

New Fluorine Derivatives of Methylcyclohexasilane

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ABSTRACT

1,1-Difluorodecamethyl- and 1,1,4,4-tetrafluorooctamethylcyclohexasilane were synthesized by the reaction of LiF with the corresponding trifluoromethanesulfonic derivatives and were characterized by spectroscopic methods, mainly by modern NMR techniques. The stability of the fluorinated cyclosilanes decreases with an increase of fluorine substituents. This seems to be the reason for the instability of perfluorinated cyclosilanes.

INTRODUCTION

A small number of partially fluorinated cyclosilanes are known at present, whereas perfluorinated derivatives have not yet been prepared. In contrast, perchloro-, bromo- and iodocyclosilanes were prepared and isolated by our group some years ago [1, 2, 3], starting from perphenylcyclosilanes. It is relatively easy to remove phenyl groups from cyclosilanes by cleaving the Si-C bond with hydrogen halides, using aluminum halides as catalysts. It is, however, difficult to do the same with methyl groups.

Using HX/AlX_3 ($X = Cl, Br, I$), the cyclosilanes Si_nX_{2n} ($n = 4, 5, 6$) were prepared from Si_nPh_{2n} and reduced to Si_5H_{10} and Si_6H_{12} [4, 5]. Methylphenylcyclosilanes, $Si_nMe_mPh_{2n-m}$, react to form methylhalocyclosilanes $Si_nMe_mX_{2n-m}$, described later in this work. The reason for the large difference of the reactivities lies in the reaction mechanism, which

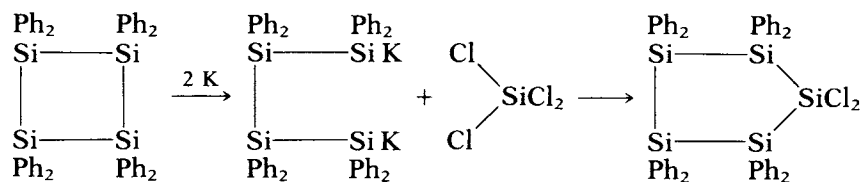
was shown to be of electrophilic nature [6]. Toly groups, possessing a higher σ^* constant, are removed more easily than phenyl groups. This fact can be used for preparative purposes [7]. Attempts to prepare perfluorocyclosilanes failed because of the formation of polymeric materials, even when halogen exchange reactions, proven successful for the preparation of disilane derivatives, were used. ZnF_2 in the presence of catalytic amounts of silver allowed us to effect the preparation of fluorophenyldisilanes [8] from chloro- and bromodisilanes. AgF and SbF_3 , however, were reduced to the metals by the Si-Si bond.

When ZnF_2 reacts with perchlorocyclosilanes under the same reaction conditions, polymeric silanes with varying Cl/F contents are formed. Similar polymers are obtained with SbF_3 , LiF or KF/18-crown-6. The previously unknown, 1,1-dichlorooctaphenylcyclopentasilane (I), which we prepared from 1,4-dipotassiumoctaphenyltetrasilane and $SiCl_4$, reacts with ZnF_2 , forming octaphenylcyclo-tetrasilane and polymeric $(SiF_2)_n$, but no 1,1-difluorooctaphenylcyclopentasilane (Scheme 1).

Obviously, formation of difluorosilylene occurs during the reaction, followed by a rearrangement of the ring skeleton and polymerization of the silylene. Interestingly, the fluorination of 2,2-dibromohexamethyltrisilane with ZnF_2 can be carried out in high yields without formation of $(SiF_2)_n$ [9].

Cyclosilanes with just one fluorine atom attached to an Si atom are much more stable than those containing SiF_2 groups. Thus hexafluorohexamethylcyclohexasilane $(SiFMe)_6$ was easily prepared from hexachlorohexamethylcyclohexasilane, which was synthesized by reacting $(SiMePh)_6$ with $HCl/AlCl_3$ [10].

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SCHEME 1

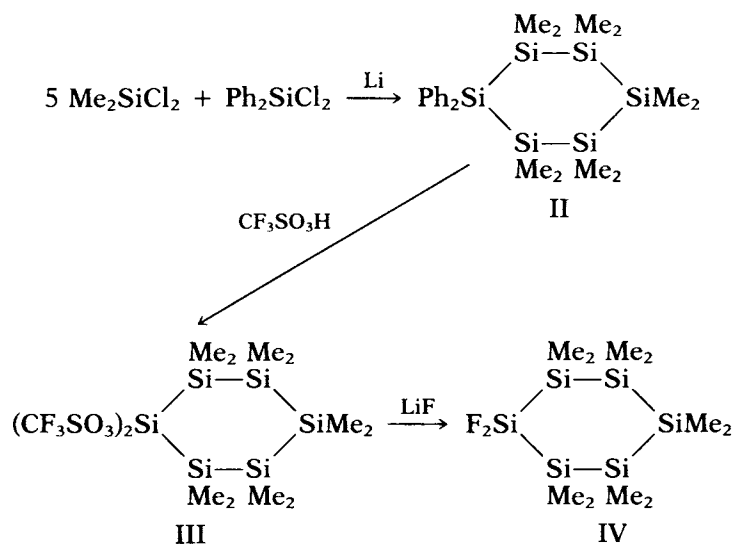
The question therefore arose whether or not cyclosilanes containing SiF_2 units could be prepared. A positive answer will be given in this work for the cyclohexasilane system.

RESULTS

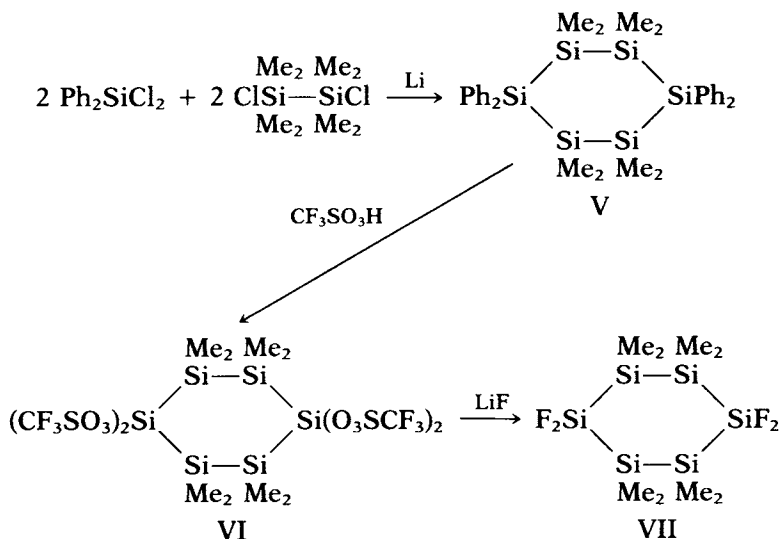
The synthesis of 1,1-difluorodecamethylcyclohexasilane starts from 1,1-diphenyldecamethylcyclo-

hexasilane (II) obtained from Ph_2SiCl_2 and Me_2SiCl_2 (1:5 ratio) in a condensation reaction with Li [9]. The phenyl groups are removed with trifluoromethanesulfonic acid. The 1,1-bis(trifluoromethylsulfonyloxy)decamethylcyclohexasilane intermediate (III) reacts smoothly with LiF to give 1,1-difluorodecamethylcyclohexasilane (IV) (Scheme 2).

Using 1,1-dichlorodecamethylcyclohexasilane



SCHEME 2



SCHEME 3

as an intermediate poses some problems because $(\text{SiMe}_2)_5\text{SiPh}_2$ may undergo rearrangement reactions when treated with HCl/AlCl_3 .

In an analogous way, 1,1,4,4-tetrafluorooctamethylcyclohexasilane (VII) was prepared from 1,1,4,4-tetraphenyloctamethylcyclohexasilane (V) by first reacting it with trifluoromethanesulfonic acid followed by treatment of the intermediate 1,1,4,4-tetrakis(trifluoromethanesulfonic)-compound (VI) with LiF (Scheme 3).

The two fluoro derivatives IV and VII show a marked difference of thermal stabilities. IV melts without decomposition at 44°C , whereas VII decomposes at 80°C . The mass spectrum of VII shows a relatively weak parent peak when compared to IV, vanishing when VII is heated to 80°C . The fragmentation pattern can be interpreted in terms of SiF_2 loss, though SiF_2^+ could not be detected (probably because of secondary reactions). Our results indicate that an increase of the number of SiF_2 units in cyclohexasilanes reduces the thermal stability of the compounds. This may explain why all attempts to prepare $(\text{SiF}_2)_6$ failed.

EXPERIMENTAL

Attempts to Prepare Perfluorocyclosilanes

Reactions of $\text{Si}_5\text{Cl}_{10}$, $\text{Si}_5\text{Br}_{10}$ and $\text{Si}_6\text{Cl}_{12}$ with ZnF_2 in tetrachloroethane or in hexachloro-1,3-butadiene always delivered reaction products of the solvent with Si-fluorinated ring fragments (reaction temperature up to 40°C). If the reaction of $\text{Si}_5\text{Cl}_{10}$ with ZnF_2 is carried out in diethyl ether at room temperature, the main product is an Si polymer containing Cl and F as substituents. Reaction of perchlorocyclosilanes with $\text{KF}/18\text{-crown-6}$ at room temperature in benzene or in cyclohexane also gave similar polymers as main products.

The reaction of decamethoxycyclopentasilane with boron trifluoride, carried out in diethyl ether at -60°C , yields a polymer containing fluorine and methoxy groups as substituents.

1,1-Dichlorooctaphenylcyclopentasilane (I)

Twenty g of octaphenylcyclotetrasilane (27.5 mmol) in 200 mL of THF was stirred with 2.5 g potassium (64 mmol) at room temperature. After two hours the ring-cleavage was complete and the dark red solution of 1,4-di-potassiumoctaphenyltetrasilane was filtered into a dropping funnel. This solution and 4.6 g of tetrachlorosilane (27 mmol) dissolved in 200 mL of THF were added simultaneously to 100 mL of THF at -80°C over a period of 3 h. The solvent was removed after warming to room temperature, and 400 mL of toluene were added to the residue. Afterwards, the solvent was filtered from the salts and evaporated. Recrystallization from cyclohexane ($3\times$) gave 5.8 g (26%) of pure $\text{Si}_5\text{Ph}_8\text{Cl}_2$:

mp: $220\text{--}222^\circ\text{C}$; Anal. (Calcd./found) for $\text{Si}_5\text{C}_{48}\text{H}_{40}\text{Cl}_2$: Si 16.96/17.04%, Cl 8.56/8.72%; ^{29}Si -NMR δ : 16.9 (Si1), -24.15 (Si2), -35.27 (Si3); MS: $m/z = 826$ (M^+). IR [cm^{-1}]: 992w, 970w, 728s, 690s, 685sh, 569m, 545s, 515w, 468m, 455sh, 333m, 312w, 249m, 232s, 211s.

Attempts to Prepare

1,1-Difluorooctaphenylcyclopentasilane

Fluorination with ZnF_2 . Reactions were carried out in hexachloro-1,3-butadiene. Below 60°C no reaction was detectable, but catalytic amounts of silver powder accelerated the reaction. Surprisingly, the ^{29}Si -NMR spectra of the reaction mixture showed octaphenylcyclotetrasilane to be the main product.

The coupling reaction between tetrafluorosilane and 1,4-dipotassiumoctaphenyltetrasilane, carried out in the same way as the synthesis of the dichloro-derivative, gave complex mixtures of compounds. Using the previously unknown bis(trifluoromethylsulfonyloxy)-difluorosilane $\text{Si}(\text{OSO}_2\text{CF}_3)_2\text{F}_2$ ($\delta_{\text{Si}} = -70.70$ ppm, $^1J_{\text{SiF}} = 284.8$ Hz), which can easily be prepared by the reaction of trifluoromethanesulfonic acid with SiPh_2F_2 [11], instead of tetrafluorosilane in the coupling reaction, gave similar results. Though there is some evidence for the formation of the desired compound in the NMR- and mass-spectra, we had no success in trying to separate the mixture.

1,1-Diphenyldecamethylcyclohexasilane (II)

A suspension of 18.5 g of lithium (2.64 mol) in 1000 mL THF was heated to reflux. A mixture of 142 g of dichlorodimethylsilane (1.1 mol) and 55.7 g of dichlorodiphenylsilane (0.22 mol) was added dropwise at a rate such that reflux continued without further heating. Excess Li was destroyed by adding 500 mL of a dilute aqueous solution of ammonium chloride. The organic layer was separated and dried over potassium sulfate. The solvent was distilled off and the crude product was fractionated in vacuo. The fraction between 160 and 180°C consisted mainly of $\text{Si}_6\text{Me}_{10}\text{Ph}_2$. Further purification was achieved with liquid chromatography, using a silica gel column and heptane as eluent, giving 11 g (11%) of colorless crystals: mp: 96°C , MS: $m/z = 472$ (M^+). NMR: δ ^1H : 0.16(12H), 0.22(6H), 0.35(12H), 7.15-7.57(10H); δ ^{13}C : -5.29 , -5.24 , -3.93 , 128.62, 129.22, 137.11, 137.18; δ ^{29}Si : -33.67 , -41.18 , -41.99 , -42.28 ; IR [cm^{-1}]: 840sh, 832s, 825s, 795s, 765sh, 725m, 690m, 680sh, 642m, 554vw, 502s, 444m, 390w, 353w, 315vw, 294w, 265m, 255m, 230s, 215s.

1,1-Bis(trifluoromethylsulfonyloxy)-decamethylcyclohexasilane (III)

Two g $\text{Si}_6\text{Me}_{10}\text{Ph}_2$ (4.24 mmol) in 30 mL of hexane was cooled to -30°C . Over a period of 30 minutes

1.27 g trifluoromethanesulfonic acid (8.4 mmol) was added. The solution was then stirred for 2 h at that temperature and allowed to warm to room temperature. No further purification was necessary to convert this product to the fluoro derivative. Because of the extreme sensitivity of this compound, the characterization was done by ^{29}Si -NMR spectroscopy only. ^{29}Si -NMR [ppm]: 47.19(SiTf_2), -35.35, -41.61, -42.11.

1,1-Difluorodecamethylcyclohexasilane (IV)

$\text{Si}_6\text{Me}_{10}(\text{OSO}_2\text{CF}_3)_2$, prepared as described above, was dissolved in 50 mL of diethyl ether and cooled to -30°C . Then 0.5 g of LiF (15.4 mmol) was added and the mixture was allowed to warm to room temperature. The ether was removed in vacuo, 50 mL of petroleum ether was added to the residue, and the salts were filtered off. Purification was achieved by vacuum sublimation at $60^\circ\text{C}/0.04$ Torr. This procedure gave 1 g of colorless crystals; this was a yield of 63% according to the charged 2 g of $\text{Si}_6\text{Me}_{10}\text{Ph}_2$: mp: $42\text{--}44^\circ\text{C}$; NMR δ ^{19}F : -138.06; ^{29}Si : 35.93(SiF_2), -41.96, -42.93, -44.59; $^{19}\text{F}\text{--}^{29}\text{Si}$ couplings: $^1J = 398.1$, $^2J = 15.9$, $^3J = 6.3$ Hz; IR [cm^{-1}]: 835s, 820m, 795s, 770sh, 730w, 688w, 650w, 637m, 575vw, 518s, 435m, 406s, 345vw, 283w, 263s, 250s, 235s; MS [m/z(intensity) fragment]: 356(100) $\text{Si}_6\text{Me}_{10}\text{F}_2$, 341(6) $\text{Si}_6\text{Me}_9\text{F}_2$, 298(23) $\text{Si}_5\text{Me}_8\text{F}_2$, 290(8) $\text{Si}_5\text{Me}_{10}$, 264(22) $\text{Si}_5\text{Me}_7\text{F}$, 232(14) Si_4Me_8 , 217(24) Si_4Me_7 , 202(19) Si_4Me_6 , 187(25) Si_4Me_5 , 174(11) Si_3Me_6 , 157(22) Si_4Me_3 , 131(13) Si_2Me_5 , 116(12) Si_2Me_4 , 73(100) SiMe_3 .

1,1,4,4-Tetraphenyloctamethylcyclohexasilane (V)

A mixture of 666 g of 1,2-dichlorotetramethyldisilane (3.56 mol) and 900 g of dichlorodiphenylsilane (3.56 mol) was added dropwise to a suspension of 100 g of Li powder in 2000 mL of THF at a rate maintaining reflux of the solution. The reaction mixture was cooled with ice and excess Li was destroyed with a dilute aqueous solution of HCl. The organic layer was extracted with petroleum ether and dried over potassium sulfate. After evaporation of the solvent, the oily residue was fractionated in vacuo. The fraction brought off from 150 to 300°C was dissolved in acetone. At a temperature of -30°C , $\text{Si}_6\text{Me}_8\text{Ph}_4$ crystallized together with $\text{Si}_6\text{Me}_{12}$. $\text{Si}_6\text{Me}_{12}$ was then removed by vacuum sublimation at $120^\circ\text{C}/0.1$ Torr. Recrystallization from benzene yielded 20 g (2%) of colorless crystals of $\text{Si}_6\text{Me}_8\text{Ph}_4$: mp: $230\text{--}233^\circ\text{C}$; Anal. (Calcd./Found) for $\text{Si}_6\text{C}_{32}\text{H}_{44}$: C: 64.36/64.19%, H: 7.43/7.36%; ^{29}Si -NMR δ : -33.25(SiPh_2), -40.96; IR/Ra [cm^{-1}]: 832vs/-, 800vvs/-, 730vs/737w,b, -/714vww, 693vs/691s, 680sh/-, -/660s, 645m/642w, 630m/628w,b, -/518m,

505sh/-, 495vs/-, -/473w, 448s/-, 430m/435vw, 405w/408w,sh, 390vw/396vs, 360w/-, 340vw/-, 330vw/331vw, 312vs/312vw, 285mw/283vs, 260m/-, -/239s.

1,1,4,4-Tetrakis(trifluoromethylsulfonyloxy)-octaphenylcyclohexasilane (VI)

The compound was prepared by the same procedure used for compound (III). Starting materials: 1.5 g $\text{Si}_6\text{Me}_8\text{Ph}_4$ (2.52 mmol) in 50 mL of hexane and 1.51 g of trifluoromethanesulfonic acid (10 mmol). ^{29}Si -NMR: δ 36.97, -39.55.

1,1,4,4-Tetrafluorooctamethylcyclohexasilane (VII)

Five ml of diethyl ether was added to the solution described above. After cooling to -30°C , 0.5 g of LiF (19.2 mmol) was added, and the mixture was stirred at this temperature for 3 h. The solvent was evaporated, the residue was suspended in hexane, and the salts were filtered off. Vacuum sublimation of the crude product at $45^\circ\text{C}/0.01$ Torr gave 0.5 g of pure, colorless, crystalline $\text{Si}_6\text{Me}_8\text{F}_4$ (55% according to charged $\text{Si}_6\text{Me}_8\text{Ph}_4$): mp: $67\text{--}69^\circ\text{C}$; NMR: δ ^{19}F : -137.39; ^{29}Si : 35.14(SiF_2), -46.42; $^{19}\text{F}\text{--}^{29}\text{Si}$ couplings: $^1J = 397.0$, $^2J = 16.8$, $^3J = 6.3$, $^4J = 1.5$ Hz; IR [cm^{-1}]: 907m, 845s, 820s, 783s, 755m, 724s, 678m, 645m, 510s, 463w, 417m, 398w, 388m, 350w, 311m, 292w, 280w, 257m, 225m; MS: [m/z(intensity) fragment]: 364(8) $\text{Si}_6\text{Me}_8\text{F}_4$, 349(11) $\text{Si}_6\text{Me}_7\text{F}_4$, 298(9) $\text{Si}_5\text{Me}_8\text{F}_2$, 232(8) Si_4Me_8 , 217(5) Si_4Me_7 , 202(14) Si_4Me_6 , 174(4) Si_3Me_6 , 157(11) Si_4Me_3 , 131(6) Si_2Me_5 , 116(8) Si_2Me_4 , 101(9) Si_2Me_3 , 73(100) SiMe_3 .

NMR INVESTIGATIONS

The characterization of the synthesized new cyclohexasilanes is mainly based on NMR spectroscopy. Therefore the assignment of all ^{29}Si chemical shifts is done by the determination of the $^{29}\text{Si}\text{--}^{29}\text{Si}$ coupling constants between one and two bonds (Table 1). The $^1J_{\text{SiSi}}$ are measured by the INADEQUATE-technique we described previously [12], and $^2J_{\text{SiSi}}$ are determined by INEPT-INADEQUATE [13]. In combination with the known molecular weights (derived from the mass-spectra) these data give sure proof of the proposed ring structures. Looking to the fluoro-derivatives, this problem can also be solved by analyzing the $^{19}\text{F}\text{--}^{29}\text{Si}$ couplings.

The example of the 1,1-diphenyl-derivative shows that all of the ^1H and ^{13}C chemical shifts can be determined with two-dimensional $^{29}\text{Si}\text{--}^1\text{H}$ and $^{13}\text{C}\text{--}^1\text{H}\text{--}J$ correlation spectroscopy, provided the silicon chemical shifts are assigned. Therefore, the proton resonances are assigned with a 2D- $^{29}\text{Si}\text{--}^1\text{H}$ -DEPT sequence first [14] and then the carbon chem-

TABLE 1 ^{29}Si -Chemical Shifts (Relative to TMS) and Silicon-Silicon Coupling Constants [Hz] of the New Cyclohexasilane-Derivatives

Compound	$\delta_{\text{Si}1}$	$\delta_{\text{Si}2}$	$\delta_{\text{Si}3}$	$\delta_{\text{Si}4}$	$^1J_{1,2}$	$^1J_{2,3}$	$^1J_{3,4}$	$^2J_{1,3}$	$^2J_{2,4}$
II(Ph)	-33.67	-41.99	-41.18	-42.28	60.1	58.5	61.5	9.6	9.5
III(triflate)	47.19	-35.35	-41.61	-42.11	48.8	60.5	— ^a	16.2	9.2
IV(F)	35.93	-44.59	-42.93	-41.96	77.6	— ^b	— ^a	15.1	9.5
V(Ph)	-33.26	-40.74	—	—	60.1	—	—	9.6	—
VI(triflate)	36.97	-39.55	—	—	58.8	—	—	13.6	—
VII(F)	35.14	-46.42	—	—	71.3	—	—	14.6	—

^a These values can not be measured because of the small shift difference.

^b Because of the ^{19}F - ^{29}Si -coupling the signals are overlapping so that the silicon-silicon coupling can not be determined.

Assignment of the ^1H - and ^{13}C -chemical shifts (relative to TMS) of compound II:

^1H : 2- CH_3 0.35, 3- CH_3 0.16, 4- CH_3 0.22, o-H 7.19, m-H 7.59, p-H 7.13;

^{13}C : 2- CH_3 -3.93, 3- CH_3 -5.29, 4- CH_3 -5.24, C-*i* 137.18, C-*o* 128.62, C-*m* 137.11, C-*p* 129.22.

ical shifts are assigned (modified 2D-DEPT sequence, giving a fully proton decoupled ^1H -NMR spectrum in the F1 projection [15]).

All spectra were recorded on a Bruker MSL 300 instrument equipped with a 10 mm selective ^{29}Si probe operating at 59.627 MHz, and with a 10 mm broadband probe. To get a suitable signal to noise ratio in a moderate time, 0.5 to 0.7 g of the samples were dissolved in 2 mL deuteriobenzene. Working with these concentrations, it was necessary to accumulate 600 FID's for the INADEQUATE spectra using a relaxation delay of 50 seconds and 320 FID's for the INEPT-INADEQUATE spectra with a delay of 6 seconds. Sample temperature was 20°C (70°C for $\text{Si}_6\text{Me}_8\text{Ph}_4$ because of its low solubility). Pulse width was 6000 Hz in all cases using a block size of 16 k data points.

The 2D-spectra were obtained with data matrices of 1 * 0.5 k data points. Therefore 256 rows each with 8 FID's had to be recorded. The resolution in the F1 dimension is enhanced by Gauß-multiplication.

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