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Syntheses, Structures, and Sensory Characteristics of the Perfume Ingredient Majantol and Its Analogs Sila-majantol and Germa-majantol: A Study on C/Si/Ge Bioisosterism[§]

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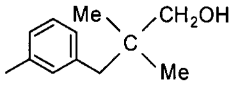
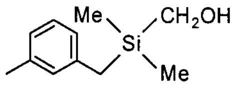
The perfume ingredient majantol [2,2-dimethyl-3-(3-methylphenyl)propan-1-ol (**1a**)] and its silicon- and germanium-containing analogs sila-majantol [(hydroxymethyl)dimethyl(3-methylbenzyl)silane (**1b**)] and germa-majantol [(hydroxymethyl)dimethyl(3-methylbenzyl)-germane (**1c**)], respectively, were synthesized from *i*-PrC(O)Ph (four steps, → **1a**), $Me_2Si(CH_2Cl)Cl$ (three steps, → **1b**), or Cl_3GeCH_2Cl (four steps, → **1c**). The structures of the C/Si/Ge analogs **1a**/**1b**/**1c** were determined by crystal structure analyses and computational studies [RI-MP2 calculations (TZVP level)]. The odor of majantol (**1a**) was found to be strong fresh-floral, aqueous-aldehydic, and characteristic of lily-of-the-valley flowers, whereas that of sila-majantol (**1b**) was considerably less intense than that of **1a**. It lacked the aqueous-aldehydic freshness, but possessed nevertheless the characteristic lily-of-the-valley odor, but it was more terpineol-like. The odor of germa-majantol (**1c**) was very weak and not characteristic; the majantol impression could be recognized only as a shade.

Introduction

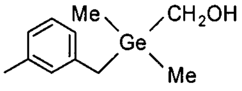
Since the first report on sila-analogs of organic perfume ingredients,[1] a series of papers dealing with silicon-[2] and germanium-based[2b,c,i,k] fragrance materials have been published. In context with our systematic studies on C/Si/Ge bioisosterism (for a recent review, see ref 3; for recent papers, see ref 4), we are investigating the effects of C/Si exchange (sila-substitution) and C/Ge exchange (germa-substitution) in organic perfume ingredients. As part of this project, we have studied the effects of sila- and germa-substitution of the fragrance material majantol (**1a**), a commercial synthetic product[5] with a muguet-type fragrance.[6] We report here the syntheses of majantol (**1a**), sila-majantol (**1b**), and germa-majantol (**1c**) and their sensory characterization. The structures of these C/Si/Ge analogs were determined by X-ray diffraction and computational methods. Preliminary results of these studies have been reported elsewhere.[7]



1a



1b



1c

[§] Dedicated to Professor Edmund Lukevics on the occasion of his 65th birthday.

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[‡] Haarmann & Reimer GmbH.

(1) Wrobel, D.; Tacke, R.; Wannagat, U.; Harder, U. *Chem. Ber.* **1982**, *115*, 1694−1704.

(2) (a) Wrobel, D.; Wannagat, U. *Liebigs Ann. Chem.* **1982**, 734−738. (b) Wrobel, D.; Wannagat, U.; Harder, U. *Monatsh. Chem.* **1982**, *113*, 381−388. (c) Wrobel, D.; Wannagat, U. *J. Organomet. Chem.* **1982**, *225*, 203-210. (d) Wrobel, D.; Wannagat, U. *Liebigs Ann. Chem.* **1983**, 211−219. (e) Münstedt, R.; Wannagat, U. *Liebigs Ann. Chem.* **1985**, 944−949. (f) Wannagat, U.; Münstedt, R.; Harder, U. *Liebigs Ann. Chem.* **1985**, 950−958. (g) Münstedt, R.; Wannagat, U. *Monatsh. Chem.* **1985**, *116*, 693−700. (h) Wannagat, U.; Damrath, V.; Schliephake, A.; Harder, U. *Monatsh. Chem.* **1987**, *118*, 779−788. (i) Tacke, R.; Wiesenberger, F. *Z. Naturforsch., B* **1991**, *46*, 275−279. (j) Tang, S.; Li, Y.; Cao, Y.; Wang, X. *Chin. J. Chem.* **1991**, *9*, 68−75; *Chem. Abstr.* **1991**, *115*, 29450a. (k) Wannagat, U.; Damrath, V.; Huch, V.; Veith, M.; Harder, U. *J. Organomet. Chem.* **1993**, *443*, 153−165. (l) Tang, S.; Xue, J.; Wu, J.; Cao, Y.; Zhi, J.; Wang, X. *Chem. Res. Cin. Univ.* **1993**, *9*, 121−126; *Chem. Abstr.* **1994**, *121*, 108909j. (m) Wannagat, U.; Damrath, V.; Harder, U. *Monatsh. Chem.* **1994**, *125*, 1159−1169. (n) Obara, R.; Olejniczak, T.; Wawrzeńczyk, C. *J. Soc. Cosmet. Chem.* **1995**, *46*, 321−328. (o) Obara, R.; Wawrzeńczyk, C. *J. Cosmet. Sci.* **1998**, *49*, 299−308. (p) Cao, Y.; Liu, Z. *Yingyong Huaxue* **1999**, *16*, 77−79; *Chem. Abstr.* **2000**, *132*, 180622e. (q) Liu, Z.; Cao, Y. *Gaodeng Xuexiao Huaxue Xuebao* **2000**, *21*, 1515−1519; *Chem. Abstr.* **2001**, *134*, 42184d.

(3) Tacke, R.; Heinrich, T.; Kornek, T.; Merget, M.; Wagner, S. A.; Gross, J.; Keim, C.; Lambrecht, G.; Mutschler, E.; Beckers, T.; Bernd, M.; Reissmann, T. *Phosphorus, Sulfur Silicon* **1999**, *150*/*151*, 69−87.

(4) (a) Tacke, R.; Reichel, D.; Jones, P. G.; Hou, X.; Waelbroeck, M.; Gross, J.; Mutschler, E.; Lambrecht, G. *J. Organomet. Chem.* **1996**, *521*, 305−323. (b) Tacke, R.; Kosub, U.; Wagner, S. A.; Bertermann, R.; Schwarz, S.; Merget, S.; Günther, K. *Organometallics* **1998**, *17*, 1687−1699. (c) Tacke, R.; Merget, M.; Bertermann, R.; Bernd, M.; Beckers, T.; Reissmann, T. *Organometallics* **2000**, *19*, 3486-3497. (d) Merget, M.; Günther, K.; Bernd, M.; Günther, E.; Tacke, R. *J. Organomet. Chem.* **2001**, *628*, 183−194. (e) Tacke, R.; Kornek, T.; Heinrich, T.; Burschka, C.; Penka, M.; Pülm, M.; Keim, C.; Mutschler, E.; Lambrecht, G. *J. Organomet. Chem.* **2001**, *640*, 140−165.

(5) Hafner, W.; Gebauer, H.; Regiert, M.; Ritter, P. Consortium für elektrochemische Industrie GmbH, DE 3531585 A1, March 3 1987; *Chem. Abstr.* **1987**, *106*, 156034g. Majantol is a registered trademark of Haarmann & Reimer GmbH, Holzminden, Germany.

(6) For muguet materials, see: Rossiter, K. J. In *Flavours and Fragrances*; Swift, K. A. D., Ed.; Royal Society of Chemistry: Cambridge, UK, 1997; pp 21−35, and literature cited therein.

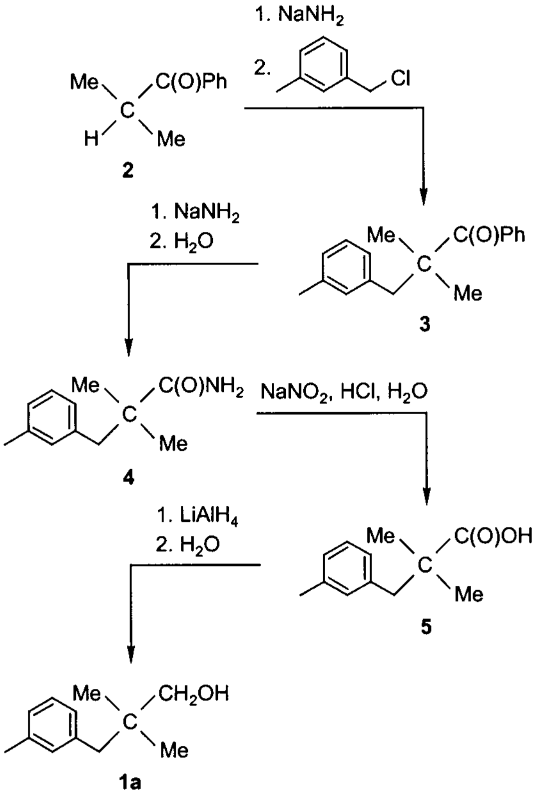
(7) Schmid, T.; Burschka, C.; Hofmann, M.; Penka, M.; Surburg, H.; Tacke, R. *33rd Organosilicon Symposium*; Saginaw, 2000, Abstract PB-17.

10.1021/om010816o CCC: $22.00

Results and Discussion

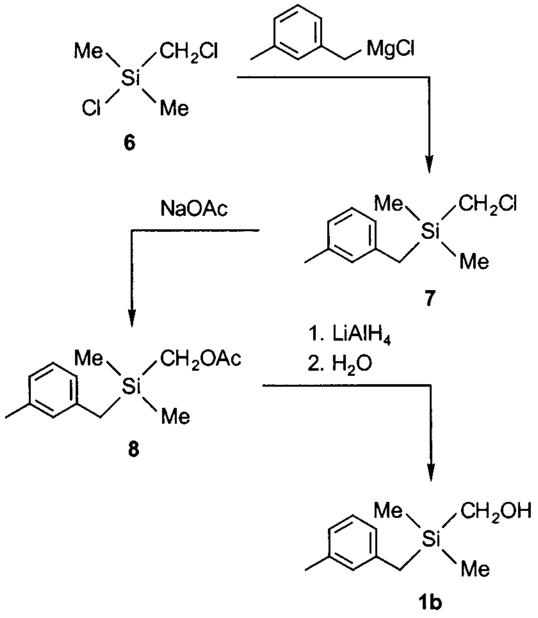
Syntheses. Majantol (**1a**) was prepared by a four-step synthesis, starting from 2-methyl-1-phenylpropanone (**2**) (Scheme 1). Except for the last step [preparation of **1a** (yield 89%) by treatment of 2,2-dimethyl-3-(3-methylphenyl)propanoic acid with lithium aluminum hydride in diethyl ether, followed by hydrolysis], all reaction steps (**2** → **3** → **4** → **5**) were performed according to ref 8.

Scheme 1



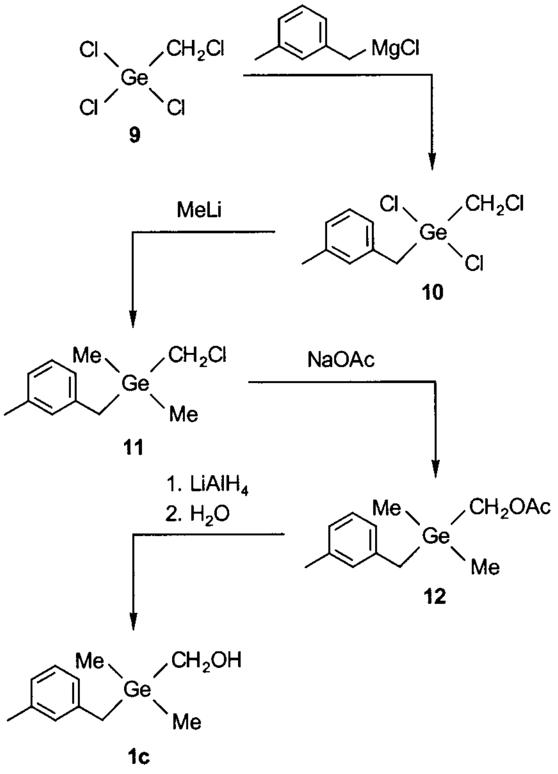
Sila-majantol (**1b**) was prepared by a three-step synthesis (Scheme 2), starting from chloro(chloromethyl)dimethylsilane (**6**). Treatment of **6** with 3-methylbenzylmagnesium chloride in diethyl ether gave (chloromethyl)dimethyl(3-methylbenzyl)silane (**7**) (yield 65%), which on reaction with sodium acetate in dimethylformamide afforded (acetoxymethyl)dimethyl(3-methylbenzyl)silane (**8**) (yield 69%). Treatment of **8** with lithium aluminum hydride in diethyl ether, followed by hydrolysis, finally gave (hydroxymethyl)dimethyl(3-methylbenzyl)silane (sila-majantol, **1b**) (yield 91%).

Scheme 2



Germa-majantol (**1c**) was prepared by a four-step synthesis, starting from trichloro(chloromethyl)germane (**9**) (Scheme 3). Treatment of **9** with 3-methylbenzylmagnesium chloride in diethyl ether gave dichloro(chloromethyl)(3-methylbenzyl)germane (**10**) (yield 39%), which on reaction with methyllithium in diethyl ether afforded (chloromethyl)dimethyl(3-methylbenzyl)germane (**11**) (yield 90%). Treatment of **11** with sodium acetate in dimethylformamide gave (acetoxymethyl)dimethyl(3-methylbenzyl)germane (**12**) (yield 87%). Subsequent reduction with lithium aluminum hydride in diethyl ether, followed by hydrolysis, finally yielded (hydroxymethyl)dimethyl(3-methylbenzyl)germane (germa-majantol, **1c**) (yield 86%).

Scheme 3



Compounds **1a**, **1b**, **1c**, **7**, **8**, and **10**−**12** were isolated as colorless liquids. Their identities were established by elemental analyses (C, H) and solution NMR studies (^{1}H, ^{13}C, ^{29}Si). In addition, the C/Si/Ge analogs **1a**/**1b**/**1c** were structurally characterized by single-crystal X-ray diffraction studies.

Crystal Structure Analyses. Compounds **1a**, **1b**, and **1c** were studied by single-crystal X-ray diffraction. The silane **1b** and the germane **1c** crystallize in the

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(8) Haller, A.; Bauer, E. *Ann. Chim.* **1918**, *9*, 21−27.

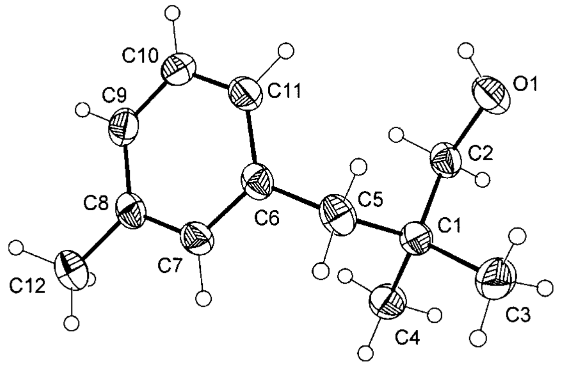

Figure 1. Molecular structure of **1a** in the crystal (probability level of displacement ellipsoids 50%), showing the atomic numbering scheme. Subsequent difference Fourier maps showed the position of the oxygen-linked hydrogen atom to be disordered between two positions. Both of these positions revealed reasonable distances for potential O−H···O hydrogen bonds [O1−H1 0.81(4), H1···O1 1.91(4), O1···O1 2.71(4) Å, O1−H1···O1 169(4)°; O1−H1 0.78(4), H1···O1 1.97(4), O1···O1 2.73(4) Å, O1−H1···O1 161(4)°],[10] each resulting in an infinite $(OH)_x$ chain along [0 0 1].

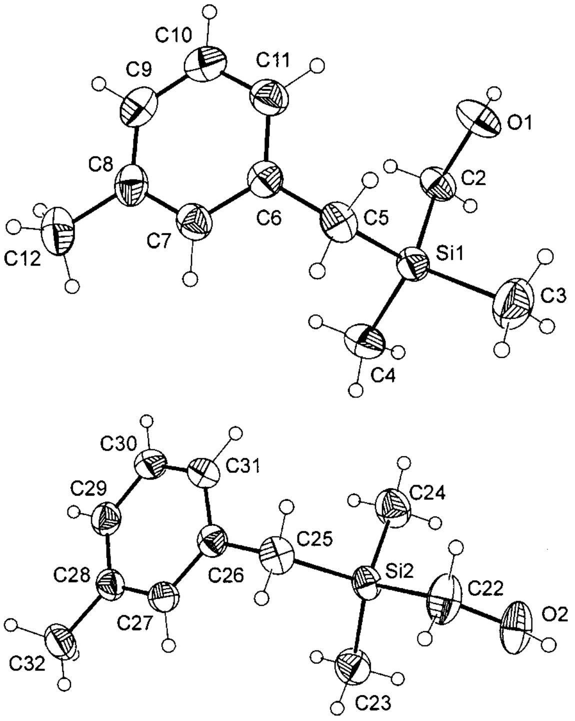

Figure 2. Molecular structures of the conformers **1b**-α (above) and **1b**-*β* (below) in the crystal of **1b** (probability level of displacement ellipsoids 50%), showing the atomic numbering scheme. These conformers form intermolecular O−H···O hydrogen bonds in the crystal [O1−H1 0.84(3), H1···O2 1.91(3), O1···O2 2.7223(18) Å, O1−H1···O2 160(3)°; O2−H2 0.81(3), H2···O1 1.92(3), O2···O1 2.7345(18) Å, O2−H2···O1 176(2)°],[10] resulting in an infinite $(OH)_x$ chain along [0 0 1].

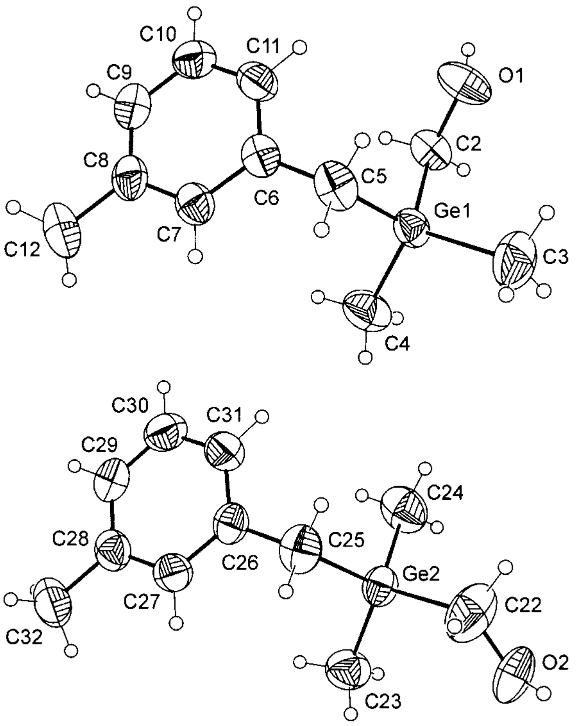

Figure 3. Molecular structures of the conformers **1c**-α (above) and **1c**-*β* (below) in the crystal of **1c** (probability level of displacement ellipsoids 50%), showing the atomic numbering scheme. The conformers form intermolecular O−H···O hydrogen bonds in the crystal [O1−H1 0.77(5), H1···O2 2.02(5), O1···O2 2.755(4) Å, O1−H1···O2 159(5)°; O2−H2 0.90(5), H2···O1 1.88(5), O2···O1 2.766(3) Å, O2−H2···O1 170(5)°],[10] resulting in an infinite $(OH)_x$ chain along [0 0 1].

space group $P2_1/c$, with two molecules (conformers **1b**-α/**1b**-*β* and **1c**-α/**1c**-*β*, respectively) in the asymmetric unit. The crystal structures of these two compounds are isotypic. The carbon analog **1a** crystallizes in the space group $C2/c$,[9] with a single molecule in the asymmetric unit. The structures of **1a**, **1b**-α/**1b**-*β*, and **1c**-α/**1c**-*β* in the crystal are depicted in Figures 1−3. The crystal data and the experimental parameters used for the crystal structure analyses are summarized in Table 1. Selected interatomic distances and angles are listed in Tables 2 and 3.

As can be seen from Figure 4 and Tables 2 and 3, the respective Si/Ge-analogous conformers **1b**-α (**1b**-*β*) and **1c**-α (**1c**-*β*) are almost isostructural, and the structures of the α-conformers are very similar to that of the conformer found in the crystal of **1a**. Thus, the structural chemistry of the C/Si/Ge analogs is characterized by distinct similarities. This finding is supported by the results obtained in the computational studies (see below).

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[9] The space group *Cc* is also consistent with the observed conditions limiting possible reflections. With the space group *C*2/*c*, a structural model could be easily obtained by direct methods and least squares refinement. Subsequent difference Fourier maps showed the position of the oxygen-linked hydrogen atom to be disordered between two positions. Both of these positions revealed reasonable distances for potential O−H···O hydrogen bonds, each resulting in an infinite $(OH)_x$ chain along [0 0 1]. This particular type of disorder for the O*H* hydrogen atoms could not be completely resolved in the space group *Cc*.

[10] In the case of **1a**, the hydrogen-bonding system was analyzed by using the program SHELXL-97: Sheldrick, G. M. *SHELXL-97*; University of Göttingen: Germany, 1997. In the case of **1b** and **1c**, the hydrogen-bonding systems were analyzed by using the program PLATON: Spek, A. L. *PLATON*; University of Utrecht: The Netherlands, 1998.

Table 1. Crystal Data and Experimental Parameters for the Crystal Structure Analyses of 1a, 1b, and 1c

	1a	**1b**	**1c**
empirical formula	$C_{12}H_{18}O$	$C_{11}H_{18}OSi$	$C_{11}H_{18}GeO$
formula mass, g mol^{-1}	178.26	194.34	238.84
collection *T*, K	173(2)	173(2)	263(2)
λ(Mo Kα), Å	0.71073	0.71073	0.71073
cryst syst	monoclinic	monoclinic	monoclinic
space group (no.)	*C*2/*c* (15)	$P2_1/c$ (14)	$P2_1/c$ (14)
a, Å	25.127(5)	9.7441(19)	9.774(2)
b, Å	9.784(2)	27.492(6)	27.597(6)
c, Å	8.9928(18)	8.9331(18)	9.0082(18)
β, deg	104.11(3)	92.46(3)	91.26(3)
V, Å^3	2144.1(7)	2390.9(8)	2429.3(8)
Z	8	8	8
D(calcd), g cm^{-3}	1.104	1.080	1.306
μ, mm^{-1}	0.068	0.161	2.486
F(000)	784	848	992
cryst dimens, mm	0.5 × 0.4 × 0.4	0.5 × 0.5 × 0.4	0.5 × 0.5 × 0.4
2θ range, deg	4.48−52.74	4.18−52.76	4.76−49.42
index ranges	$-31 \le h \le 31$, $-12 \le k \le 12$, $-11 \le l \le 11$	$-12 \le h \le 11$, $-27 \le k \le 34$, $-11 \le l \le 11$	$-11 \le h \le 7$, $-32 \le k \le 32$, $-10 \le l \le 10$
no. of collected reflns	10881	13824	11159
no. of ind reflns	2181	4848	4115
R_{int}	0.0513	0.0504	0.0782
no. of reflns used	2181	4848	4115
no. of params	128	247	248
S^a	1.079	0.973	0.938
weight params *a*/*b*^{b}	0.0698/0.6751	0.0742/0.0000	0.0573/0.0000
$R1^c\ [I > 2\sigma(I)]$	0.0440	0.0394	0.0387
$wR2^d$(all data)	0.1262	0.1142	0.1004
max./min. residual electron density, e Å^{-3}	+0.279/−0.174	+0.234/−0.260	+0.506/−0.544

^{a} $S = \{\sum[w(F_o^2 - F_c^2)^2]/(n - p)\}^{0.5}$; n = no. of reflections; p = no. of parameters. ^{b} $w^{-1} = \sigma^2(F_o^2) + (aP)^2 + bP$, with $P = [\max(F_o^2, 0) + 2F_c^2]/3$. ^{c} $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. ^{d} $wR2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{0.5}$.

Table 2. Selected Interatomic Distances (Å) and Angles (deg) for 1a, 1b-α, and 1c-α

	1a	**1b**-α	**1c**-α
El	C1	Si1	Ge1
El−C2	1.5225(17)	1.8823(17)	1.951(3)
El−C3	1.5272(17)	1.865(2)	1.944(4)
El−C4	1.5266(17)	1.8614(19)	1.940(4)
El−C5	1.5475(17)	1.8792(19)	1.956(4)
C2−El−C3	109.88(10)	109.09(9)	109.57(18)
C2−El−C4	107.18(10)	106.99(8)	107.16(16)
C2−El−C5	111.46(10)	109.53(8)	108.86(16)
C3−El−C4	108.91(10)	111.25(11)	111.1(2)
C3−El−C5	108.47(10)	109.06(10)	108.99(18)
C4−El−C5	110.91(10)	110.87(8)	111.08(18)
El−C5−C6	115.80(10)	114.36(11)	113.7(2)
El−C2−O1	113.39(11)	111.06(10)	111.0(2)

Table 3. Selected Interatomic Distances (Å) and Angles (deg) for 1b-β and 1c-β

	1b-β	**1c**-β
El	Si2	Ge2
El−C22	1.8738(18)	1.956(4)
El−C23	1.854(2)	1.933(4)
El−C24	1.8567(19)	1.939(4)
El−C25	1.8842(18)	1.961(4)
C22−El−C23	110.00(10)	110.4(2)
C22−El−C24	110.87(10)	110.5(2)
C22−El−C25	103.68(7)	103.95(18)
C23−El−C24	110.60(9)	111.14(18)
C23−El−C25	111.55(8)	111.80(18)
C24−El−C25	109.95(9)	108.83(18)
El−C25−C26	114.28(10)	114.3(2)
El−C22−O2	113.41(11)	114.5(2)

Computational Studies. RI-MP2[11] studies (TZVP[12] level) with the program TURBOMOLE[13] revealed a high conformational flexibility of the C/Si/Ge analogs **1a**/**1b**/**1c**. The conformations of the calculated minima[14] of **1a**, **1b**-α, and **1c**-α (starting geometries derived from the respective experimentally established conformations in the crystal) are shown in Figure 5; the calculated interatomic distances and angles are listed in Table 4. As can be seen from Tables 2−4, the calculated structures are in good agreement with those established experimentally.

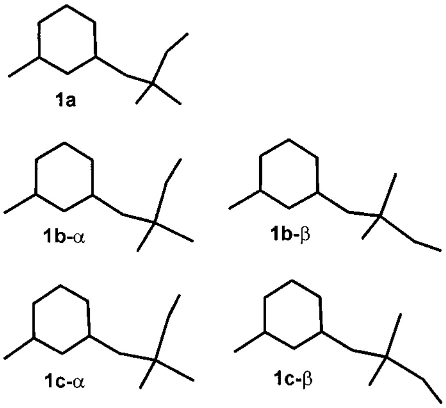

Figure 4. Backbones of the conformers **1a**, **1b**-α, and **1c**-α (left) and the conformers **1b**-β and **1c**-β (right) in the crystals of **1a**, **1b**, and **1c**.

The electrostatic potentials and the electron densities of the C/Si/Ge analogs **1a**/**1b**/**1c** were calculated with the program GAUSSIAN 98[15] (B3LYP[16]/TZVP level) by using the respective minimum conformations **1a**, **1b**-α,

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[11] (a) Weigend, F.; Häser, M. *Theor. Chem. Acc.* **1997**, *97*, 331−340. (b) Weigend, F.; Häser, M.; Patzelt, H.; Ahlrichs, R. *Chem. Phys. Lett.* **1998**, *294*, 143−152.

[12] Schäfer, A.; Huber, C.; Ahlrichs, R. *J. Chem. Phys.* **1994**, *100*, 5829−5835.

[13] Program system TURBOMOLE: Ahlrichs, R.; Bär, M.; Häser, M.; Horn, H.; Kömel, C. *Chem. Phys. Lett.* **1989**, *162*, 165−169.

[14] Calculated energies (C_1 symmetry) [RI-MP2 + *E*(vib0) energies (Hartree)]: **1a**, −541.5862513; **1b**-α, −792.6252565; **1c**-α, −2579.1622626.

[15] Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Baboul, A. G.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B. G.; Chen, W.; Wong, M. W.; Andres, J. L.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*, revision A.7; Gaussian, Inc.: Pittsburgh, PA, 1998.

[16] (a) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785−789. (b) Miehlich, B.; Savin, A.; Stoll, H.; Preuss, H. *Chem. Phys. Lett.* **1989**, *157*, 200−206. (c) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648−5652.

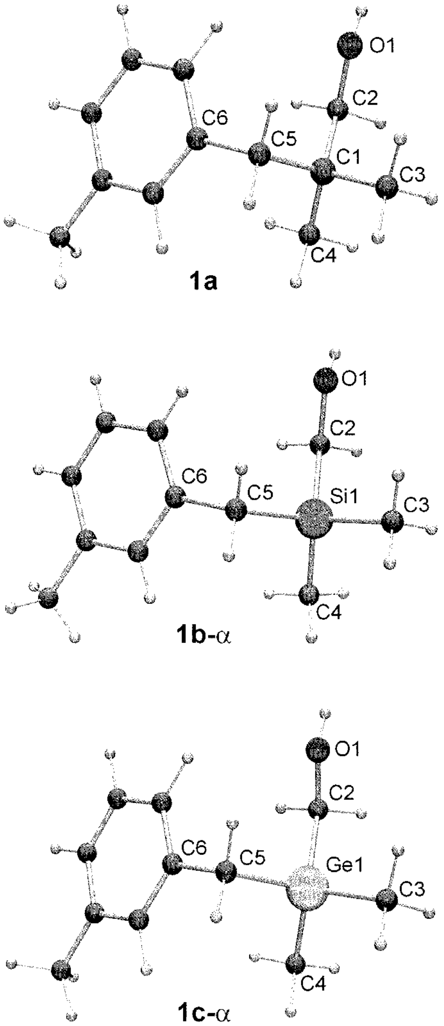

Figure 5. Calculated structures of the conformers **1a**, **1b**-α, and **1c**-α.

Table 4. Calculated Interatomic Distances (Å) and Angles (deg) for 1a, 1b-α, and 1c-α

	1a	**1b**-α	**1c**-α
El	C1	Si1	Ge1
El−C2	1.521	1.903	1.968
El−C3	1.528	1.885	1.954
El−C4	1.526	1.887	1.955
El−C5	1.545	1.901	1.971
C2−El−C3	109.8	109.6	109.2
C2−El−C4	107.7	108.2	109.0
C2−El−C5	110.5	106.6	105.8
C3−El−C4	109.7	111.4	111.7
C3−El−C5	108.5	110.7	111.2
C4−El−C5	110.8	110.1	109.8
El−C5−C6	114.3	110.4	109.4
El−C2−O1	109.1	107.2	106.5

and **1c**-α obtained in the RI-MP2 studies. The electrostatic potentials (±0.08 au) mapped on the calculated isosurfaces of the electron density (0.02 au) are depicted in Figure 6. According to these studies, sila- and germa-substitution of majantol does not affect the electrostatic potential significantly.

Sensory Characterization. The sensory properties of the C/Si/Ge analogs **1a**/**1b**/**1c** were determined using 10% solutions of the respective compounds in diethyl ether applied to a blotter. The odor of **1a** turned out to be identical with that of the industrial standard majantol (**1a**): strong fresh-floral, aqueous-aldehydic, and characteristic of lily-of-the-valley flowers. The odor of sila-majantol (**1b**) was found to be considerably less intense than that of **1a**. It lacked the aqueous-aldehydic freshness, but possessed nevertheless the characteristic lily-of-the-valley odor, but it was more terpineol-like. The odor of germa-majantol (**1c**), on the other hand, was very weak and not characteristic; the majantol impression could be recognized only as a shade. Compared to the parent compound **1a**, the sensory intensities of the sila-analog **1b** and the germa-analog **1c** were considerably less pronounced.

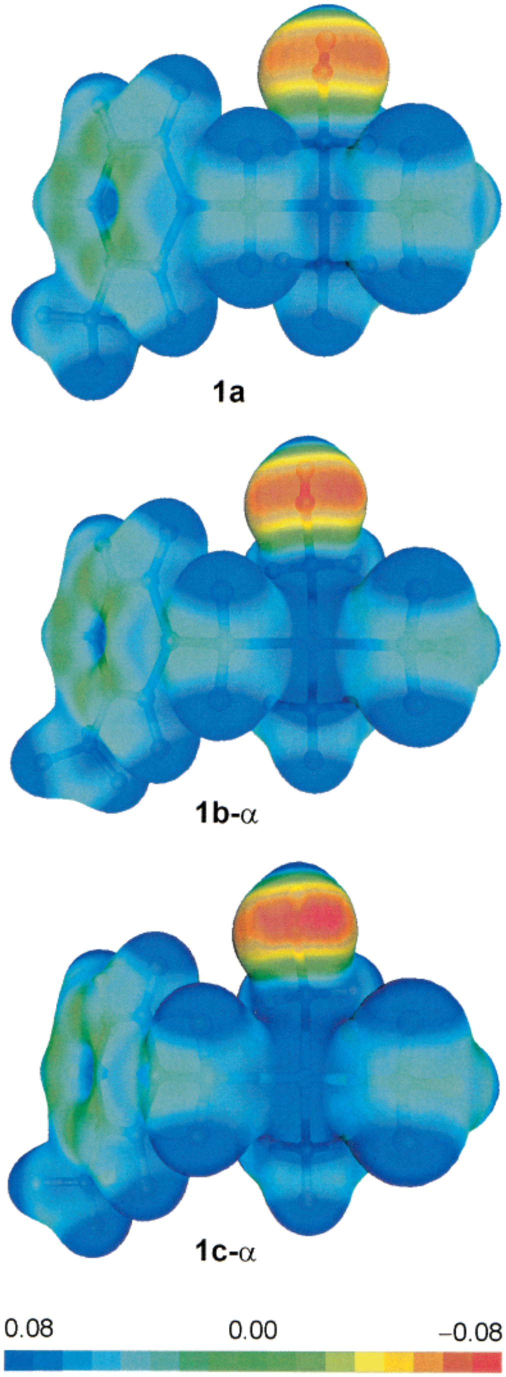

Figure 6. Electrostatic potentials (±0.08 au) mapped on the calculated isosurfaces of the electron density (0.02 au) of the conformers **1a** (min. −0.074 au), **1b**-α (min. −0.078 au), and **1c**-α (min. −0.077 au).

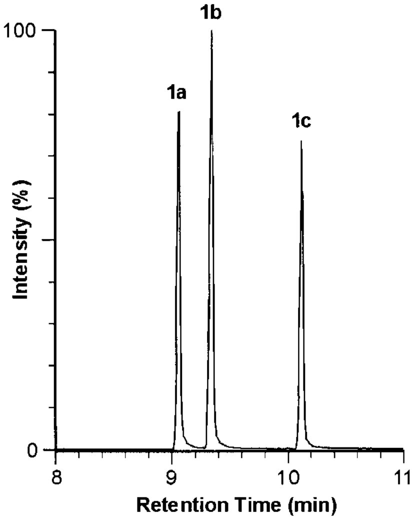

Figure 7. Gas chromatogram obtained with a mixture of the C/Si/Ge analogs **1a**/**1b**/**1c** (see Experimental Section).

Due to the different covalent radii of carbon, silicon, and germanium, the majantol, sila-majantol, and germa-majantol molecules differ somewhat in their size, but the structural chemistry of these C/Si/Ge analogs is characterized by strongly pronounced similarities. Their electrostatic potentials are also very similar. Despite all of these similarities, significant differences in their sensory properties were observed. These differences may be explained by the different volatilities of compounds **1a**, **1b**, and **1c** (**1a** > **1b** > **1c**). These different volatilities are clearly reflected by the gas chromatogram shown in Figure 7.

Experimental Section

General Procedures. All reactions were carried out under dry nitrogen. Dimethylformamide (DMF) and diethyl ether were dried and purified according to standard procedures and stored under nitrogen. ^{1}H, ^{13}C, and ^{29}Si NMR spectra were recorded at 22 °C on a Bruker DRX-300 NMR spectrometer (^{1}H, 300.1 MHz; ^{13}C, 75.5 MHz; ^{29}Si, 59.6 MHz) using $CDCl_3$ as solvent. Chemical shifts (ppm) were determined relative to internal $CHCl_3$ (^{1}H, δ 7.24), internal $CDCl_3$ (^{13}C, δ 77.0), and external TMS (^{29}Si, δ 0). Assignment of the ^{13}C NMR data was supported by DEPT 135 and ^{13}C HMQC experiments. The GC studies were performed with a ThermoQuest gas chromatograph MS-8060 (J&W Scientifics DB-5MS capillary column, 30 m, i.d. 0.32 mm; injector, split (1:10), 225 °C; detector, ThermoQuest mass spectrometer TRIO 1000, EI MS, 70 eV; carrier gas, helium; temperature program, 80 °C (2 min) with 3 °C/min).

Preparation of 2,2-Dimethyl-3-(3-methylphenyl)propan-1-ol (Majantol, 1a). A solution of **5** (3.38 g, 17.6 mmol) in diethyl ether (34 mL) was added dropwise at 0 °C over a period of 30 min to a stirred suspension of lithium aluminum hydride (LAH) (1.33 g, 35.0 mmol) in diethyl ether (15 mL). The mixture was stirred for 1 h at room temperature and then added to a mixture of 2 M hydrochloric acid (90 mL) and diethyl ether (40 mL) at 0 °C. The organic phase was separated and the aqueous layer extracted with diethyl ether (30 mL). The combined organic extracts were dried over anhydrous Na_2SO_4, the solvent was removed under reduced pressure, and the residue was purified by Kugelrohr distillation (oven temperature 87 °C, 0.01 mbar) to give **1a** in 89% yield as a colorless liquid (2.78 g, 15.6 mmol). ^{1}H NMR ($CDCl_3$): δ 0.87 (s, 6 H, CCH_3), 1.46 (s, 1 H, OH), 2.31 (s, 3 H, CCH_3), 2.52 (s, 2 H, CCH_2C), 3.30 (s, 2 H, CCH_2O) 6.93−7.01 (m, 3 H, H-2, H-4, H-6, C_6H_4), 7.11−7.17 (m, 1 H, H-5, C_6H_4). ^{13}C NMR ($CDCl_3$): δ 21.4 (CCH_3), 24.0 (CCH_3), 36.4 (CC_4), 44.6 (CCH_2C), 71.2 (CCH_2O), 126.7 (C-4 or C-6, C_6H_4), 127.5 (C-4 or C-6, C_6H_4), 127.7 (C-5, C_6H_4), 131.2 (C-2, C_6H_4), 137.3 (C-1 or C-3, C_6H_4), 138.7 (C-1 or C-3, C_6H_4). Anal. Calcd for $C_{12}H_{18}O$: C, 80.85; H, 10.18. Found: C, 80.8; H, 10.0.

Preparation of (Hydroxymethyl)dimethyl(3-methylbenzyl)silane (Sila-majantol, 1b). A solution of **8** (3.07 g, 13.0 mmol) in diethyl ether (25 mL) was added dropwise at 0 °C over a period of 30 min to a stirred suspension of LAH (980 mg, 25.8 mmol) in diethyl ether (11 mL). The mixture was stirred for 1 h at room temperature and then added to a mixture of 2 M hydrochloric acid (70 mL) and diethyl ether (30 mL) at 0 °C. The organic phase was separated and the aqueous layer extracted with diethyl ether (20 mL). The combined organic extracts were dried over anhydrous Na_2SO_4, the solvent was removed under reduced pressure, and the residue was purified by Kugelrohr distillation (oven temperature 100 °C, 0.01 mbar) to give **1b** in 91% yield as a colorless liquid (2.29 g, 11.8 mmol). ^{1}H NMR ($CDCl_3$): δ 0.04 (s, 6 H, $SiCH_3$), 1.07 (s, 1 H, OH), 2.14 (s, 2 H, $SiCH_2C$), 2.30 (s, 3 H, CCH_3), 3.38 (s, 2 H, $SiCH_2O$), 6.83−6.91 (m, 3 H, H-2, H-4, H-6, C_6H_4), 7.09−7.14 (m, 1 H, H-5, C_6H_4). ^{13}C NMR ($CDCl_3$): δ −5.3 ($SiCH_3$), 21.4 (CCH_3), 23.5 ($SiCH_2C$), 54.7 ($SiCH_2O$), 124.9 (C-4 or C-6, C_6H_4), 125.0 (C-4 or C-6, C_6H_4), 128.2 (C-5, C_6H_4), 128.8 (C-2, C_6H_4), 137.8 (C-1 or C-3, C_6H_4), 139.5 (C-1 or C-3, C_6H_4). ^{29}Si NMR ($CDCl_3$): δ −0.1. Anal. Calcd for $C_{11}H_{18}OSi$: C, 67.98; H, 9.34. Found: C, 67.6; H, 9.3.

Preparation of (Hydroxymethyl)dimethyl(3-methylbenzyl)germane (Germa-majantol, 1c). A solution of **12** (2.30 g, 8.19 mmol) in diethyl ether (20 mL) was added dropwise at 0 °C over a period of 30 min to a stirred suspension of LAH (750 mg, 19.8 mmol) in diethyl ether (30 mL). The mixture was stirred for 3 h at room temperature and then added to a mixture of 2 M hydrochloric acid (40 mL) and diethyl ether (20 mL) at 0 °C. The organic phase was separated and the aqueous layer extracted with diethyl ether (10 mL). The combined organic extracts were dried over anhydrous Na_2SO_4, the solvent was removed under reduced pressure, and the residue purified by Kugelrohr distillation (oven temperature 110 °C, 0.01 mbar) to give **1c** in 86% yield as a colorless liquid (1.69 g, 7.07 mmol). ^{1}H NMR ($CDCl_3$): δ 0.14 (s, 6 H, $GeCH_3$), 1.10 (s, 1 H, OH), 2.26 (s, 2 H, $GeCH_2C$), 2.28 (s, 3 H, CCH_3), 3.60 (s, 2 H, $GeCH_2O$), 6.81−6.88 (m, 3 H, H-2, H-4, H-6, C_6H_4), 7.07−7.12 (m, 1 H, H-5, C_6H_4). ^{13}C NMR ($CDCl_3$): δ −5.6 ($GeCH_3$), 21.4 (CCH_3), 23.4 ($GeCH_2C$), 55.9 ($GeCH_2O$), 124.6 (C-4 or C-6, C_6H_4), 124.9 (C-4 or C-6, C_6H_4), 128.3 (C-5, C_6H_4), 128.4 (C-2, C_6H_4), 137.9 (C-1 or C-3, C_6H_4), 140.7 (C-1 or C-3, C_6H_4). Anal. Calcd for $C_{11}H_{18}GeO$: C, 55.31; H, 7.60. Found: C, 55.2; H, 7.4.

2-Methyl-1-phenylpropanone (2). This compound was commercially available (Aldrich).

Preparation of 2,2-Dimethyl-3-(3-methylphenyl)-1-phenylpropanone (3). This compound was synthesized according to ref 8.

Preparation of 2,2-Dimethyl-3-(3-methylphenyl)propanamide (4). This compound was synthesized according to ref 8.

Preparation of 2,2-Dimethyl-3-(3-methylphenyl)propanoic acid (5). This compound was synthesized according to ref 8.

Chloro(chloromethyl)dimethylsilane (6). This compound was commercially available (ABCR).

Preparation of (Chloromethyl)dimethyl(3-methylbenzyl)silane (7). A solution of 3-methylbenzyl chloride (15.0 g, 107 mmol) in diethyl ether (35 mL) was added dropwise over a period of 30 min at −10 °C to a stirred suspension of magnesium turnings (3.10 g, 128 mmol) in diethyl ether (5 mL). The mixture was stirred for 1 h at −10 °C and then added dropwise within 30 min at room temperature to a stirred solution of **6** (15.3 g, 107 mmol) in diethyl ether (80 mL). After the mixture was stirred for 16 h, water (100 mL) was added. The phases were separated, and the aqueous layer was extracted with diethyl ether (2 × 30 mL). The combined organic extracts were dried over anhydrous Na_2SO_4, the solvent was removed under reduced pressure, and the residue was distilled in vacuo (115 °C, 10 mbar) to give **7** in 65% yield as a colorless liquid (14.9 g, 70.0 mmol). ^{1}H NMR ($CDCl_3$): δ 0.12 (s, 6 H, SiCH_3), 2.20 (s, 2 H, SiCH_2C), 2.32 (s, 3 H, CCH_3), 2.76 (s, 2 H, SiCH_2Cl), 6.84−6.94 (m, 3 H, H-2, H-4, H-6, C_6H_4), 7.11−7.16 (m, 1 H, H-5, C_6H_4). ^{13}C NMR ($CDCl_3$): δ −4.9 (SiCH_3), 21.4 (C*C*H_3), 23.4 (Si*C*H_2C), 29.6 (SiCH_2Cl), 125.11 (C-4 or C-6, C_6H_4), 125.13 (C-4 or C-6, C_6H_4), 128.2 (C-5, C_6H_4), 128.9 (C-2, C_6H_4), 137.9 (C-1 or C-3, C_6H_4), 138.8 (C-1 or C-3, C_6H_4). ^{29}Si NMR ($CDCl_3$): δ 3.0. Anal. Calcd for $C_{11}H_{17}ClSi$: C, 62.09; H, 8.05. Found: C, 62.3; H, 8.0.

Preparation of (Acetoxymethyl)dimethyl(3-methylbenzyl)silane (8). A mixture of sodium acetate (2.83 g, 34.5 mmol) and **7** (5.00 g, 23.5 mmol) in DMF (50 mL) was stirred for 3 days at 80 °C. After the mixture was cooled to room temperature, water (35 mL) and diethyl ether (40 mL) were added. The phases were separated, and the organic layer was washed with water (2 × 10 mL) and then dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure and the residue distilled in vacuo (0.01 mbar, 70 °C) to give **8** in 69% yield as a colorless liquid (3.86 g, 16.3 mmol). ^{1}H NMR ($CDCl_3$): δ 0.04 (s, 6 H, SiCH_3), 2.02 (s, 3 H, CCH_3), 2.12 (s, 2 H, SiCH_2C), 2.28 (s, 3 H, C(O)CH_3) 3.74 (s, 2 H, SiCH_2O), 6.78−6.90 (m, 3 H, H-2, H-4, H-6, C_6H_4), 7.07−7.12 (m, 1 H, H-5, C_6H_4). ^{13}C NMR ($CDCl_3$): δ −5.0 (SiCH_3), 20.7 (C(O)*C*H_3), 21.4 (C*C*H_3), 23.7 (Si*C*H_2C), 56.1 (SiCH_2O), 125.0 (C-4 or C-6, C_6H_4), 125.1 (C-4 or C-6, C_6H_4), 128.2 (C-5, C_6H_4), 128.9 (C-2, C_6H_4), 137.8 (C-1 or C-3, C_6H_4), 138.8 (C-1 or C-3, C_6H_4), 171.8 (C=O). ^{29}Si NMR ($CDCl_3$): δ 0.3. Anal. Calcd for $C_{13}H_{20}O_2Si$: C, 66.05; H, 8.53. Found: C, 66.4; H, 8.5.

Preparation of Trichloro(chloromethyl)germane (9). This compound was synthesized according to ref 17a (see also ref 17b).

Preparation of Dichloro(chloromethyl)(3-methylbenzyl)germane (10). A solution of 3-methylbenzyl chloride (4.31 g, 30.7 mmol) in diethyl ether (20 mL) was added dropwise over a period of 30 min at −10 °C to a suspension of magnesium turnings (751 mg, 30.9 mmol) in diethyl ether (5 mL). The mixture was stirred for 1 h at this temperature and then added dropwise within 30 min at room temperature to a stirred solution of **9** (7.00 g, 30.6 mmol) in diethyl ether (40 mL). After the mixture was stirred for 16 h at room temperature and heated under reflux for 1 h, *n*-pentane (50 mL) was added. The resulting precipitate was filtered off and washed with *n*-pentane (2 × 20 mL). The filtrate and wash solutions were combined, the solvent was removed under reduced pressure, and the residue was distilled in vacuo (0.01 mbar, 90 °C) to give **10** in 39% yield as a colorless liquid (3.60 g, 12.1 mmol). ^{1}H NMR ($CDCl_3$): δ 2.34 (s, 3 H, CCH_3), 3.17 (s, 2 H, GeCH_2C), 3.38 (s, 2 H, GeCH_2Cl), 7.03−7.07 (m, 3 H, H-2, H-4, H-6, C_6H_4), 7.18−7.21 (m, 1 H, H-5, C_6H_4). ^{13}C NMR ($CDCl_3$): δ 21.4 (C*C*H_3), 31.0 (Ge*C*H_2C), 32.5 (GeCH_2Cl), 126.0 (C-4 or C-6, C_6H_4), 127.7 (C-4 or C-6, C_6H_4), 128.9 (C-5, C_6H_4), 129.7 (C-2, C_6H_4), 132.0 (C-1 or C-3, C_6H_4), 138.7 (C-1 or C-3, C_6H_4). Anal. Calcd for $C_9H_{11}Cl_3Ge$: C, 36.26; H, 3.72. Found: C, 36.4; H, 3.8.

Preparation of (Chloromethyl)dimethyl(3-methylbenzyl)germane (11). A 1.6 M solution of methyllithium in diethyl ether (15 mL, 24.0 mmol of MeLi) was diluted with diethyl ether (20 mL) and the resulting solution then added dropwise over a period of 45 min at −10 °C to a solution of **10** (3.60 g, 12.1 mmol) in diethyl ether (60 mL). The mixture was stirred for 1 h at −10 °C and then warmed to room temperature and stirred for another 3 h. The solvent was removed under reduced pressure and the residue distilled in vacuo (0.01 mbar, 79 °C) to give **11** in 90% yield as a colorless liquid (2.80 g, 10.9 mmol). ^{1}H NMR ($CDCl_3$): δ 0.21 (s, 6 H, SiCH_3), 2.29 (s, 3 H, CCH_3), 2.31 (s, 2 H, GeCH_2C), 2.89 (s, 2 H, GeCH_2Cl), 6.81−6.90 (m, 3 H, H-2, H-4, H-6, C_6H_4), 7.08−7.13 (m, 1 H, H-5, C_6H_4). ^{13}C NMR ($CDCl_3$): δ −5.1 (GeCH_3), 21.4 (C*C*H_3), 23.3 (Ge*C*H_2C), 29.8 (GeCH_2Cl), 124.7 (C-4 or C-6, C_6H_4), 125.1 (C-4 or C-6, C_6H_4), 128.3 (C-5, C_6H_4), 128.5 (C-2, C_6H_4), 137.9 (C-1 or C-3, C_6H_4), 139.7 (C-1 or C-3, C_6H_4). Anal. Calcd for $C_{11}H_{17}ClGe$: C, 51.35; H, 6.66. Found: C, 51.6; H, 6.8.

Preparation of (Acetoxymethyl)dimethyl(3-methylbenzyl)germane (12). A mixture of sodium acetate (1.66 g, 20.2 mmol) and **11** (2.60 g, 10.1 mmol) in DMF (13 mL) was heated under reflux for 5 h. After the mixture was cooled to room temperature, water (10 mL) and diethyl ether (20 mL) were added. The phases were separated, and the organic layer was extracted with water (2 × 5 mL) and then dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure and the residue distilled in vacuo (0.01 mbar, 98 °C) to give **12** in 87% yield as a colorless liquid (2.48 g, 8.83 mmol). ^{1}H NMR ($CDCl_3$): δ 0.15 (s, 6 H, GeCH_3), 2.01 (s, 3 H, C(O)CH_3), 2.26 (s, 2 H, GeCH_2C), 2.28 (s, 3 H, CCH_3), 2.89 (s, 2 H, GeCH_2Cl), 6.78−6.88 (m, 3 H, H-2, H-4, H-6, C_6H_4), 7.06−7.11 (m, 1 H, H-5, C_6H_4). ^{13}C NMR ($CDCl_3$): δ −5.0 (GeCH_3), 20.7 (C(O)*C*H_3), 21.4 (C*C*H_3), 23.8 (Ge*C*H_2C), 57.5 (GeCH_2O), 124.8 (C-4 or C-6, C_6H_4), 125.0 (C-4 or C-6, C_6H_4), 128.2 (C-5, C_6H_4), 128.5 (C-2, C_6H_4), 137.8 (C-1 or C-3, C_6H_4), 140.0 (C-1 or C-3, C_6H_4), 171.7 (C=O). Anal. Calcd for $C_{13}H_{20}GeO_2$: C, 55.58; H, 7.18. Found: C, 55.2; H, 6.8.

Single-Crystal X-ray Diffraction Studies. Suitable single crystals of **1a**, **1b**, and **1c** were obtained by crystallization from solutions in *n*-pentane at −20 °C. The crystals were mounted in inert oil (perfluoroalkyl ether, ABCR) on a glass fiber and then transferred to the cold nitrogen gas stream of the diffractometer [Stoe IPDS; graphite-monochromated Mo Kα radiation (λ = 0.71073 Å)]. The data for **1a** and **1b** were collected at 173 K and the data for **1c** at 263 K. Initial models for the refinement of the structures of **1a**, **1b**, and **1c** were obtained by direct methods.[18,19] All non-hydrogen atoms were refined anisotropically.[20] Hydrogen atoms could be located from the peak lists of subsequent difference Fourier maps and were refined using a riding model and geometrical recalculation at ideal positions. Only those hydrogen atoms linked to the oxygen atoms were refined freely with their temperature factors tied to 1.5 times of the corresponding oxygen atom temperature factors.

Computational Studies. RI-MP2[11] geometry optimizations (TZVP[12] level) of the C/Si/Ge analogs **1a**/**1b**/**1c** were performed using the TURBOMOLE program system.[13] The experimentally established conformations **1a**, **1b**-α, and **1c**-α in the crystal served as starting geometries for these calculations. Each critical point of the respective potential energy surface was characterized as a local minimum by calculation of the vibrational frequencies. The calculated energies[14] of **1a**, **1b**-α, and **1c**-α include the MP2 energies and the zero-point vibrational energies obtained by SCF calculations. The electrostatic potentials and electron densities of **1a**, **1b**-α, and **1c**-α (conformations obtained in the RI-MP2 calculations) were calculated with the program GAUSSIAN 98[15] using the DFT method (B3LYP[16]/TZVP level).

Sensory Characterization. To get highly pure samples for the sensory characterization, the NMR-spectroscopically pure compounds **1a**, **1b**, and **1c** were additionally purified by thin-layer chromatography on silica gel (PLC plates, 20 × 20 cm, silica gel 60 F254, 1 mm; Merck, 1.13895) using *n*-hexane/diethyl ether [10:1 (v/v)] as solvent. To remove traces of silica,

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(17) (a) Tacke, R.; Becker, B. *J. Organomet. Chem.* **1988**, *354*, 147−153. (b) Seyferth, D.; Rochow, E. G. *J. Am. Chem. Soc.* **1955**, *77*, 907−910.

(18) Sheldrick, G. M. *SHELXS-97*; University of Göttingen: Germany, 1997.

(19) Sheldrick, G. M. *Acta Crystallogr., Sect. A* **1990**, *46*, 467−473.

(20) Sheldrick, G. M. *SHELXL-97*; University of Göttingen: Germany, 1997.

the compounds were afterward gently distilled in vacuo (Kugelrohr apparatus). As demonstrated by GC studies, the purities of the samples used for the sensory characterization were >99.5%. The sensory properties were determined using 10% solutions of the respective compounds in diethyl ether applied to a blotter.

Acknowledgment. Financial support of this work by the Fonds der Chemischen Industrie is gratefully acknowledged.

Supporting Information Available: Tables of atomic coordinates and equivalent isotropic displacement parameters, anisotropic displacement parameters, experimental details of the X-ray diffraction studies, and bond lengths and angles for **1a**, **1b**, and **1c**. This material is available free of charge via the Internet at http://pubs.acs.org. In addition, crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-160855 (**1a)**, CCDC-160856 (**1b**), and CCDC-160857 (**1c**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: (+44) 1223/336033; e-mail: deposit@ccdc.cam.ac.uk].

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