hydroanthracene, respectively, were observed in the reaction of $HGeCl_3$ superacid with anthracene and 9-methylanthracene in the presence of oxygen.

2. The change in the direction of these reactions in an inert atmosphere and in the presence of oxygen confirms the existence of the cryptoradical steps that we previously observed in the reaction of HGeCl₃ with 9-methylanthracene in an N_2 atmosphere.

3. Some chemical transformations of the product of double germylation of 9-methylanthracene, on the basis of which the geometrical configuration of trans-9,10-bis(trichlorogermy1)-9-methyl-9,10-dihydroanthracene was assigned to it, were studied.

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REACTION OF HGeC1₃ SUPERACID WITH AROMATIC COMPOUNDS. COMMUNICATION 4. REACTION WITH DIPHENYL ETHER. CRYSTAL AND MOLECULAR STRUCTURE OF 1,3,5-TRIS(TRIMETHYLGERMYL)-1-(p-PHENOXYPHENYL)CYCLOHEXANE

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It is known that $HGeCl_3$ superacid [2] adds under mild conditions to the aromatic multiple bonds of a number of derivatives of benzene, naphthalene, anthracene, and thiophene [1, 3-5].

We have observed that, in addition to hydrogermylation of the aromatic multiple bonds, unusual alkylation of diphenyl ether (I) occurs in the reaction of HGeCl₃ with excess I:



1,3,5-Tris(trichlorogermy1)-1-(p-phenoxypheny1)cyclohexane (II) was characterized in the form of methylated derivative III. The overall yield of III was 70% (based on HGeCl₃). The structure of III indicates that the reaction of HGeCl₃ with I should include steps involving the hydrogermylation of one of the pheny1 rings (PR), cleavage of ether C-O bond,

*For Communication 3, see [1].

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and alkylation of excess I by the carbonium ion formed after cleavage of the C-O bond. It might be assumed that the addition of three $HGeCl_3$ molecules to diphenyl ether occurs in the first step:



The formation of 1-methoxy-1,3,5-tris(trichlorogermy1)cyclohexane in the reaction of $HGeCl_3$ with anisole [3, 4] constitutes evidence in favor of this reaction pathway:



Cleavage of the ether C-O bond in IV to give ion pair V is then possible:



It should be noted here that cleavage of the C-O bond of ethers is known to be characteristic for $HGeCl_3$ [6].

Finally, carbonium ion pair V alkylates excess diphenyl ether in the para position relative to the phenoxy group:

$$(V) + (I) \rightarrow (II) + HGeCl_s$$

The alkylating function of HGeCl₃ as Friedel—Crafts acid has been demonstrated for the first time in this research. The GeCl₃ gegenion, which in contrast to the gegenions of classical superacids [7], has high nucleophilicity, usually recombines with carbonium ions. The existence of ion pair V, however, can probably be associated with the instability of the recombination product, which contains two geminally oriented GeCl₃ groups.

It is significant that ion pair V with the indicated structure can exist only if the $GeCl_3$ substituent has a strong stabilizing mesomeric effect on the carbonium center, for otherwise, considering the destabilizing influence of the negative inductive effect of this substituent, a hydride shift must occur:



However, the structure of III demonstrates that alkylation proceeds at the C atom of the cyclohexane ring bonded to a germyl substituent, and this sort of isomerization consequently does not occur.

Finally, one may assume a step involving electron transfer in V to give a radical pair, since there is no doubt that the GeCl₃ substituent has a stabilizing effect on the radical center:



In this case the final step in the alkylation of excess diphenyl ether will be realized via a radical-substitution mechanism:

$$(VI) + (I) \rightarrow (II) + HGeCl_a$$

The structure of III was confirmed by the results of elementary analysis and the ¹H and ¹³C NMR spectra and was proved unambiguously by an x-ray diffraction study (Fig. 1).

The III crystal contains two independent molecules A and B connected by a noncrystallographic symmetry element, viz., local "slip plane" $n(x, y \sim 0.3)$, since the coordinates of the corresponding atoms in the A and B molecules satisfy the expressions $X_B = X_A + \frac{1}{2}$, $Y_B =$ $Y_A = -\frac{1}{2}$, $Z_B = 0.6 - Z_A$. These expressions are well-satisfied for the atoms of the cyclo-hexane ring, the Ge atoms, and the atoms of the $C^7 - C^{12}$ phenyl ring, to a lesser extent for the CH₃ groups, and very approximately for the atoms of the C¹³-C¹⁸ phenyl ring. At the same time, the bond lengths and bond angles in the A and B molecules coincide within the limits of 3σ. A quantitative comparison of the geometries of the A molecule and the inverted B molecule by the method in [8] led to the following values of the S criterion: S = 0.05 with allowance for the atoms of the cyclohexane ring and the Ge atoms, S = 0.07 with allowance for the same fragment, the atoms of the C^7-C^{12} phenyl ring, and the 0^1 atom, S = 0.17 when the CH₃ groups are added, and S = 0.61 when the A and B molecules as a whole are compared. According to the classification adopted in [8], the first two S values fall into the first group, i.e., comparable fragments of the molecules are identical. The third value of the S criterion corresponds to molecules with similar geometries; however, considering the high values of the isotropic equivalent heat factors (Beq) of the C atoms of the CH3 groups, the small difference in the orientations of these groups in the A and B molecules can be disregarded, and, on the basis of the first two S values, the geometries of the A molecule and the inverted B molecule (excluding the C¹³-C¹⁸ phenyl ring) can be considered to be identical.

In the description of the molecular geometry of III below we will therefore use only the geometrical parameters of the A molecule.

The marked increase in the value of the S criterion in the fourth case shows that the principal difference in the A and B molecules consists in nonidentical rotation of the C^{13} - C^{18} phenyl ring about the 0^1-C^{10} bond. Thus the $C^9C^{10}0^1C^{13}$ torsion angles in the A and B molecules are 82(1) and $-33(2)^\circ$, respectively. The orientation of the plane of the $C^{13}-C^{18}$ phenyl ring (satisfied with an accuracy of 0.02 Å in A and 0.01 Å in B) relative to the ether bridge also differs in the two molecules; torsion angle $C^{10}0^1C^{13}C^{14}$ is $0(1)^\circ$ in A and $42(1)^\circ$ in B. The planes of the $C^{13}-C^{18}$ and C^7-C^{12} phenyl rings (the latter is satisfied with an accuracy of 0.02 Å in A and 0.01 Å in B) form a dihedral angle of 78.5° with one another in the A molecule and 115.0° in the B molecule. Packing effects in the crystal are evidently the probable reason for the different orientations of the phenyl rings in the independent molecules, although there are no shortened (as compared with the sums of the van der Waals radii) intermolecular contacts in the III structure.

Because of the strong thermal vibrations of the 0^1 and $C^{13}-C^{18}$ fragments and, as a consequence, the low accuracy in the determination of the bond lengths and bond angles in them, a discussion of this part of the molecules is not warranted. One may note only the usual [9] increase in the endocyclic angle at the ipso C^{13} atom to $126(2)^{\circ}$ in both molecules due to the electron-acceptor character of the oxyphenyl substituent. The increase in exocyclic angles $0^1C^{13}C^{14}$ as compared with angles $0^1C^{13}C^{18}$ is associated with participation of the C^{14} atoms of both molecules in the shortened (as compared with the doubled van der Waals radius of the C atom of 3.42 Å [10]) intramolecular $C^{14}...C^{1\circ}$ [$\frac{2}{6}.82(2)$ and 2.99(2) Å] and $C^{14}...C^{9}$ [3.31(2) and 3.19(2) Å] contacts for the Å and B molecules, respectively.

The C7-C12 phenyl ring is virtually perpendicular to the Ge1-C1 bond; torsion angle Ge1C1C7C8 is equal to 91(1)°, and the angle between this bond and the plane of the phenyl ring is 79.0°. This orientation is most favorable with respect to decreasing the steric interaction of the C⁷-C¹² phenyl ring with the C²⁰H₃ and C²¹H₃ groups attached to the Ge1 atom. The cyclohexane ring has a chair conformation with 50.4 and 49.7° deflection of angles C²C¹C⁶ and C₃²C⁵C⁴ to different sides of the C²C³C⁵C⁶ plane, which is satisfied with an accuracy of 0.01 Å. The parameters of this ring determined by a modification [11] of the Kramer-Pople method have the following values: Q = 1.14 Å, $\theta = 178.71^{\circ}$, $\psi = 30.22^{\circ}$, and $\sigma = 0.88^{\circ}$, i.e., the conformation of the cyclohexane ring is actually a virtually ideal chair. The deviations of the Ge¹, Ge², Ge³, and C⁷ atoms from the root-mean-square plane of the cyclohexane ring are 0.540(2), 0.323(2), 0.355(2), and -1.78(2) Å, and all three GeMe₃ groups are consequently



Fig. 1. Geometry of the A molecule (the H atoms are not shown).

TABLE 1. Coordinates of the Nonhydrogen Atoms ($\cdot 10^3$; $\cdot 10^4$ for the Ge and O atoms) in the III Molecule

| | Molecule A | | | Molecule B | | |
|--|---|--|---|--|---|--|
| Atom | x | Y | z | X | ¥ | Z |
| $\begin{array}{c} Ge^1\\ Ge^2\\ Ge^3\\ G^1\\ C^2\\ C^3\\ C^4\\ C^5\\ C^6\\ C^7\\ C^8\\ C^9\\ C^{10}\\ C^{11}\\ C^{12}\\ C^{13}\\ C^{14}\\ C^{15}\\ C^{16}\\ C^{17}\\ C^{18}\\ C^{19}\\ C^{21}\\ C^{22}\\ C^{22} \end{array}$ | $\begin{array}{c} 3261 (1) \\ 597 (1) \\ -958 (1) \\ 4570 (7) \\ 218 (1) \\ 186 (1) \\ 97 (1) \\ 1 \\ 1 \\ 1 \\ (1) \\ 30 (1) \\ 121 (1) \\ 274 (1) \\ 330 (1) \\ 330 (1) \\ 330 (1) \\ 333 (1) \\ 274 (1) \\ 339 (1) \\ 333 (1) \\ 274 (1) \\ 329 (1) \\ 329 (1) \\ 329 (1) \\ 329 (1) \\ 329 (1) \\ 329 (1) \\ 329 (1) \\ 328 (1) \\ 454 (1) \\ 20 (1) \end{array}$ | $\begin{array}{c} 8670(1)\\ 9490(1)\\ 6076(2)\\ 12073(8)\\ 872(1)\\ 904(1)\\ 898(1)\\ 758(1)\\ 758(1)\\ 759(1)\\ 959(1)\\ 1069(1)\\ 1156(1)\\ 1126(1)\\ 1016(1)\\ 933(1)\\ 1256(1)\\ 1229(1)\\ 1281(1)\\ 1356(2)\\ 1333(1)\\ 761(1)\\ 811(1)\\ 1007(1)\\ 849(1)\\ \end{array}$ | $\begin{array}{c} 3730(1)\\ 3292(1)\\ 5510(1)\\ 7341(6)\\ 437(1)\\ 374(1)\\ 374(1)\\ 445(1)\\ 511(1)\\ 445(1)\\ 511(1)\\ 445(1)\\ 511(1)\\ 445(1)\\ 511(1)\\ 664(1)\\ 586(1)\\ 664(1)\\ 602(1)\\ 792(1)\\ 792(1)\\ 792(1)\\ 785(1)\\ 848(1)\\ 919(1)\\ 922(1)\\ 861(1)\\ 265(1)\\ 444(1)\\ 339(1)\\ 217(1) \end{array}$ | $\begin{array}{c} 8246 (1) \\ 5607 (1) \\ 3916 (1) \\ 9203 (11) \\ 714 (1) \\ 680 (1) \\ 593 (1) \\ 494 (1) \\ 518 (1) \\ 609 (1) \\ 762 (1) \\ 826 (1) \\ 826 (1) \\ 877 (1) \\ 863 (1) \\ 802 (1) \\ 750 (1) \\ 951 (1) \\ 885 (2) \\ 926 (2) \\ 1026 (2) \\ 1090 (1) \\ 1053 (1) \\ 763 (1) \\ 855 (1) \\ 950 (1) \\ 507 (1) \end{array}$ | $\begin{array}{c} 3634(2)\\ 4577(2)\\ 919(2)\\ 6583(9)\\ 363(1)\\ 408(1)\\ 403(1)\\ 286(1)\\ 241(1)\\ 247(1)\\ 247(1)\\ 441(1)\\ 556(1)\\ 630(1)\\ 587(1)\\ 403(1)\\ 760(1)\\ 778(2)\\ 886(2)\\ 964(2)\\ 945(1)\\ 838(1)\\ 263(1)\\ 304(1)\\ 509(1)\\ 356(1) \end{array}$ | $\begin{array}{c} 1509(1)\\ 3240(1)\\ 392(1)\\ -1479(6)\\ 128(1)\\ 215(1)\\ 210(1)\\ 174(1)\\ 86(1)\\ 100(1)\\ 177(1)\\ 76(1)\\ 100(1)\\ -79(1)\\ -100(1)\\ -176(1)\\ -104(1)\\ -176(1)\\ 240(1)\\ 441(1)\\ 190(1)\\ 411(1)\\ \end{array}$ |
| $\begin{array}{c} {\rm C}^{23} \\ {\rm C}^{24} \\ {\rm C}^{25} \\ {\rm C}^{26} \\ {\rm C}^{27} \end{array}$ | $ \begin{array}{c c} 183(1) \\ -62(1) \\ -50(1) \\ -191(1) \\ -172(1) \end{array} $ | 1103 (1) 937 (1) 559 (1) 619 (2) 489 (1) | 312(1) 376(1) 619(1) 622(1) 447(1) | 689(1) 451(1) 435(1) 279(1) 339(1) | $ \begin{array}{c c} 607(1) \\ 455(1) \\ 49(1) \\ 89(2) \\ -16(1) \end{array} $ | $ \begin{array}{c c} 366(1) \\ 308(1) \\ -78(1) \\ 27(1) \\ 118(1) \end{array} $ |

equatorially oriented, whereas the p-phenoxyphenyl substituent is axially oriented. All three GeMe₃ groups in both molecules have skew orientations relative to the Ge-C bonds that connect them with the cyclohexane ring.

The remaining geometrical parameters of the III structure (bond lengths and bond angles) have the normal values within the limits of the experimental accuracy, which is not very high because of the intensive thermal vibrations. In particular, the average length of the Ge-C bond of 1.95(3) Å is close to the standard value of 1.98 Å [12].

EXPERIMENTAL

1,3,5-Tris(trimethylgermyl)-1-(p-phenoxyphenyl)cyclohexane (III). A mixture of 17.0 g (0.1 mole) of diphenyl ether and 18.0 g (0.1 mole) of HGeCl₃ [13] was heated with a reflux

| Rond | d, | Å | Bond | d, A | |
|---|--|---|--|---|---|
| Bolid | molecule A | molecule B | | molecule A | molecule B |
| $\begin{array}{c} Ge^{1}-C^{1}\\ Ge^{1}-C^{19}\\ Ge^{1}-C^{20}\\ Ge^{2}-C^{21}\\ Ge^{2}-C^{22}\\ Ge^{2}-C^{22}\\ Ge^{2}-C^{23}\\ Ge^{3}-C^{25}\\ Ge^{3}-C^{25}\\ Ge^{3}-C^{25}\\ Ge^{3}-C^{26}\\ Ge^{3}-C^{27}\\ O^{1}-C^{10}\\ O^{1}-C^{13}\\ C^{1}-C^{2}\\ C^{1}-C^{6}\\ G^{1}-C^{7}\\ \end{array}$ | $\begin{array}{c} 1,99\ (2)\\ 1,95\ (1)\\ 1,90\ (2)\\ 1,89\ (2)\\ 2,03\ (2)\\ 1,97\ (1)\\ 1,93\ (2)\\ 1,97\ (2)\\ 1,97\ (2)\\ 1,97\ (2)\\ 1,97\ (2)\\ 1,94\ (2)\\ 1,94\ (2)\\ 1,40\ (2)\\ 1,44\ (2)\\ 1,51\ (2)\\ 1,50\ (2)\\ 150\ (2)\ (2)\ (2)\ (2)\ (2)\ (2)\ (2)\ (2)$ | $\begin{array}{c} 1,94 (2) \\ 1,93 (2) \\ 1,94 (2) \\ 1,91 (2) \\ 1,97 (1) \\ 1,94 (2) \\ 1,94 (2) \\ 1,96 (2) \\ 1,95 (1) \\ 2,00 (2) \\ 1,95 (1) \\ 2,00 (2) \\ 1,93 (2) \\ 1,44 (2) \\ 1,36 (2) \\ 1,52$ | $\begin{array}{c} C^2-C^3\\ C^3-C^4\\ C^4-C^5\\ C^5-C^6\\ C^7-C^8\\ C^9-C^{12}\\ C^8-C^9\\ C^9-C^{11}\\ C^{11}-C^{12}\\ C^{13}-C^{14}\\ C^{13}-C^{14}\\ C^{13}-C^{14}\\ C^{15}-C^{16}\\ C^{16}-C^{17}\\ C^{17}-C^{18}\\ \end{array}$ | $\begin{array}{c} 1,48 (3) \\ 1,50 (2) \\ 1,52 (2) \\ 1,55 (3) \\ 1,37 (2) \\ 1,38 (2) \\ 1,38 (2) \\ 1,38 (2) \\ 1,38 (2) \\ 1,38 (2) \\ 1,38 (2) \\ 1,38 (2) \\ 1,38 (2) \\ 1,38 (2) \\ 1,39 (2) \\ 1,42 (3) \\ 1,42 (3) \\ 1,39 (5) \\ 1,41 (4) \end{array}$ | $\begin{array}{c} 1,45 (3) \\ 1,52 (2) \\ 1,54 (2) \\ 1,53 (3) \\ 1,39 (2) \\ 1,39 (2) \\ 1,39 (2) \\ 1,38 (2) \\ 1,38 (2) \\ 1,39 (2) \\ 1,36 (4) \\ 1,36 (3) \\ 1,36 (3) \\ 1,35 (4) \\ 1,38 (3) \end{array}$ |

TABLE 2. Bone Lengths (d) in the III Molecule

TABLE 3. Bond Angles (ω) in the III Molecule

| A 1. | ω, deg | | 4 1 | ω , deg | |
|--|---|--|--|--|--|
| Angle | molecule A molecule B | | Angie | molecule A | molecule B |
| $\begin{array}{c} C^{1}Ge^{1}C^{19}\\ C^{1}Ge^{1}C^{20}\\ C^{1}Ge^{1}C^{21}\\ C^{19}Ge^{1}C^{21}\\ C^{20}Ge^{1}C^{21}\\ C^{20}Ge^{2}C^{22}\\ C^{3}Ge^{2}C^{23}\\ C^{22}Ge^{2}C^{24}\\ C^{22}Ge^{2}C^{24}\\ C^{22}Ge^{2}C^{24}\\ C^{23}Ge^{2}C^{24}\\ C^{5}Ge^{3}C^{25}\\ C^{5}Ge^{3}C^{25}\\ C^{5}Ge^{3}C^{25}\\ C^{5}Ge^{3}C^{25}\\ C^{25}Ge^{3}C^{26}\\ C^{25}Ge^{3}C^{27}\\ C^{25}G$ | Imorecure A 108,8 (7) 112,9 (7) 105,8 (8) 108,5 (8) 108,7 (8) 106,0 (7) 108,7 (8) 108,7 (8) 108,7 (8) 108,7 (8) 108,7 (8) 108,7 (8) 108,7 (8) 108,7 (8) 108,7 (8) 108,7 (8) 101,1 (9) 105,3 (8) 110,1 (9) 105,3 (8) 108(1) 109(1) | 108,6 (7) 110,4 (8) 112,5 (4) 106,0 (8) 110,2 (8) 108,8 (8) 107,7 (8) 110,3 (7) 109,4 (8) 109,9 (8) 108,3 (8) 111,2 (9) 108,1 (8) 110,5 (8) 111,8 (9) 106,6 (8) 106,6 (8) 106,6 (8) 106,9 (9) 124 (2) 112 (1) 113 (1) | Ge ² C ³ C ² Ge ² C ³ C ⁴ C ² C ³ C ⁴ G ² C ⁴ C ⁵ G ² C ⁵ C ⁵ C ⁴ C ⁷ C ¹² C ⁷ C ¹² C ⁷ C ¹² C ⁷ C ⁸ C ⁹ C ⁹ C ⁹ C ¹⁰ O ⁴ C ¹⁰ C ¹¹ C ⁹ C ¹⁰ C ¹¹ C ¹⁰ C ¹¹ C ¹² C ⁷ C ¹² C ¹¹ C ¹⁰ C ¹¹ C ¹² C ¹⁰ C ¹³ C ¹⁴ C ¹⁴ C ¹³ C ¹⁴ O ¹ C ¹³ C ¹⁴ C ¹⁴ C ¹³ C ¹⁴ C ¹⁴ C ¹³ C ¹⁴ | molecule A 111(1) 113(1) 114(1) 112(1) 112(1) 112(1) 123(1) 123(1) 123(1) 123(2) 117(2) 121(2) 121(2) 121(2) 121(2) 121(2) 124(2) 111(2) 126(2) 121(2) | 113 (1) 112 (1) 112 (1) 113 (1) 113 (1) 113 (1) 113 (1) 113 (1) 113 (1) 124 (1) 122 (1) 124 (1) 122 (1) 119 (2) 121 (2) 119 (2) 123 (2) 120 (2) 122 (2) 112 (2) 126 (2) 126 (2) |
| Ge ² C ¹ C ⁶ C ² C ¹ C ⁶ C ⁶ C ¹ C ⁷ C ¹ C ² C ³ | 104,8 (9) 110(1) 114(1) 111(1) 112(1) | 107,0(9) 104(1) 108(1) 112(1) 118(1) | C14C15C16 C15C16C17 C16C17C18 C13C18C17 | 120 (2) 116 (2) 122 (2) 122 (2) 113 (2) | 117 (2) 118 (2) 124 (3) 120 (2) 115 (2) |

condenser for 3 h. The temperature of the reaction mixture ranged from 100°C at the start of the reaction to 150°C at the end, at which point it was treated with an ether solution of MeMgBr (0.6 mole). After the usual workup, distillation gave 14.5 g of a fraction with bp 230-258°C (1.5 mm), which crystallized completely during storage. Recrystallization from alcohol gave 13.7 g (70%) of III with mp 128°C. PMR spectrum (CDCl₃, δ , ppm): -0.03 s (9H, GeCH₃), 0.10 s (18H, GeCH₃), 1.16 and 1.62 mm (6H, CH₂), 2.40 broad d (2H, CH), and 6.95-7.40 m (9H, CH_{arom}). ¹³C NMR spectrum (CDCl₃, δ , ppm): -5.20 (3CH₃), -4.57 (6CH₃, CH₃ groups attached to Ge atoms), 23.02 (2CH), 30.75 (CH₂), 32.97 (2CH₂), 36.70 (C, cyclohexane ring), 118.60, 118.76, 122.88, 127.64, 129.62 (9CH), 139.47, 153.52, 157.76 (3C, phenyl ring). The spectra were recorded with a Bruker WM-250 spectrometer.

<u>X-Ray Diffraction Studies</u>. The transparent acicular crystals of III ($C_{26}H_{42}Ge_{30}$) were triclinic and had the following parameters at 20°C: a = 17.096(5), b = 16.479(6), c = 15.185(3) Å, $\alpha = 101.27(2)$, $\beta = 80.21(2)$, $\gamma = 133.005(6)^{\circ}$, $d_{calc} = 1.28$ g/cm³, Z = 4, and space group PI. The cell parameters and the intensities of 4998 independent reflections were measured with a Hilger-Watts automatic four-circle diffractometer ($\lambda Cu K_{\alpha}$, graphite mono-chromator, $\theta/2\theta$ scanning, $\theta \leq 66^{\circ}$). Refinement of the structure was carried out with respect to 3629 independent reflections with I $\geq 2\sigma$. The structure was decoded by the direct

method by means of the MULTAN program and was refined successively within the isotropic and anisotropic approximations for all of the nonhydrogen atoms. The H atoms of the cyclohexane ring and the C^7-C^{12} phenyl ring in the two molecules and some of the H atoms of the CH₃ groups were revealed from a differential series. The positions of some of the other H atoms of the CH₃ groups were calculated on the basis of this. The H atoms of the $C^{13}-C^{16}$ rings of the two molecules were disregarded because of the strong thermal vibrations of these rings. The contribution of the H atoms (with a fixed B_{1SO} value of 6 Å²) was then taken into account in the F_{calc} values, but their position parameters were not refined. The final R value was 0.071 (R_W = 0.069). All of the calculations were made with an Eclipse S/200 computer by means of modified* EXTL programs.

The coordinates of the nonhydrogen atoms^{\dagger} are presented in Table 1, and the bond lengths and bond angles are presented in Tables 2 and 3, respectively. The geometry of the A molecule (without the hydrogen atoms) is shown in Fig. 1.

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CONCLUSIONS

1. The reaction of HGeCl₃ superacid with excess diphenyl ether leads to 1,3,5-tris(trichlorogermyl)-1-(p-phenoxyphenyl)cyclohexane, which is converted by the action of MeMgBr to 1,3,5-tris(trimethylgermyl)-1-(p-phenoxyphenyl)cyclohexane.

2. The structures of the indicated products constitute evidente for alkylation of diphenyl ether in the reaction. The alkylating function of $HGeCl_3$ as a Friedel-Crafts acid was thereby demonstrated for the first time.

3. The crystal and molecular structure of 1,3,5-tris(trimethylgermyl)-l-(p-phenoxyphenyl) cyclohexane was determined by x-ray diffraction. The crystal contains independent A and B mole cules that differ only with respect to inversion of the phenoxy group. The cyclohexane ring has a chair configuration with three equatorially oriented trimethylgermyl substituents.

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[†]The coordinates of the H atoms, as well as the isotropic temperature factors, can be obtained from the authors.