to the procedure for **26**: 1-methoxygermatrane (**28**; 0.3 g, 1.2 mmol) and dichloroacetic acid (0.16 g, 1.2 mmol). Yield: 0.35 g (88%); m.p. 207–208°C. – NMR ($CDCl_3$): ^1H: δ = 5.89 (s, 1H, CH), 3.97 (t, 6H, OCH_2), 2.98 (t, 6H, NCH_2). – ^{13}C: δ = 170.0 (C=O), 66.12 (CH), 57.50 (OCH_2), 51.84 (NCH_2). – $C_8H_{13}Cl_2GeNO_5$ (346.49): calcd. C 27.72, H 3.78, N 4.04; found C 27.29, H 3.55, N 3.99. – MS (70 eV); *m/z* (%): 225 (33) [M^+ – C_2HClO_2 – CH_2O], 220 (17) [A = M^+ – $OCOCHCl_2$], 195 [M^+ – C_2HClO_2 – 2 CH_2O] (18), 86 (100).

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