Silicon Analogues of the Musk Odorant Versalide

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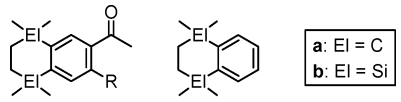
*Summary: Twofold sila-substitution (C/Si exchange) of the musk odorant Versalide (**1a**) provides Disila-versalide (**1b**). The silicon compound **1b** and its derivatives **2b** (Et/Me exchange) and **3b** (Et/H exchange) were synthesized by starting from 1,2-bis(ethynyldimethylsilyl)ethane. The silicon compounds **1b**−**3b** and their carbon analogues **1a**−**3a** were studied for their olfactory properties and their biodegradability.*

Introduction

Versalide (**1a**) is a powerful musk odorant[1] with fixative properties close to those of macrocyclic musks, an outstanding stability, and an inexpensive industrial access. Discovered by



1: R = Et
2: R = Me
3: R = H

4

a: El = C
b: El = Si

Carpenter of Givaudan in 1954,[2] it was placed on the market the following year and soon earned its reputation as the finest polycyclic musk (PCM). In 1976, however, it was discovered that it induced a blue discoloration of internal organs and a vacuolar degeneration of the brain in a 13 week subacute dermal test on rats,[3] which was due to the formation of 1,1′-(5,5,8,8-tetramethyl-5,6,7,8-tetrahydro-2,3-naphthdiyl)diethanone upon oxidation of the ethyl group under biological conditions. Versalide (**1a**) was thus withdrawn from the market in March 1978[3] but remained an excellent benchmark for a PCM in terms of olfactory properties and was therefore chosen as the lead structure in the present study.

Silicon chemistry has proven to be a powerful source of chemical diversity in the design of odorants,[4] and in context with our systematic studies on the C/Si switch strategy we report here on (i) the syntheses of Disila-versalide (**1b**) and its derivatives **2a**, **2b**, **3a**, and **3b**,[5] (ii) computational studies of the model system 1,1,4,4-tetramethyl-1,2,3,4-tetrahydronaphthalene (**4a**) and its disila-analogue **4b**, and (iii) studies concerning the olfactory properties and the biodegradation of the C/Si pairs **1a**/**1b**, **2a**/**2b**, and **3a**/**3b**.

Results and Discussion

Syntheses. Compounds **1b**, **2a**, **2b**, **3a**, and **3b** were synthesized according to Scheme 1.

Disila-versalide (**1b**) was prepared from 1,2-bis(ethynyldimethylsilyl)ethane (**5**) in a cobalt-catalyzed ($CpCo(CO)_2$) cyclization with 3-hexyn-2-one (**6**) to provide the title compound in 24% yield. 1-(3,5,5,8,8-Pentamethyl-5,6,7,8-tetrahydro-2-naphthyl)ethanone (**2a**) was synthesized in 87% yield by reaction of 1,1,4,4,6-pentamethyl-1,2,3,4-tetrahydronaphthalene (**7**) with acetyl chloride in the presence of aluminum chloride. The corresponding disila-analogue, 1-(3,5,5,8,8-pentamethyl-5,8-disila-5,6,7,8-tetrahydro-2-naphthyl)ethanone (**2b**), was prepared in 26% yield analogously to the synthesis of **1b** by using 3-pentyn-2-one (**8**) instead of the alkyne **6**. 1-(5,5,8,8-Tetramethyl-5,6,7,8-tetrahydro-2-naphthyl)ethanone (**3a**) was synthesized in 75% yield analogously to the synthesis of **2a** by using 1,1,4,4-tetramethyl-1,2,3,4-tetrahydronaphthalene (**4a**) instead of **7**. The disila-analogue of **3a**, 1-(5,5,8,8-tetramethyl-5,8-disila-5,6,7,8-tetrahydro-2-naphthyl)ethanone (**3b**), was prepared in a multistep synthesis by starting from the diyne **5**. Thus, treatment of **5** with 3-(trimethylsilyloxy)-1-butyne (**9**) in the presence of $CpCo(CO)_2$, followed by treatment with acetic acid/methanol, provided *rac*-1-(5,5,8,8-tetramethyl-5,8-disila-5,6,7,8-tetrahydro-2-naphthyl)ethanol (*rac*-**10**; 21% yield), which upon oxidation afforded **3b** (83% yield).

Computational Studies. Geometry optimizations for the C/Si model systems **4a** and **4b** were performed with the Turbomole program system at the RI-MP2 level using a TZP basis set and a TZVP auxiliary basis for the fit of the charge density.[6] Due

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(1) For recent reviews on musk odorants, see: (a) Kraft, P. In *Perspectives in Flavor and Fragrance Research*; Kraft, P., Swift, K. A. D., Eds.; Verlag Helvetica Chimica Acta: Zürich, Switzerland, 2005, and Wiley-VCH: Weinheim, Germany, 2005; pp 127−144. (b) Kraft, P. In *Chemistry and Technology of Flavors and Fragrances*; Rowe, D. J., Ed.; CRC Press: Boca Raton, FL, 2005, and Blackwell: Oxford, U.K., 2005; pp 143−168.

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(3) (a) Opdyke, D. L. J. *Food Cosmet. Toxicol.* **1979**, *17*, 357−390. (b) Spencer, P. S.; Sterman, A. B.; Horoupian, D.; Bischoff, M. *Neurotoxicology* **1979**, *1*, 221−237. (c) Spencer, P. S.; Sterman, A. B.; Horoupian, D. S.; Foulds, M. M. *Science* **1979**, *204*, 633−635.

(4) For recent papers on silicon-based odorants, see: (a) Tacke, R.; Schmid, T.; Burschka, C.; Penka, M.; Surburg, H. *Organometallics* **2002**, *21*, 113−120 and references cited therein. (b) Tacke, R.; Schmid, T.; Hofmann, M.; Tolasch, T.; Francke, W. *Organometallics* **2003**, *22*, 370−372. (c) Schmid, T.; Daiss, J. O.; Ilg, R.; Surburg, H.; Tacke, R. *Organometallics* **2003**, *22*, 4343−4346. (d) Doszczak, L.; Gasperi, T.; Saint-Dizier, A.; Loreto, M. A.; Enders, D. In *Perspectives in Flavor and Fragrance Research*; Kraft, P., Swift, K. A. D., Eds.; Verlag Helvetica Chimica Acta AG: Zürich, Switzerland, 2005, and Wiley-VCH: Weinheim, Germany, 2005; pp 89−103.

(5) Syntheses of **2a** and **3a** have already been reported elsewhere but were adapted in order to obtain olfactorily pure samples. (a) Synthesis of **2a**: Dawson, M. I.; Jong, L.; Hobbs, P. D.; Cameron, J. F.; Chao, W.; Pfahl, M.; Lee, M.-O.; Shroot, B.; Pfahl, M. *J. Med. Chem.* **1995**, *38*, 3368−3383. (b) Synthesis of **3a**: Kagechika, H.; Kawachi, E.; Hashimoto, Y.; Himi, T.; Shudo, K. *J. Med. Chem.* **1988**, *31*, 2182−2192.

(6) For further computational details, see the Supporting Information.

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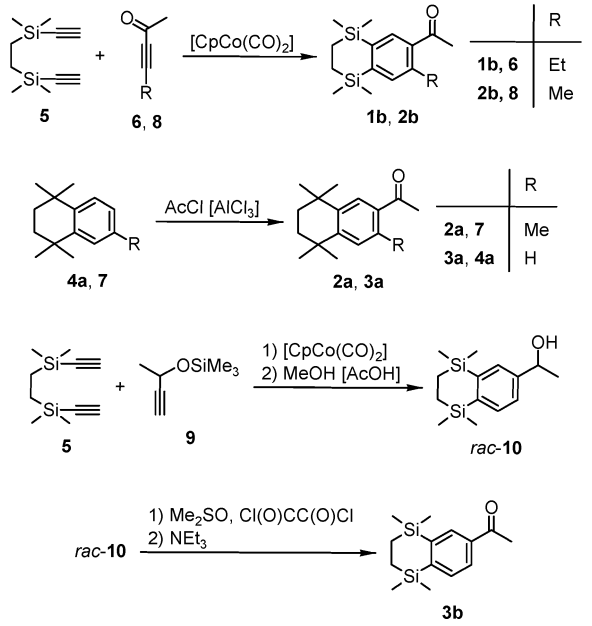
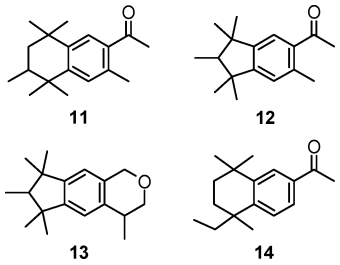
Scheme 1



to the different covalent radii of carbon and silicon, **4a** and **4b** differ distinctly in their size and shape (Figure 1). The influence of the C/Si switch on the electron density and electrostatic potential was calculated with the program Gaussian 98 (MP2/TZP level) from the respective lowest energy conformations obtained in the RI-MP2 studies.[6] As shown in Figure 2, the electrostatic potentials (−0.135 au, +0.055 au) mapped on the calculated isosurfaces of the electron density (0.02 au) differ significantly.

Olfactory Characterization. The lead structure Versalide (**1a**), with its typical strong and distinct musk odor reminiscent of PCMs such as Fixolide (**11**) and Phantolide (**12**) as well as of some macrocyclic musks, unequivocally constitutes the most intense musk odorant investigated in this study. Disila-versalide



(**1b**) still smells musky, but much less so than **1a**, and it is also less intense. Its musk character resembles that of the PCM Galaxolide (**13**), but its main odor note is floral-green with woody facets and a chalklike nuance. Transition to the *nor* structures **2a** and **2b** diminishes the musk character of both, but while **2a** still is a floral-woody musk odorant of soft, velvety tonality and fruity-green nuance, the silicon compound **2b** is already too weak to be considered an odorant. It is also less musky than **1a**, **1b**, and **2a** and only slightly recalls a musky impression with an animalic sensuality accompanied by uncharacteristic green, woody-earthy aspects. The absence of an alkyl substituent on the carbon atom C3 makes the musk odor completely disappear in the case of **3a**, with a somewhat floral odor, while musky facets are clearly discernible in the disila-analogue **3b**. Albeit weaker than **3a**, the disila-analogue **3b** smells fruity-musky, reminiscent of blackberries, with some floral-green undertones recalling lily of the valley.

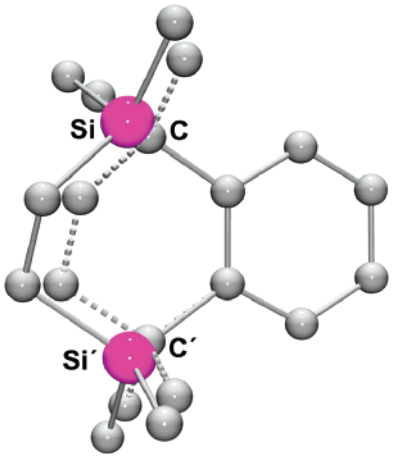


Figure 1. Superposition of the calculated structures of **4a** (dashed bonds) and **4b** (solid bonds) obtained by geometry optimizations. The hydrogen atoms are omitted for clarity.

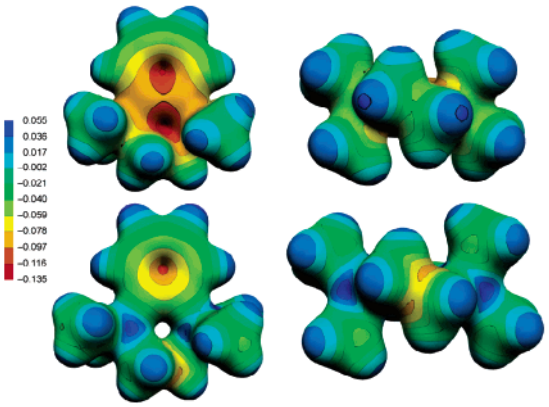


Figure 2. Electrostatic potentials (−0.135 au/+0.055 au) mapped on the calculated isosurfaces of the electron density (0.02 au) of the calculated structures of **4a** (minimum −0.135 au, maximum +0.038 au; top) and **4b** (minimum −0.106 au, maximum +0.056 au; bottom): (left) view from above of the bicyclic ring system; (right) frontal view of the $Me_2ElCH_2CH_2ElMe_2$ (El = C, Si) moiety.

The odor descriptions of the carbon compounds **1a**−**3a** are in accordance with those in the literature.[2d,7] Wood[7d] described **2a** as a musk odorant, while the derivative **3a** had "no appreciable musk odor". Homologues, in which one of the two methyl groups of one of the two *gem*-dimethyl moieties was replaced by an ethyl substituent, did not exhibit a musk odor.[7d] Only when the remaining methyl group was replaced by a hydrogen atom did a weak musk odor result.[2d] With cyclopentadecanone set to 1.0, Theimer and Davies[7c] rated the "relative muskiness" of Versalide (**1a**) as 0.7 and that of the derivative **2a** as 0.2; the derivative **3a** was not considered, and they reported only a weak intensity for compound **14**.[7c] Increasing the steric bulk around the quaternary carbon atoms also diminished the musk intensity of related indane musks significantly.[7a,b]

In summary, we found the following rank order for the muskiness of the compounds investigated: **1a** ≫ **2a** ≫ **1b** >

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2b > **3b** > **3a**. With regard to the odor intensity, the following order was observed: **1a** ≫ **2a** > **3a** > **1b** ≫ **2b** > **3b**.

Biodegradability Studies. The disila-substitution of **1a**−**3a** results not only in an increased van der Waals (vdW) volume but also in increased bond polarizations and different electrostatic potentials (see Figure 2). On the basis of the increase of bond polarization, one would have expected a decreased lipophilicity and perhaps a better bioavailability, but the measured octanol/water partition coefficients (P_{OW}) indicated the opposite, demonstrating that the increased vdW volume is dominating. For Versalide (**1a**), a value of log $P_{OW} = 5.7$ was determined, while the disila-analogue **1b** was so hydrophobic that only log $P_{OW} > 6.0$ could be stated. For the C/Si analogues **2a** and **2b,** the octanol/water partition coefficient increased from log $P_{OW} = 4.8$ (**2a**) to log $P_{OW} = 6.0$ (**2b**), and for **3a** and **3b** it increased from log $P_{OW} = 4.8$ (**3a**) to log $P_{OW} = 5.5$ (**3b**). None of the compounds studied underwent any biodegradation, as monitored by the biological oxygen demand according to the OECD guideline No. 301 F,[8] and all have to be considered "not readily biodegradable".

Conclusions. While a longitudinal extension of the hydrophobic bulk region of PCMs is usually well tolerated,[1b] the latitudinal dimensions are more restricted. Disila-substitution of **1a**−**3a** (→**1b**−**3b**) results mainly in a latitudinal extension of the molecular structures (see Figure 1), and this may account for the reduced musk intensities. Indeed, all disila-analogues were weaker in odor intensity and musk character, except for the weakest pair **3a**/**3b**, of which only the silicon compound **3b** was slightly musky. Disila-substitution of compounds **1a**−**3a** did not improve their biodegradability, and the disila-analogs **1b**−**3b** proved to be more lipophilic than their carbon counterparts **1a**−**3a**. The results clearly demonstrate that the C/Si switch can significantly affect the physicochemical and olfactory properties of odorants and therefore represents a challenging tool for the development of new odorants.[4]

Experimental Section

Chemistry. General Procedures. All syntheses were carried out under dry nitrogen. The organic solvents used were dried and purified according to standard procedures and stored under dry nitrogen. A Büchi GKR 50 apparatus was used for the bulb-to-bulb distillations. Melting points were determined with a Büchi B-540 melting point apparatus using samples in sealed glass capillaries. The ^{1}H, ^{13}C, and ^{29}Si NMR spectra were recorded at 22 °C on a Bruker Avance 500 NMR spectrometer (^{1}H, 500.1 MHz; ^{13}C, 125.8 MHz; ^{29}Si, 99.4 MHz), and $CDCl_3$ was used as the solvent. Chemical shifts were determined relative to internal $CHCl_3$ (^{1}H, δ 7.24; $CDCl_3$), $CDCl_3$ (^{13}C, δ 77.0; $CDCl_3$), or external TMS (^{29}Si, δ 0; $CDCl_3$). Assignment of the ^{1}H NMR data was supported by ^{1}H,^{1}H gradient-selected COSY, ^{13}C,^{1}H gradient-selected HMQC and gradient-selected HMBC, and ^{29}Si,^{1}H gradient-selected HMQC experiments (optimized for $^2J_{SiH} = 7$ Hz). Assignment of the ^{13}C NMR data was supported by DEPT 135 and the aforementioned ^{13}C,^{1}H correlation experiments.

Preparation and Properties of 1-(3-Ethyl-5,5,8,8-tetramethyl-5,8-disila-5,6,7,8-tetrahydro-2-naphthyl)ethanone (Disila-Versalide, 1b). A solution of cyclopentadienylcobalt dicarbonyl ($CpCo(CO)_2$; 3.28 g, 18.2 mmol) in *m*-xylene (50 mL) was added dropwise over a period of 7 h to a stirred boiling solution of **5** (14.2 g, 73.0 mmol), **6** (7.00 g, 72.8 mmol), and $CpCo(CO)_2$ (3.28 g, 18.2 mmol) in *m*-xylene (50 mL). (To avoid heating of the $CpCo(CO)_2$ solution before its addition, the dropping funnel containing this catalyst was separated from the refluxing reaction mixture by a glass tube (length, 20 cm), through which the $CpCo(CO)_2$ solution was allowed to drop freely into the refluxing mixture.) The solvent was removed by vacuum distillation (45 °C/25 mbar), and the black tarry residue was applied to the top of a pad of silica gel in a glass frit (frit dimensions, 6 × 8 cm; silica gel (32−63 μm, ICN 02826), 200 g), and the product was washed out of the residue with *n*-hexane/ethyl acetate (95:5 (v/v), 4 × 200 mL). The wash solutions were combined, the solvent was removed under reduced pressure, and the resulting residue was purified by column chromatography on silica gel (column dimensions, 60 × 5 cm; silica gel (32−63 μm, ICN 02826), 500 g; eluent, *n*-hexane/ethyl acetate (95:5 (v/v))). The relevant fractions (GC control) were combined, the solvent was removed under reduced pressure, and the residue was purified by twofold bulb-to-bulb distillation (140−180 °C/0.2 mbar) to give a yellowish oil, which was crystallized from methanol (10 mL; crystallization at 4 °C over a period of 5 days), followed by twofold recrystallization from methanol, to afford **1b** in 24% yield as a colorless crystalline solid (5.08 g, 17.5 mmol), mp 38−39 °C. ^{1}H NMR: δ 0.221 (s, 6 H, SiCH_3), 0.225 (s, 6 H, SiCH_3), 1.00 (s, 4 H, SiCH_2C), 1.20 (t, $^3J_{HH} = 7.5$ Hz, 3 H, CH_2CH_3), 2.57 (s, 3 H, C(O)CH_3), 2.82 (q, $^3J_{HH} = 7.5$ Hz, 2 H, CH_2CH$_3$), 7.35−7.37 (m, 1 H, *H*-4, Naph (=5,5,8,8-tetramethyl-5,8-disila-5,6,7,8-tetrahydro-2-naphthyl)), 7.63−7.65 (m, 1 H, *H*-1, Naph). ^{13}C NMR: δ −1.7 (2 C, SiCH$_3$), −1.5 (2 C, SiCH$_3$), 7.36 (SiCH$_2$C), 7.43 (SiCH$_2$C), 16.0 (C(O)CH$_3$), 27.1 (CH$_2$CH$_3$), 30.0 (CH$_2$CH$_3$), 133.1 (*C*-1, Naph), 135.5 (*C*-4, Naph), 137.9 (*C*-2, Naph), 142.8 (*C*-3, Naph), 142.9 (*C*-8a, Naph), 150.3 (*C*-4a, Naph), 203.0 (*C*=O). ^{29}Si NMR: δ −6.8, −6.7. Anal. Calcd for $C_{16}H_{26}OSi_2$: C, 66.14; H, 9.02. Found: C, 66.3; H, 9.0. Odor: weaker and less musky than Versalide (**1a**), mainly floral and slightly green with musky and woody facets, and a chalklike nuance; the musk tonality is in the direction of Galaxolide (**13**) but not pronounced. Lipophilicity: log $P_{OW} > 6.0$. Biodegradability: Not readily biodegradable (30 days).

Preparation and Properties of 1-(3,5,5,8,8-Pentamethyl-5,8-disila-5,6,7,8-tetrahydro-2-naphthyl)ethanone (2b). A solution of $CpCo(CO)_2$ (7.68 g, 42.7 mmol) in *m*-xylene (50 mL) was added dropwise over a period of 8 h to a stirred boiling solution of **5** (33.1 g, 170 mmol), **8** (14.0 g, 171 mmol), and $CpCo(CO)_2$ (7.68 g, 42.7 mmol) in *m*-xylene (50 mL). (To avoid heating of the $CpCo(CO)_2$ solution before its addition, the dropping funnel containing this catalyst was separated from the refluxing reaction mixture by a glass tube (length, 20 cm), through which the $CpCo(CO)_2$ solution was allowed to drop freely into the refluxing mixture.) The solvent was removed by vacuum distillation (45 °C/25 mbar), and the black tarry residue was applied to the top of a pad of silica gel in a glass frit (frit dimensions, 6 × 8 cm; silica gel (32−63 μm, ICN 02826), 200 g), and the product was washed out of the residue with *n*-hexane/ethyl acetate (95:5 (v/v)). The wash solutions were combined, the solvent was removed under reduced pressure, and the residue was purified by column chromatography on silica gel (column dimensions, 60 × 5 cm; silica gel (32−63 μm, ICN 02826), 500 g; eluent, *n*-hexane/ethyl acetate (95:5 (v/v))). The relevant fractions (GC control) were combined, the solvent was removed under reduced pressure, and the residue was purified by twofold bulb-to-bulb distillation (140−200 °C/0.2 mbar) to give a yellowish oil, which was further purified by column chromatography on silica gel (column dimensions, 80 × 3 cm; silica gel (15−40 μm, Merck 1.15111), 240 g; eluent, *n*-hexane/ethyl acetate (90:10 (v/v))). The relevant fractions (GC control) were combined, the solvent was removed under reduced pressure, and the residue was purified by twofold bulb-to-bulb distillation (150−180 °C/0.2 mbar). The resulting colorless oil was crystallized from methanol (20 mL; crystallization at −20 °C over a period of 6 days), followed by recrystallization from methanol, to give **2b** in 26% yield as a

(8) OECD, Guidelines for the Testing of Chemicals−All Test Guidelines up to and Including the 12th Addendum January 2001/Les lignes directrices de l'OCDE pour essays de produits chimiques−Tout les essays jusque'au 12e addenda janvier 2001; CD-ROM; OECD Publishing: Paris, 2001; 117 (1989) and 301 F (1992).

colorless crystalline solid (12.4 g, 44.8 mmol), mp 30−31 °C. ^{1}H NMR: δ 0.22 (s, 6 H, SiCH_3), 0.23 (s, 6 H, SiCH_3), 1.00 (s, 4 H, SiCH_2C), 2.48−2.50 (m, 3 H, CCH_3), 2.57 (s, 3 H, C(O)CH_3), 7.32−7.34 (m, 1 H, *H*-4, Naph), 7.71−7.73 (m, 1 H, *H*-1, Naph). ^{13}C NMR: δ −1.7 (2 C, Si*C*H$_3$), −1.5 (2 C, Si*C*H$_3$), 7.3 (Si*C*H$_2$C), 7.4 (Si*C*H$_2$C), 21.5 (C*C*H$_3$), 29.6 (C(O)*C*H$_3$), 133.5 (*C*-1, Naph), 137.0 (*C*-4, Naph), 137.1 (*C*-3, Naph), 137.6 (*C*-2, Naph), 142.9 (*C*-8a, Naph), 150.6 (*C*-4a, Naph), 202.3 (*C*═O). ^{29}Si NMR: δ −6.8, −6.7. Anal. Calcd for $C_{15}H_{24}OSi_2$: C, 65.15; H, 8.75. Found: C, 65.2; H, 8.8. Odor: weak, slightly musky with a touch of animalic sensuality and somewhat green, woody-earthy aspects; much weaker and less musky than the parent carbon compound **2a**. Lipophilicity: log P_{OW} = 6.0. Biodegradability: not readily biodegradable (30 days).

Preparation and Properties of 1-(5,5,8,8-Tetramethyl-5,8-disila-5,6,7,8-tetrahydro-2-naphthyl)ethanone (3b). A solution of dimethyl sulfoxide (1.23 g, 15.7 mmol) in dichloromethane (8 mL) was added dropwise at −55 °C (±5 °C) over a period of 30 min to a stirred solution of oxalyl chloride (960 mg, 7.56 mmol) in dichloromethane (15 mL), and the resulting mixture was stirred for 30 min at −55 °C (±5 °C). Subsequently, a solution of *rac*-**10** (1.82 g, 6.88 mmol) in dichloromethane (8 mL) was added dropwise at −55 °C (±5 °C) within 1 h, the mixture was stirred for 30 min, and triethylamine (3.48 g, 34.4 mmol) was added dropwise at the same temperature over a period of 30 min. The resulting mixture was stirred for a further 15 min at −55 °C and then warmed to 5 °C over a period of 2 h. The mixture was washed with water (2 × 25 mL), the organic phase was separated, the first aqueous wash solution (A) was extracted with diethyl ether (25 mL), the resulting ethereal extract was used to extract the second aqueous wash solution (B), and the organic extract was separated, followed by a second extraction of the wash solutions A and B with a fresh portion of diethyl ether (25 mL), using the same protocol as described for the first extraction sequence. The combined organic solutions were dried over anhydrous sodium sulfate, and the solvent was removed under reduced pressure to give a yellowish oil, which was purified by column chromatography on silica gel (column dimensions, 60 × 3.5 cm; silica gel (15−40 μm, Merck 1.15111), 180 g; eluent, *n*-hexane/ethyl acetate (80:20 (v/v))). The relevant fractions (GC control) were combined, the solvent was removed under reduced pressure, and the residue was purified by bulb-to-bulb distillation (90−100 °C/0.3 mbar) to give a colorless oil, which was further purified by column chromatography on silica gel (column dimensions, 48 × 2.5 cm; silica gel (15−40 μm, Merck 1.15111), 90 g; eluent, *n*-hexane/ethyl acetate (90:10 (v/v))). The relevant fractions (GC control) were combined, the solvent was removed under reduced pressure, and the residue was finally subjected to a threefold bulb-to-bulb distillation (100−110 °C/0.8 mbar) to give a colorless oil, which was crystallized from ethanol (10 mL; crystallization at −78 °C over a period of 10 h), followed by recrystallization from ethanol, to give a crystalline solid. When the temperature was raised to 20 °C, compound **3b** was isolated in 83% yield as a colorless oil (1.50 g, 5.71 mmol). ^{1}H NMR: δ 0.23 (s, 6 H, SiCH_3), 0.25 (s, 6 H, SiCH_3), 1.02 (s, 4 H, SiCH_2C), 2.58 (s, 3 H, C(O)CH_3), 7.58 (dd, $^3J_{HH}$ = 7.7 Hz, $^5J_{HH}$ = 0.6 Hz, 1 H, *H*-4, Naph), 7.84 (dd, $^3J_{HH}$ = 7.7 Hz, $^4J_{HH}$ = 1.8 Hz, 1 H, *H*-3, Naph), 8.03 (dd, $^4J_{HH}$ = 1.8 Hz, $^5J_{HH}$ = 0.6 Hz, 1 H, *H*-1, Naph). ^{13}C NMR: δ −1.7 (2 C, Si*C*H$_3$), −1.6 (2 C, Si*C*H$_3$), 7.3 (Si*C*H$_2$C), 7.4 (Si*C*H$_2$C), 26.6 (C(O)*C*H$_3$), 127.4 (*C*-3, Naph), 132.5 (*C*-1, Naph), 133.6 (*C*-4, Naph), 136.1 (*C*-2, Naph), 146.5 (*C*-8a, Naph), 152.7 (*C*-4a, Naph), 198.7 (*C*═O). ^{29}Si NMR: δ −6.3 (2 Si). Anal. Calcd for $C_{14}H_{22}OSi_2$: C, 64.06; H, 8.45. Found: C, 64.3; H, 8.3. Odor: weak, slightly musky and fruity, with the fruity aspects in the direction of blackberries, and some floral-green undertones reminiscent of lily of the valley; in comparison with the carbon compound **3a**, the odor of the disila-analogue **3b** is less intense, and in contrast to **3a**, some musky facets are present in the case of **3b**. Lipophilicity: log P_{OW} = 5.5. Biodegradability: not readily biodegradable (32 days).

Preparation of *rac*-1-(5,5,8,8-Tetramethyl-5,8-disila-5,6,7,8-tetrahydro-2-naphthyl)ethanol (*rac*-10). A solution of $CpCo(CO)_2$ (9.00 g, 50.0 mmol) in *m*-xylene (50 mL) was added dropwise over a period of 6 h to a stirred boiling solution of **5** (48.6 g, 250 mmol), **9** (49.8 g, 350 mmol), and $CpCo(CO)_2$ (4.50 g, 25.0 mmol) in *m*-xylene (200 mL). (To avoid heating of the $CpCo(CO)_2$ solution before its addition, the dropping funnel containing this catalyst was separated from the refluxing reaction mixture by a glass tube (length, 20 cm), through which the $CpCo(CO)_2$ solution was allowed to drop freely into the refluxing mixture.) The solvent was removed by vacuum distillation (25 °C/10 mbar), and the residue was purified by column chromatography on silica gel (column dimensions, 60 × 5.0 cm; silica gel (32−63 μm, ICN 02826), 500 g; eluent, *n*-hexane/ethyl acetate (92:8 (v/v))). The relevant fractions (GC control) were combined, the solvent was removed under reduced pressure, and the residue was purified by bulb-to-bulb distillation (100−150 °C/0.2 mbar) to give a yellowish oil, which was added to a solution of acetic acid (3.05 g, 50.8 mmol) in methanol (200 mL). The resulting mixture was heated under reflux for 2 days, cooled to 20 °C, and diluted with diethyl ether (200 mL), followed by addition of a half-saturated aqueous sodium hydrogencarbonate solution (200 mL). The organic layer was separated and the aqueous layer extracted with diethyl ether (3 × 100 mL), the organic solutions were combined and dried over anhydrous sodium sulfate, and the solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel (column dimensions, 60 × 5.0 cm; silica gel (32−63 μm, ICN 02826), 500 g; eluent, *n*-hexane/ethyl acetate (80:20 (v/v))). The relevant fractions (GC control) were combined, the solvent was removed under reduced pressure, and the residue was purified by bulb-to-bulb distillation (100−140 °C/0.5 mbar) to give a yellowish oil, which was crystallized from *n*-hexane (35 mL; crystallization at −20 °C over a period of 8 days) to give *rac*-**10** in 21% yield as a colorless crystalline solid (13.9 g, 52.5 mmol), mp 48−49 °C. ^{1}H NMR: δ 0.210 (s, 3 H, SiCH_3), 0.212 (s, 3 H, SiCH_3), 0.222 (s, 3 H, SiCH_3), 0.225 (s, 3 H, SiCH_3), 1.00 (s, 4 H, SiCH_2C), 1.50 (d, $^3J_{HH}$ = 6.5 Hz, 3 H, CH(OH)CH_3), 1.75 (br s, 1 H, CH(O*H*)CH$_3$), 4.86 (q, $^3J_{HH}$ = 6.5 Hz, 1 H, C*H*(OH)CH$_3$), 7.33−7.36 (m, 1 H, *H*-3, Naph), 7.46−7.50 (m, 2 H, *H*-1, *H*-4, Naph). ^{13}C NMR: δ −1.49 (2 C, Si*C*H$_3$), −1.48 (2 C, Si*C*H$_3$), 7.5 (Si*C*H$_2$C), 7.6 (Si*C*H$_2$C), 24.9 (CH(OH)*C*H$_3$), 70.6 (*C*H(OH)CH$_3$), 125.2 (*C*-3, Naph), 130.4 (*C*-1, Naph), 133.7 (*C*-4, Naph), 145.0 (*C*-4a, Naph), 145.2 (*C*-2, Naph), 146.2 (*C*-8a, Naph). ^{29}Si NMR: δ −7.1, −6.9. Anal. Calcd for $C_{14}H_{24}OSi_2$: C, 63.57; H, 9.15. Found: C, 63.8; H, 8.8.

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Supporting Information Available: Text giving experimental details of the syntheses of **1a**−**3a**, **4a**, and **5**−**9**, the computational studies of **4a**/**4b**, the olfactory properties and biodegradability studies of **1a**/**1b**, **2a**/**2b**, and **3a**/**3b**, and the determination of the log P_{OW} values of **1a**/**1b**, **2a**/**2b**, and **3a**/**3b**. This material is available free of charge via the Internet at http://pubs.acs.org.

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