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SILICON-CONTAINING HETEROCYCLIC COMPOUNDS
IV*. PREPARATION AND CHARACTERIZATION OF 1,6-DISILA[4.4.4]-PROPELLANE AND RELATED COMPOUNDS. EVIDENCE FOR A (TRIALKYLSILYL)MAGNESIUM COMPOUND

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SUMMARY

The reaction of 4a,8a-dichloro-4a,8a-disiladecalin with $ClMg(CH_2)_4MgCl$ in tetrahydrofuran gave the title compound (4% yield) along with 10-butyl-5,10-disilaspiro [4.9]tetradecane (12% yield). Strong evidence has been obtained for the latter product having arisen from a silicon–magnesium compound formed as a fairly stable species. The disilapropellane absorbs ultraviolet light at 212 nm.

INTRODUCTION

As part of a continuing program to investigate the stereochemistry of silicon–silicon containing heterocyclic compounds[1-3], we report here the preparation of 1,6-disilatricyclo[4.4.4.$0^{1,6}$]tetradecane (V), hereafter named 1,6-disila[4.4.4]propellane according to the "propellane" nomenclature[4].

In our previous papers[2,3], it was mentioned that a substantial amount of strain is involved in a silicon–silicon containing six-membered heterocycle. Indeed, inspection of molecular models reveals that the tricyclic compound (V) is highly strained. However, it may become strain-free if both the silicon atoms assume trigonal bipyramidal configuration with either of them coinciding with an apical position of the other bipyramid (Fig. 1). This shape of the molecule will provide each silicon atom with a vacant, relatively low energy orbital available for the attack of an electron-donating agent. With this in mind, we initiated the studies.

RESULTS AND DISCUSSION

The preparative route is summarized in Scheme 1, and new compounds together with their physical properties and analytical data are listed in Table 1.

1,1,2,2-Tetraphenyl-1,2-disilacyclohexane (I), which has been reported as unpublished work by Gilman *et al.*[5], and its precursors were prepared by the reported

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[*] For Part III see ref. 3b.
[**] On leave from Toray Industries Inc., Apr. 1969–Aug. 1970.

SCHEME 1

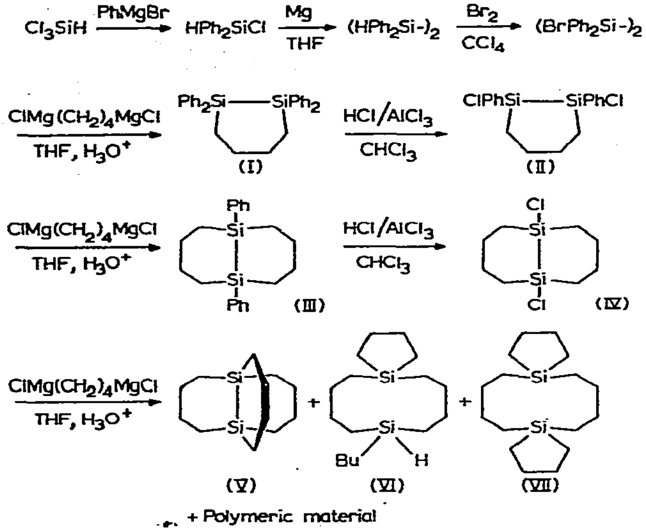


TABLE 1

PHYSICAL PROPERTIES AND ANALYTICAL DATA FOR NEW COMPOUNDS

Compound	No.	M.p. (°C)	B.p. (°C/mm)	C (%)		H (%)	
				Found	(Calcd.)	Found	(Calcd.)
$C_{16}H_{18}Cl_2Si_2$	(II)	68–69.5	148–151/0.03	56.77	(56.96)	5.61	(5.38)[a]
$C_{20}H_{26}Si_2$	(III)	104–105	*ca.* 188–190/4	74.45	(74.46)	8.34	(8.12)
$C_8H_{16}Cl_2Si_2$	(IV)	29.5–31.0	90/4	40.07	(40.15)	6.85	(6.74)[b]
$C_{12}H_{24}Si_2$	(V)	114–115.5		64.41	(64.20)	10.92	(10.78)
$C_{16}H_{34}Si_2$	(VI)		124–126/1[c]	67.74	(68.00)	12.10	(12.12)
$C_{16}H_{32}Si_2$	(VII)	89.5–90.5		68.69	(68.49)	11.38	(11.49)
$C_{17}H_{36}Si_2$	(IX)		124–126/1	69.13	(68.83)	12.24	(12.23)
$C_{10}H_{22}Br_2Si_2$	(X)	105–109	118–122/1	33.86	(33.52)	6.22	(6.19)[d]
$C_{18}H_{40}Si_2$	(XI)		132–134/2[e]	69.30	(69.14)	12.84	(12.89)

[a] Cl, 21.39 (21.02). [b] Cl, 29.98 (29.63). [c] n_D^{20} 1.5050; d_4^{20} 0.9207; MR_D found 91.05, calcd. 91.32. [d] Br, 45.38 (44.61). [e] n_D^{20} 1.4834; d_4^{20} 0.8785; MR_D found 101.72, calcd. 102.35.

methods[6,7]. 1,2-Dichloro-1,2-diphenyl-1,2-disilacyclohexane (II) was prepared in 76% yield by aluminum chloride catalyzed chlorodephenylation of (I) by hydrogen chloride in chloroform at room temperature. This reaction proceeded with cleavage of only one phenyl group from each silicon atom.

4a,8a-Diphenyl-4a,8a-disiladecalin (III) was obtained in 76% yield from (II) by treatment with the di-Grignard reagent from 1,4-dichlorobutane in tetrahydrofuran (THF). The product was homogeneous by GLC whereas analogously prepared *cis*- and *trans*-4a,8a-dimethyl-4a,8a-disiladecalin (VIII)[3] were distinguishable. It has previously been described[3] that the ^1H NMR spectrum of *cis*-(VIII) shows two distinct groups of multiplet bands due to the ring methylene hydrogens whereas that of *trans*-(VIII) exhibits a much more complex pattern. In view of the NMR spectrum of (III) where the methylene hydrogen resonances appear in two discrete groups of

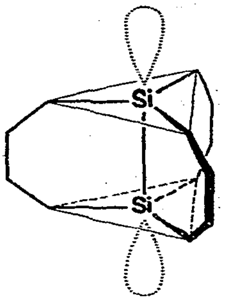


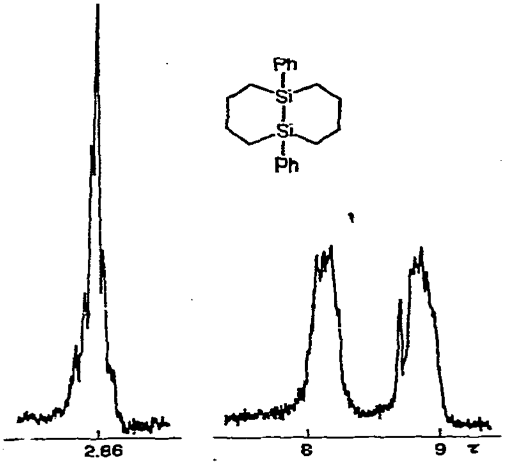
Fig. 1. A strain-relieved model of 1,6-disila[4.4.4]propellane with two trigonal-bipyramidal silicon atoms.

multiplets (Fig. 2), it may have the *cis* configuration.

Chlorodephenylation of (III) by hydrogen chloride in the presence of aluminum chloride in chloroform gave 4a,8a-dichloro-4a,8a-disiladecalin (IV) in 89% yield.

Isomer ratios in compounds (II) and (IV) are not clear, because, despite they were both homogeneous by GLC, upon methylation a mixture of *cis* and *trans* isomers was obtained in either case, *i.e.*, known *cis*- and *trans*-1,2-diphenyl-1,2-dimethyl-1,2-disilacyclohexane[2] in the ratio of *ca.* 6/1 from (II) while *cis*- and *trans*-(VIII)[3] in the ratio of *ca.* 3/1 from (IV).

The reaction of compound (IV) with tetramethylenedimagnesium dichloride in THF afforded mainly non-volatile, polymeric material (*ca.* 70%). However, from the volatile fraction consisting of several products, we could isolate by preparative GLC 1,6-disila[4.4.4]propellane (V) in 4% yield, together with 10-butyl-5,10-disilaspiro[4.9]tetradecane (VI) in 12% yield, and possibly 5,10-disiladispiro[4.4.4.4]-octadecane (VII) in 3% yield, in the pure state.



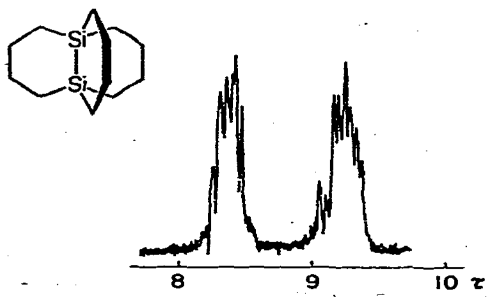


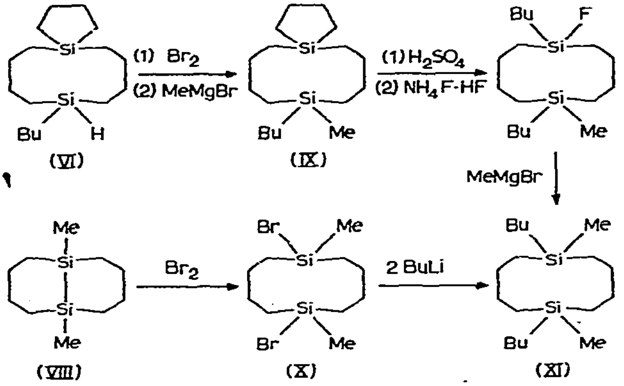
Fig. 2. ^{1}H NMR spectrum of 4a,8a-diphenyl-4a,8a-disiladecalin in carbon tetrachloride at room temperature (60 Mc).

Fig. 3. ^{1}H NMR spectrum of 1,6-disila[4.4.4]propellane in carbon tetrachloride at room temperature (60 Mc).

Compound (V) is stable in air, whose NMR spectrum at room temperature shows two groups of multiplets due to methylene hydrogens (Fig. 3). It has an UV absorption maximum at 211.5 nm in cyclohexane (ε 7700) and acetonitrile (ε7100) showing a bathochromic shift of some 20 nm from hexamethyldisilane (near 198 nm, ε 8500–7230^8 or 193.5 nm, ε 10800^9). This absorption may be attributed to either the destabilization of the ground state due to the internal strain involved in the molecule or the appearance of low lying vacant level(s) owing to the rehybridization involving *d* orbitals which may occur in order to reduce the ring strain as mentioned above, or to both of these two effects. Details will be discussed elsewhere in connection with the absorption properties of related cyclic compounds.

The presence of the silacyclopentane ring(s) in compounds (VI) and (VII) was established by a group absorption bands in the IR spectra characteristic of such a ring, for which Nametkin *et al.*^{10} reported a medium band at 1075 and a weak doublet at 1030 and 1020 cm^{-1}. The IR spectrum of (VI) showed also the intense absorption of ν(Si–H) at 2090 cm^{-1} and its NMR spectrum displayed a multiplet resonance near τ 6.3 due to a hydrogen linked to silicon in addition to multiplets due to the ring methylene hydrogens. Crucial evidence for the structure of (VI) could be obtained by converting it into 1,6-dibutyl-1,6-dimethyl-1,6-disilacyclodecane (XI), an authentic sample of which was prepared independently from 4a,8a-dimethyl-4a,8a-disiladecalin (VIII)^3 (Scheme 2).

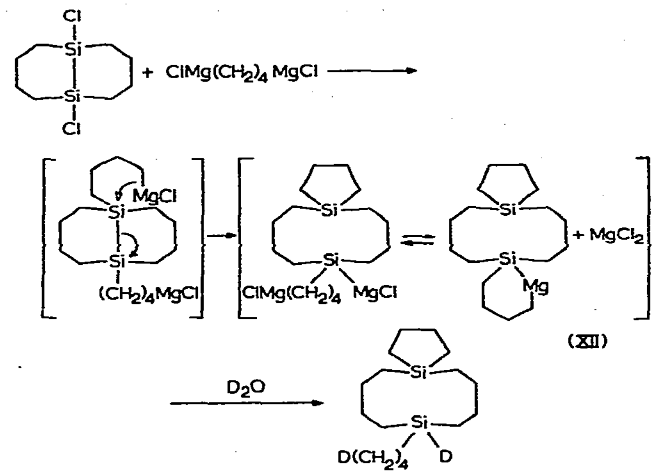
SCHEME 2



Compound (VI) reacted with one equivalent of bromine with evolution of hydrogen bromide to give, after treatment with methylmagnesium bromide, 10-butyl-10-methyl-5,10-disilaspiro[4.9] tetradecane (IX), survival of the silacyclopentane ring being again shown by the IR spectrum. The action of concentrated sulfuric acid on (IX), as well-known^{11}, invoked fission of the five-membered ring, and successive treatments with ammonium hydrogen fluoride and with a methyl Grignard reagent led to compound (XI). Its IR spectrum showed that the silacyclopentane ring was no longer present.

The production of (VI) may suggest that a trialkylsilylmagnesium compound is formed from cleavage of the silicon–silicon bond by the action of the Grignard reagent, which leads to the observed Si–H compound upon hydrolysis. In fact, work-up of the reaction mixture with deuterium oxide in place of water afforded a dideuterated

SCHEME 3



counterpart of compound (VI) containing one Si–D and one C–D bond on the terminal carbon atom of the butyl group (Scheme 3). Structure proof came from IR studies showing the appearance of the Si–D stretching frequency at 1525 cm^{-1} and the weak C–D stretching at 2175 cm^{-1} at the cost of the disappearance of the intense band at 2090 cm^{-1} due to the Si–H stretching and the weak peak at 1380 cm^{-1} due to symmetric deformation of the terminal methyl group. The NMR spectrum also revealed no proton resonance near τ 6.3.

The intermediate formation of silyl Grignard reagents has thus far been postulated several times (for a review see *e.g.* ref. 12), for example, in the coupling of triphenylchlorosilane to hexaphenyldisilane by cyclohexylmagnesium bromide in THF[13], in the synthesis of disilanes from aryl-containing monohaloorganosilanes with magnesium in THF[6], for the formation of dimethylphenylsilane from the action of methylmagnesium iodide on pentaiodopentaphenylcyclopentasilane, $(PhISi)_5$, in benzene/ether[14], and in other cases[15–18]. It is generally recognized that aromatic groups on silicon can stabilize silyl anions and appear necessary for the formation of organosilylalkali compounds[19] and silyl Grignard reagents[13]. To our knowledge, the silyl Grignard reagent (XII) is the first fully substantiated case of so stable a silicon–magnesium bond as to survive even under reflux conditions of THF despite the silicon atom linking to magnesium bears only alkyl groups but no aryl ones.

EXPERIMENTAL

All reactions were carried out under nitrogen atmosphere. Diphenylchlorosilane was prepared in about 65% yield by adding phenylmagnesium bromide in ether to a solution of trichlorosilane in benzene. *sym*-Tetraphenyldisilane and *sym*-tetraphenyldibromodisilane were synthesized as described in refs. 6 and 7. Infrared spectra were measured on a Hitachi EPI-G3 grating spectrophotometer. NMR spectra were obtained on a JEOL Model C-60H spectrometer in carbon tetrachloride solution with benzene or TMS as an internal standard. UV spectra were measured on a Hitachi EPS-3T spectrophotometer. Molecular weights were obtained from mass spectra measured on a Hitachi RMS-4 mass spectrometer. A Varian Aerograph Model 90P, equipped with a 20 ft column packed with Apiezon-L (20% on Celite), was used for isolation and purification.

1,1,2,2-*Tetraphenyl*-1,2-*disilacyclohexane* (*I*)

In a 2-l three-necked flask, equipped with a reflux condenser, a stirrer and a pressure-equalizing addition funnel, was prepared a Grignard solution from 22.9 g (0.18 mole) of 1,4-dichlorobutane, 10.5 g (0.43 g-atom) of magnesium and 200 ml of THF. After 4-h reflux, the solution was diluted with THF up to 1.7 l. A solution of 52.4 g (0.10 mole) of *sym*-tetraphenyldibromodisilane in 300 ml of THF was added with stirring at room temperature over a period of 4 h. After the addition was completed, the reaction mixture was refluxed for 65 h. Solvent was removed by distillation and the remainder was hydrolyzed with dilute hydrochloric acid. The resulting organic layer and ether extracts from the aqueous layer were combined, washed with water and saturated solution of sodium bicarbonate, and dried over potassium carbonate. After removal of solvents, volatile materials were evaporated under reduced pressure up to 60°/6 mm. Recrystallization of the remaining mass from ethanol (*ca.* 300 ml) gave 32 g (76% yield) of (I) as white needle crystals. A second run carried out in essentially the same way, except for a shorter reflux period of 18 h, resulted in a slightly poorer yield (68%). Use of 1,4-dibromobutane in place of the chloride also led to poorer yield (52%). M.p. 109–110° (lit.[5] 110–111°).

1,2-*Diphenyl*-1,2-*dichloro*-1,2-*disilacyclohexane* (*II*)

In a 500-ml three-necked flask, equipped with a gas inlet tube, a stirrer and a reflux condenser the top of which was protected with a drying tube, was placed a mixture of 42.1 g (0.10 mole) of compound (I), 500 ml of chloroform and 2.0 g of aluminum chloride. Into the stirred mixture was passed dry hydrogen chloride at room temperature. Slightly exothermic reaction occurred. The extent of the reaction was monitored by GLC analysis (Apiezon-L, 10% on Celite 545 at 290–300°) of small samples extracted periodically from the reaction mixture. After about 12 h, the starting substance disappeared with the formation of a single product homogeneous by GLC. At this point the introduction of hydrogen chloride was discontinued and *ca.* 10 ml of acetone was added to the mixture for the purpose of deactivating the catalyst. After standing overnight, acetone/aluminum chloride complex was removed by filtration. Removal by distillation of the solvent and benzene produced during the reaction, followed by distillation of the residue through a short Vigreux column gave 25.5 g (75.5% yield) of (II) as a brown crystallizable material. The colored product was pure enough for the purpose of the next cyclization reaction and used without any further purification.

The colored matter (25.5 g) was dissolved in 50 ml of dry hexane and treated with activated carbon at 40–50° for 2 h. After filtration, the filtrate was cooled at −20 to −30° for about 5 h, giving 12 g (36%) of the colorless product.

4*a*,8*a*-*Diphenyl*-4*a*,8*a*-*disiladecalin* (*III*)

The reaction was carried out in essentially the same manner as described in the preparation of compound (I) except for use of 33.7 g (0.10 mole) of compound (II) in place of *sym*-tetraphenyldibromodisilane and 6 days' reflux of the reaction mixture. Work-up and subsequent recrystallization from ethanol (*ca.* 350 ml) afforded 24.5 g (76% yield) of compound (III) as white cubic crystals. GLC (Apiezon-L, 10% on Celite 545, 8 ft, at 280°) showed a single peak, indicating that the product contained only one isomer of *cis* and *trans* isomers, since the two isomers of its methyl analog, *i.e.* 4a,8a-dimethyl-4a,8a-disiladecalin (VIII), were distinguishable on the same column. In the light of the whole pattern of the NMR spectrum due to methylene hydrogens which fell into two groups, the product was considered to be the *cis* isomer.

4a,8a-Dichloro-4a,8a-disiladecalin (IV)

In a similar manner to that described in the preparation of compound (II), 20 g (0.062 mole) of (III) in 100 ml of chloroform was chlorodephenylated in the presence of *ca.* 1 g of aluminum chloride by passing dry hydrogen chloride at room temperature for 10 h. Work-up in the usual way and subsequent distillation gave 13.1 g (89% yield) of (IV) boiling mainly at 90°/5 mm. The colorless product thus obtained was homogeneous by GLC and crystallized upon cooling.

Methylation of (II)

To 5.0 g (14.8 mmole) of (II), purified by recrystallization from n-hexane, was added a large excess of methylmagnesium bromide (*ca.* 100 mmole) in ether (70 ml). After reflux for 4 h, the mixture was worked up and distilled to give 3.8 g (87% yield) of 1,2-diphenyl-1,2-dimethyl-1,2-disilacyclohexane, b.p. 178–183°/7 mm, as a 6/1 mixture of *cis* and *trans* isomers.

Methylation of (IV)

Compound (IV) (0.24 g; 1 mmole), which was homogeneous by GLC, was allowed to react with excess methylmagnesium bromide in ether/THF solvent. After 30-h reflux, and subsequent hydrolysis, GLC analysis of the resulting organic layer showed the formation of a *cis* and *trans* mixture (3/1) of 4a,8a-dimethyl-4a,8a-disiladecalin.

Reaction of (IV) with $ClMg(CH_2)_4MgCl$ in THF

In essentially the same manner as described in the preparation of compound (I), 12 g (0.05 mole) of 4a,8a-dichloro-4a,8a-disiladecalin (IV) was reacted with a Grignard reagent prepared from 11.4 g (0.09 mole) of 1,4-dichlorobutane and 5.3 g (0.218 g-atom) of magnesium in 1 l of THF. The reaction mixture was refluxed for 5 days. Work-up followed by distillation gave two fractions: (1) b.p. up to 170°/5 mm, 1.7 g and (2) b.p. 170–175°/5 mm, 3.9 g, leaving 8.0 g of nonvolatile viscous residue. A major product in the fraction (1) was isolated by preparative GLC (280°). The crystals (0.45 g, 4% yield) thus obtained were recrystallized from methanol and then ethanol, and identified as 1,6-disila[4.4.4]propellane (V) (mol. wt. found 224; $C_{12}H_{24}Si_2$ calcd. 224.50). A major product in the fraction (2) was isolated as a colorless liquid (1.7 g, 12% yield) by preparative GLC (280°) and was identified as 10-butyl-5,10-disilaspiro[4.9]tetradecane (VI) (mol. wt. found 282; $C_{16}H_{34}Si_2$ calcd. 282.63). The IR spectrum indicated the presence of the Si–H bond (2090 cm^{-1}) and the silacyclopentane ring (1027, 1033 and 1080 cm^{-1}). A minor product isolated from the fraction (2) was recrystallized from ethanol (0.4 g, 3% yield) and identified as 5,10-

disiladispiro[4.4.4.4]octadecane (VII) (mol. wt. found 280; $C_{16}H_{32}Si_2$ calcd. 280.61).

Reaction of (VI) with bromine followed by methylation

To a solution of 1.6 g (5.7 mmole) of (VI) in 10 ml of carbon tetrachloride was added dropwise a solution of bromine (0.9 g; 5.7 mmole) in 10 ml of carbon tetrachloride with cooling in an ice bath, under vigorous stirring. The red color immediately disappeared with evolution of hydrogen bromide. Addition of slight excess bromine caused to leave the red color, indicating the presence of only one Si–H bond and the absence of Si–Si bond in the starting material. The solvent was evaporated at reduced pressure, and the remaining viscous oil was treated with a large excess of methylmagnesium bromide in ether (ca. 50 mmole). After 3-h reflux, the reaction mixture was worked up in the usual way and then distilled to give a colorless liquid (IX, 1.2 g) boiling mainly at 124–126°/1 mm, which was homogeneous by GLC. The IR spectrum was almost identical with that of the starting material except for the disappearance of the absorption at 2090 cm^{-1} [ν(Si–H)] and the appearance of a strong band at 1250 cm^{-1} indicative of the presence of the $Si–CH_3$ group.

Reaction of compound (IX) with concentrated sulfuric acid followed by treatment with ammonium hydrogen fluoride and then with a methyl Grignard reagent

A mixture of 1.0 g of (IX) diluted with benzene (15 ml) and 30 g of concentrated sulfuric acid was stirred vigorously at 25–30°. The extent of the reaction was followed by GLC analysis of small samples extracted from the organic layer. After 15 h, the starting material disappeared from the organic phase. At that point, under cooling in an ice bath, 5 g (0.088 mole) of ammonium hydrogen fluoride was added in several portions. GLC analysis of the resulting organic layer showed the formation of a product different from the starting material, together with two products in small amounts. The organic layer and extracts (benzene 30 ml) from the acid layer were combined and the solvent was removed by distillation. To the remaining oil was added a large excess of methylmagnesium bromide in ether (*ca.* 50 mmole). Work-up, distillation (0.9 g, up to 140°/2 mm) and subsequent purification by preparative GLC afforded 0.2 g of (XI), its IR and NMR spectra and the retention time on GLC being identical with those of the authentic sample, prepared below.

1,6-*Dibromo*-1,6-*dimethyl*-1,6-*disilacyclodecane* (*X*)

To a solution of 6.0 g (30 mmole) of 4a,8a-dimethyl-4a,8a-disiladecalin (VIII; *cis*/*trans* mixture) in 30 ml of carbon tetrachloride was added a solution of 4.8 g (30 mmole) of bromine in 20 ml of carbon tetrachloride with cooling in an ice bath. The red color immediately disappeared. After removal of carbon tetrachloride by distillation, the reaction mixture was distilled to give 7.0 g (66 %) of (X) as white crystals.

1,6-*Dibutyl*-1,6-*dimethyl*-1,6-*disilacyclodecane* (*XI*)

A solution of butyllithium in hexane (60 mmole) was added to a solution of 6.3 g (17.6 mmole) of 1,6-dibromo-1,6-dimethyl-1,6-disilacyclodecane (X) in 50 ml of ether in the cold over 20 min and the mixture was stirred at room temperature for 5 h. After hydrolysis with dilute hydrochloric acid and subsequent work-up in the usual way, distillation at reduced pressure gave 5.0 g (91 % yield) of (XI) in a slightly impure state. Repeated distillation afforded a pure sample boiling mainly at 132–134°/2 mm.

Reaction of (IV) with $ClMg(CH_2)_4MgCl$, followed by treatment with deuterium oxide

Compound (IV) (1.6 g; 6.7 mmole) was added to an excess of the Grignard reagent, prepared from 6.3 g (49.6 mmole) of 1,4-dichlorobutane and 3.0 g (123.4 mmole) of magnesium in 400 ml of THF. After reflux for 8 h, the reaction mixture was treated with 8.0 g (0.4 mole) of deuterium oxide. The resulting salt and excess magnesium were filtered and washed with 200 ml of ether. The organic layer was distilled to give 0.5 g of a liquid boiling over the range of 100–140°/2 mm, leaving 1.2 g of residue. From the above fraction a product with the same retention time on GLC as that of compound (VI) was isolated by preparative GLC and identified as 10-deutero-10-(4-deuterobutyl)-5,10-disilaspiro[4.9]tetradecane (mol. wt. found 284: $C_{16}H_{32}D_2Si_2$ calcd. 284.63). In the IR spectrum, two new peaks were observed to appear at 2175 cm^{-1} (w) and 1525 cm^{-1} (s) owing to ν(C–D) and ν(Si–D), respectively, with almost disappearance of an intense band at 2090 cm^{-1} due to ν(Si–H) and of a weak peak at 1380 cm^{-1} due to symmetric deformation of the terminal methyl group. The pattern of other part of the spectrum was essentially the same as that of (VI). The ^1H NMR spectrum also revealed the absence of the silicon–hydrogen bond, since no signals occurred near τ 6.3.

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