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Synthesis and Characterization of Functional Cyclopentasilanes

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ABSTRACT

Cleavage of the exocyclic Si-Si-bond of phenyldimethylsilylnonamethylcyclopentasilane **3** *by sodium ethoxide followed by chlorination with acetyl chloride leads to the monofunctional chlorononamethylcyclopentasilane* **5.** *Subsequent hydration gives hydrononamethylcyclopentasilane* **6**, *which can be easily converted to the corresponding bromo and iodo derivatives* **7**, **8**. *Fluorononamethylcyclopentasilane can be prepared upon treatment of* **7** *with* ZnF_2. *A different but convenient synthetic pathway to the halononamethylcyclopentasilanes has also been achieved employing the corresponding trifluoromethanesulfonic acid ester* **11**. *The halogen derivatives—as expected—show a strong influence on the physical properties of the compounds.*

These functionalized cyclopentasilanes may serve as useful synthetic tools in building larger oligosilane ring systems.

Previous work in our laboratory [1, 2, 3] led to preparative pathways for various functionalized cyclohexasilane derivatives. Compound **2**, chlorodimethylsilylnonamethylcyclopentasilane, is readily accessible by a combined contraction/chlorination [4] of dodecamethylcyclohexasilane. Other structural isomers thereof were also prepared [5, 6]. Hence the aim of this work was the synthesis of monofunctional cyclopentasilanes, employing **2**. Due to their functionality all mentioned compounds are potential starting materials for the synthesis of larger silicon ring systems bearing fused and exocyclic bonded structures. In addition, their physical properties and reactivity are of primary interest. We presume that cyclopentasilanyl derivatives may serve well as synthons for coupling reactions with oligofunctional linear and cyclic polysilanes due to their sensitivity upon hydrolysis and steric factors. So far some reactions have been carried out successfully with cyclohexasilanyl derivatives [3], and present efforts concentrate on exocyclic linked oligocyclic structures starting from compounds **5**–**9**.

The synthesis of **5** was carried out, in general, as reported by Kumada [7]. Compound **2** could not be adequately purified by distillation; therefore, the crude material was directly converted to **3**. In the course of this work **4** and **5** were completely characterized for the first time. A selective cleavage of the exocyclic Si-Si-bond by catalytic reaction of $NaOC_2H_5$ in ethanolic solution gave **4** and ethoxydimethylphenylsilane. However, temperatures above 30°C and prolonged reaction times led to a number of other products arising from Si-ring cleavage. Consequently yields were significantly lowered. Therefore this reaction was closely monitored by GLC. At lower temperatures (ice cooling) no reaction occurred.

Subsequent chlorination of **5** readily led to almost quantitative yields and therefore no further purification of the ethoxy product was required.

Employing **5** we succeeded in preparing several new monofunctional cyclopentasilanes (**6**–**9**). Special interest was focused upon the complete series of the halogen derivatives (scheme).

Compound **6** is readily accessible upon hydrogenation of **5**. Treatment of **6** with tribromomethane or triiodomethane leads to compounds **7** and **8**, respectively. Initially, fluorononamethyl-

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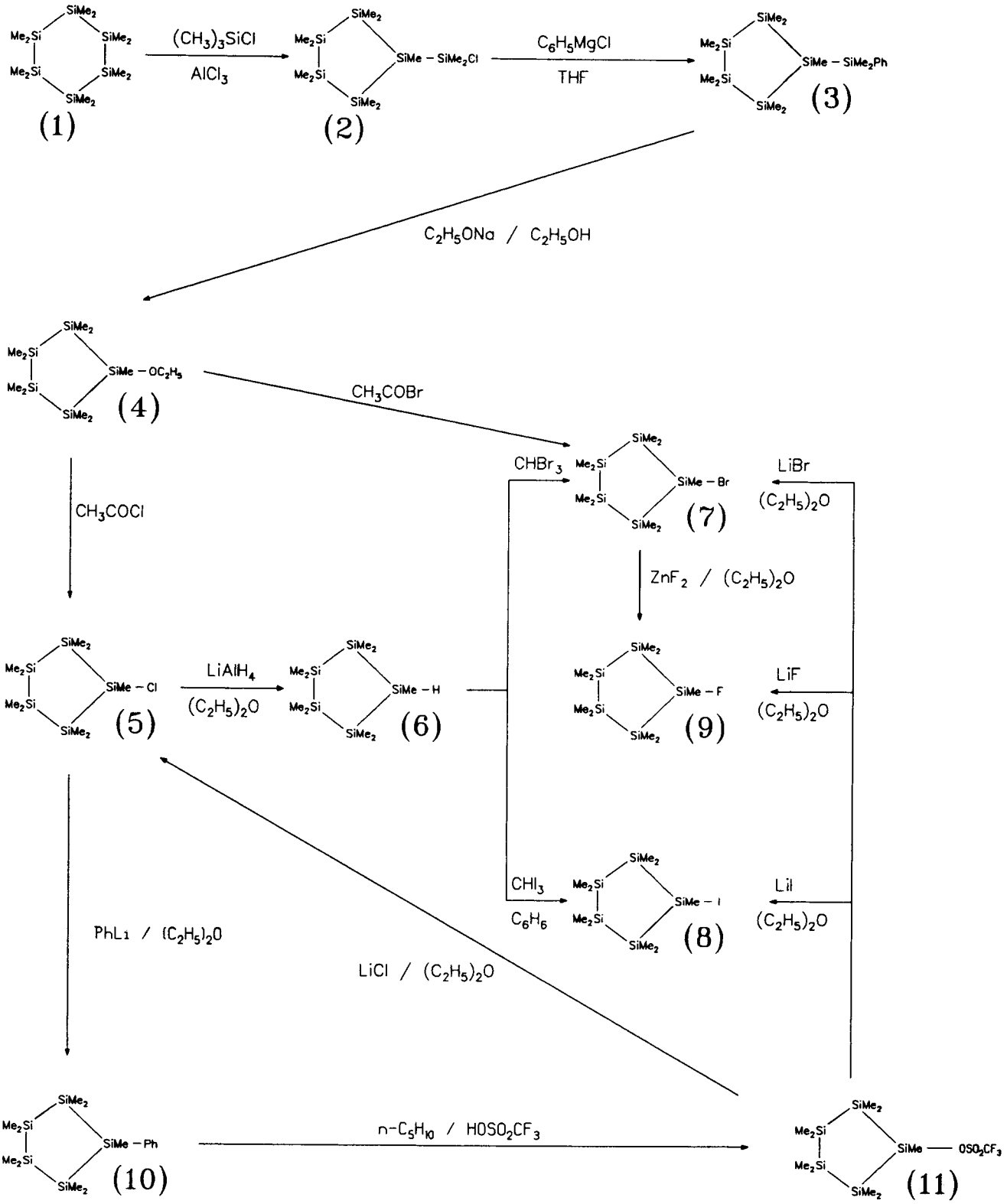

SCHEME 1

cyclopentasilane **9** was synthesized by an exchange reaction between **7** and ZnF_2, this process being favoured by the difference in electronegativities.

These compounds exhibit longer retention times (GLC) on a nonpolar phase and a significant bathochromic shift in their UV-spectra in comparison to unsubstituted decamethylcyclopentasilane and the halodimethylsilylnonamethylcyclopentasi-

lane derivatives [6]. The influence of functional groups is significantly reflected in the ^{29}Si-NMR-shifts of the α-Si:

	H	Ph	I	Br	OC_2H_5	Cl	F
δ =	−66,78	− 39,65	− 12,11	10,95	15,74	18,46	43,80

Starting from the trifluoromethanesulfonic acid ester derivative **11**, halogenation of cyclopentasilanes is readily accomplished with good yields and almost no by-product formation. Compound **5** was converted to **10** using a Grignard reaction. Compound **10** is a colourless viscous oil which is stable in air for an extended period. Upon addition of trifluoromethanesulfonic acid the very unstable and reactive **11** can be quickly prepared. Sufficient preparative yields can only obtained if this reaction is carried out below −40°C. The path of this reaction can be monitored (GLC) by following the degradation of **10**. The halocyclopentasilanes **5**, **7**, **8** and **9** are prepared upon the addition of the respective dry lithium halide. This experimental procedure is similar to that of **9** described in the experimental section (method 2).

Similar to the conversion of **4** to **5**, a simple and convenient synthesis of **7** can be achieved by reaction of **4** with acetyl bromide. An alternative synthesis of **7** (by reaction of decamethylcyclopentasilane with aluminum bromide in carbon tetrachloride solution) was described in one of our previous papers where we investigated the reactivity of various metal halides of different Lewis acidity towards medium-sized permethylated cyclosilane rings [8].

The yellow viscous oily compound **11** was used immediately after preparation and therefore was only characterized by ^{29}Si-NMR spectroscopy.

None of the cyclopentasilane derivatives could be recrystallized from common organic solvents. This is in contrast to the cyclohexasilane derivatives which appear to be more stable and mostly crystalline at room temperature.

EXPERIMENTAL

All preparative steps were carried out under an atmosphere of dry nitrogen or argon. Solvents were dried according to common methods. The lithium halides and zinc fluoride were dried under vacuum. Compounds **1**, **2** and **3** were synthesized according to literature procedures [4, 5]. NMR-spectra were recorded on a 60 MHz-instrument (Hitachi, ^{1}H) and a 300 MHz-instrument (Bruker, ^{1}H, ^{29}Si). Substances were measured as solutions in C_6D_6. IR- and UV-spectra were measured with a Perkin-Elmer 883 (CsBr-plates) and a Philips PU-8740, respectively. GLC-analyses were carried out on a HP 5890-II (12 m HP-1, ϕ 0.53 mm, (polydimethylsiloxane-phase); det.: FID (He) linked to a HP-Chemstation; mass spectra were obtained on a Finnigan-MAT-212 and a HP 5971A/5890-II, respectively.

Ethoxynonamethylcyclopentasilane (**4**)

To 300 ml dry ethanol 0.72 g (31 mmol) sodium was added portionwise and the solution was stirred until the metal was completely reacted. Subsequently 47 g (114 mmol) **3** were added and the mixture stirred for 40 hours at room temperature. At optimum yield (GLC-analysis) the mixture was neutralized with trimethylchlorosilane to pH 6 employing phenolphthalein as indicator.

The solvent was removed under reduced pressure and the residue distilled with a 30-cm-Vigreux-column at 1.5 mbar. After a fraction of ethoxydimethylphenylsilane, pure **4** was collected at a column temperature of 101°C. Yield: 24 g (62%).

MS: (M/e): 320 (16%, M^+); 291 (100%, Si_5Me_{10}); 233 (19%, Si_4Me_8); 217 (30%, Si_4Me_7); 73 (47%, $SiMe_3$); detected and theoretical isotopic pattern are in good agreement.

^{29}Si-NMR: δ = 15.74 (1 Si); −46.11 (2 Si); −44.01 (2 Si).

^{1}H-NMR: δ = 0.18 (2 Me); 0.22 (2 Me); 0.25 (2 Me); 0.35 (2 Me); 0.48 (2 Me); 1.12 (triplet); 3.57 (quartet).

IR: (cm^{-1}): 1244 s, 1158 w, 936 m, 840 s, 804 s, 787 s, 772 s, 734 s, 690 m, 652 m, 474 w, 419 w, 357 w.

UV: (ϵ/nm): 13900/227, 1500/262, 1200/282.

Chlorononamethylcyclopentasilane (**5**)

Ten g (31 mmol) (**4**) were dissolved in 90 g (1150 mmol) acetyl chloride and kept at reflux temperature for 6 hours. The excess acetyl chloride and formed ethyl acetate were distilled from the mixture at atmospheric pressure. The remaining residue was distilled with a 10-cm-Vigreux-column at 1.5 mbar and (**5**) collected at a column head temperature of 106°C. Yield: 8.0 g (83%).

MS: (M/e): 310 (85%, M^+); 215 (48%, $Si_3Me_4Cl_2$); 202 (74%, Si_4Me_6); 157 (41%, $Si_2Me_2Cl_2$); 73 (100%, $SiMe_3$); detected and theoretical isotopic pattern are in good agreement.

^{29}Si-NMR: δ = 18.46 (1 Si); −43.07 (2 Si); −41.70 (2 Si).

^{1}H-NMR: δ = 0.13 (4 Me); 0.23 (2 Me); 0.33 (2 Me); 0.60 (1 Me).

IR: (cm^{-1}): 1246 vs, 842 s, 830 s, 800 vs, 771 s, 734 s, 695 m, 652 s, 500 s, 412 w, 392 m, 358 w, 330 w, 305 w, 280 m.

UV: (ϵ/nm): 57800/237, 6500/282.

Hydrononamethylcyclopentasilane (**6**)

Four g (13 mmol) **5** were dissolved in 25 ml of diethyl ether and cooled with ice. Subsequently 2.9 ml (2.2 M) of an ethereal solution of $LiAlH_4$ (6.5 mmol) were added. The reaction was complete within 2 hours. The mixture was then neutralized to pH 7 with dilute (18%) aqueous HCl, the aqueous phase extracted with petroleum ether several times and the organic layers decanted, combined and dried over Na_2SO_4. The organic solvent was removed under reduced pressure and the pure product distilled from the residue using a 10-cm-Vigreux-column at 1.5 mbar at a column head temperature of 82°C. Yield: 3.0 g (84%).

MS: (M/e): 276 (61%, M^+); 202 (63%, Si_4Me_6); 157 (37%, Si_4Me_3); 73 (100%, $SiMe_3$); detected and theoretical isotopic pattern are in good agreement.

^{29}Si-NMR: $\delta = -66.78$ (1 Si); -40.87 (2 Si); -41.65 (2 Si).

^{1}H-NMR: $\delta = 0.19$ (4 Me); 0.20 (4 Me); 0.23 (1 Me); 0.30 (Si — H).

IR: (cm^{-1}): 2067 vs (Si — H), 1404 vs, 1246 vs, 932 m, 906 s, 870 vs, 843 s, 801 vs, 731 s, 689 s, 656 s, 634 s, 471 w, 453 w, 410 m, 392 m, 357 w.

UV: (ϵ/nm): 10100/232, 2500/256.

Calcd. for $Si_9H_{28}Si_5$: C 39.06; H 10.20.

Anal.: C 39.30; H 10.01 [with $Pb(BO_2)_2.2H_2O$].

Bromononamethylcyclopentasilane (**7**)

Method 1: 0.5 g (1.6 mmol) **4** and 10 ml (17 g, 140 mmol) acetyl bromide were kept at reflux temperature for 5 hours. Excess acetyl bromide and the formed ethyl acetate were distilled at atmospheric pressure. Pure **7** was distilled from the residue with a 10-cm-Vigreux-column at 0.06 mbar at a column head temperature of 86°C. Yield: 0.3 g (54.4%).

Method 2: 0,33 g (1,2 mmol) **6** were dissolved in 8 ml (23 g, 92 mmol) tribomomethane and stirred for 20 hours at room temperature. Residual tribromomethane and the formed dibromomethane were removed under reduced pressure and the oily residue distilled with a 10-cm-Vigreux-column. Yield: 0,28 g (66,4%).

MS: 356 (64%, M^+); 233 (33%, Si_4Me_8); 218 (40%, Si_4Me_7); 202 (55%, Si_4Me_6); 73 (100%, $SiMe_3$); detected and theoretical isotopic pattern are in good agreement.

^{29}Si-NMR: $\delta = 10.95$ (1 Si); -42.96 (2 Si); -41.70 (2 Si).

^{1}H-NMR: $\delta = 0.13$ (4 Me); 0.25 (2 Me); 0.36 (2 Me); 0.74 (1 Me).

IR: (cm^{-1}): 1247 vs, 933 w, 907 w, 879 m, 837 s, 805 s, 770 s, 734 m, 695 m, 653 m, 461 w, 434 w, 412 w, 374 w, 321 w.

UV: (ϵ/nm): 77300/240, 5400/289.

Calcd. for $C_9H_{27}BrSi_5$: C 30.39; H 7.65.

Anal.: C 30.68; H 7.56 [with $Pb(BO_2)_2.2H_2O$].

Iodononamethylcyclopentasilane (**8**)

Compound **6** (0.5 g, 1.8 mmol) and 0.79 g (2.0 mmol) iodoform were dissolved in 20 ml benzene and stirred for 1 hour at room temperature. The solvent and the formed diiodomethane were removed under reduced pressure and the oily residue distilled with a 10-cm-Vigreux-column. Pure **8** distills at 0.06 mbar and a column head temperature of 113°C. Yield: 0.65 g (86%).

MS: (M/e): 402 (64%, M^+); 317 (21%, Si_3Me_7I); 301 (39%, Si_3Me_6I); 271 (56%, Si_3Me_4I); 202 (38%, $SiMe_3I$); 73 (100%, $SiMe_3$); detected and theoretical isotopic pattern are in good agreement.

^{29}Si-NMR: $\delta = -12.11$ (1 Si); -38.80 (2 Si); -41.68 (2 Si).

^{1}H-NMR: $\delta = 0.11 - 1.08$.

IR: (cm^{-1}): 1403 vs, 1248 vs, 907 s, 878 s, 831 vs, 798 vs, 770 vs, 696 s, 664 s, 557 m, 400 w, 377 w, 358 w, 318 m, 286 w.

UV: (ϵ/nm): 68200/250, 4100/294.

Flurononamethylcyclopentasilane (**9**)

Method 1: 0.6 g (1.7 mmol) **7** and 0.2 g (1.9 mmol) dry zinc fluoride were dissolved in 10 ml of diethyl ether. After 3 hours of stirring at room temperature quantitative conversion had taken place. The solvent was removed under reduced pressure and the residue distilled at 3 mbar. Pure **9** was obtained at column head temperatures between 68–72°C. Yield: 0.20 g (40%).

Method 2: 20 ml of diethyl ether were distilled into a reaction vessel containing 0.98 g (2.3 mmol) of **11** and 0.06 g (2.3 mmol) of dry lithium fluoride were dissolved therein at -40°C. The mixture was stirred and allowed to warm to room temperature. The reaction was monitored by GLC. Subsequently the solvent was removed under reduced pressure and the residue was dissolved in petroleum ether. After removal of the salts through a glass frit, the petroleum ether was removed *in vacuo*. The remaining residue was distilled with a 10-cm-Vigreux-column.

MS: (M/e): 294 (100%, M^+); 202 (20%, Si_4Me_6); 157 (57%, Si_4Me_3); 73 (100%, $SiMe_3$); detected and theoretical isotopic pattern are in good agreement.

^{29}Si-NMR: $\delta = 43.80$ (1 Si); -46.47 (2 Si); -43.82 (2 Si).

^{19}F-NMR: $\delta = -158.76$.

^{1}H-NMR: δ = 0.130 (2 Me); 0.140 (2 Me); 0.217 (2 Me); 0.221 (2 Me); 0.338 (1 Me).

IR: (cm^{-1}): 1427 w, 1403 m, 1248 s, 1119 m, 933 w, 908 w, 875 m, 841 s, 828 s, 798 vs, 772 s, 755 m, 732 m, 689 m, 651 m, 470 m, 416 m, 399 w, 390 w, 357 w.

UV: (ϵ/nm): 16000/234, 3200/267.

Calcd. for $C_9H_{27}FSi_5$: C 36.68; H 9.23.

Anal.: C 36.40; H 9.33.

Phenylnonamethylcyclopentasilane (**10**)

Compound **5** (3.8 g, 12 mmol) was dissolved in 50 ml of diethyl ether, heated to reflux and 25 ml of a diluted solution of phenyllithium (30 mmol) in diethyl ether were added slowly. After 1 hour **5** had reacted quantitatively (GLC-analysis) and the mixture was hydrolyzed with 50 ml of a saturated solution of ammonium chloride. The aqueous phase was extracted with petroleum ether several times. The combined organic layers were dried over Na_2SO_4 and the solvent was removed under reduced pressure. Compound **10** was distilled from the residue with a 30-cm-Vigreux-column at 0.08 mbar and a column head temperature of 92–95°C. Yield: 2.15 g (50%).

MS: 352 (100%, M^+); 278 (81%, Si_5Me_9); 263 (40%, Si_5Me_8); 219 (32%, Si_4Me_7); 135 (28%, $SiMe_2Ph$); 73 (43%, $SiMe_3$); detected and theoretical isotopic pattern are in agreement.

^{29}Si-NMR; δ = −39.65 (1 Si), −42.53 (2 Si), −41.35 (2 Si).

^{1}H-NMR: δ = 0.15 − 0.48 (9 Me), 7.19 (Ph).

IR: (cm^{-1}): 3070 m, 3053 m, 2952 s, 2893 s, 1484 s, 1427 vs, 1246 s, 1110 s, 1027 s, 998 m, 836 s, 804 vs, 787 vs, 730 vs, 698 vs, 651 m, 479 m, 358 w.

UV: (ϵ/nm): 25300/249.

Calcd. for $C_{15}H_{32}Si_5$: C 51.06; H 9.14.

Anal.: C 50.87; H 9.19 [with $Pb(BO_2)_2.2H_2O$].

Nonamethylcyclopentasilanyltrifluoromethane sulfonic acid ester (**11**)

Compound **10** (0.83 g, 2.3 mmol) was dissolved in 10 ml of n-heptane at −40°C, the solution was stirred, and 0.23 ml (2.7 mmol) trifluoromethanesulfonic acid was added slowly with a glass syringe. The reaction was complete within 1 hour (GLC-analysis). The mixture was allowed to warm to room temperature and the solvent and the formed benzene were removed under reduced pressure. The residue (pale yellow oil) was diluted with diethyl ether and immediately used for further reactions.

^{29}Si-NMR: δ = 48.32 (1 Si), −44.17 (2 Si), −42.74 (2 Si).

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