[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF PURDUE UNIVERSITY, LAFAYETTE, IND.]

Aromatic Silicon Systems. I. The Preparation and Characterization of Silacyclopentadiene

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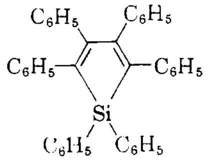
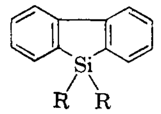
Problems concerned with the synthesis and characterization of a new class of organosilicon compounds, the silacyclopentadienes, are discussed. The principal infrared absorption bands of twelve different silacyclic structures are recorded.

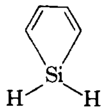
The chemical literature does not contain many examples of cyclic silicon compounds which contain functional groups attached to the carbon atoms of the ring. The reason for this void becomes apparent when one considers the difficulties inherent in the syntheses of such compounds.

The most common laboratory method of forming a silicon–carbon bond involves coupling of a silicon halide with an appropriate organometallic.[1] The latter is most often the Grignard[2] reagent or a more reactive organometallic like an organolithium[3] or organosodium[4] compound. Quite obviously the use of such reactive organometallics does not permit the functional group to be a part of the organometallic molecule which is undergoing coupling with silicon halide. Hence, it is generally not feasible to have groups such as carbonyl, nitro, amino etc. present during the coupling of the silicon halide with the organometallic.[5]

In recent years, several successful syntheses of silacyclic compounds containing unsaturation have been reported. Thus Petrov[6] has reported the synthesis of 1,1-dichloro-3-silacyclopentene by passage of 1,4-dichloro-*cis*-2-butene over a silicon–copper alloy.[7] Recently 1,1-dimethyl-3-silacyclopentene was prepared by the reaction of butadiene with dimethyldichlorosilane and sodium.[8] Fessenden prepared 1,1-dimethyl-2-silacyclopentene in low yield by the photochlorination of 1,1-dimethylsilacyclopentane, followed by treatment with quinoline.[9] Braye and Hübel have prepared hexaphenylsilacyclopentadiene (I) by the reaction of 1,4-dilithio-1,2,3,4-tetraphenylbutadiene with diphenyldichlorosilane.[10] Also Gilman has shown that α,α'-dilithiodiphenyl reacts with R_2SiCl_2 compounds to yield sila-fluorenes[11] such as compound II. Neither of these latter two routes seem applicable to the synthesis of silacyclopentadiene (III) itself.


I

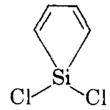

II


III

As a result of a research program designed to test the feasibility of incorporating the silicon atom into an aromatic ring system,[12] we thought it desirable to attempt the preparation of silacyclopentadiene (III). In this paper we are reporting our success in preparing and characterizing this novel silicon heterocyclic system.

Results

From the outset of our project, the synthesis of 1,1-dichlorosilacyclopentadiene (IV) was deemed a desirable target. There seemed to be little

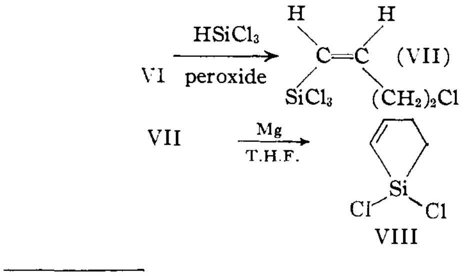

IV

doubt that compound IV would undergo reduction with lithium aluminum hydride to III, a supposition which later proved to be correct.

The first reaction sequence we attempted in the preparation of compound IV is

$$HC\equiv C{-}(CH_2)_2OH \xrightarrow{TsCl} HC\equiv C{-}(CH_2)_2OTs\,(V) \quad (1)$$

$$V \xrightarrow{LiCl} HC\equiv C(CH_2)_2Cl\,(VI) \quad (2)$$



(3)

(4)

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(1) C. Friedel and J. M. Crafts, *Ann.*, **127**, 28 (1863); C. Pape, *Ber.*, **14**, 1874 (1881).

(2) F. S. Kipping, *Proc. Chem. Soc.*, **20**, 15 (1904); F. S. Kipping, *J. Chem. Soc.*, **91**, 209 (1907); F. P. Price, *J. Am. Chem. Soc.*, **69**, 2600 (1947).

(3) R. F. Fleming, U. S. Patent 2,386,452 (1945); H. Gilman and R. N. Clark, *J. Am. Chem. Soc.*, **68**, 1675 (1946).

(4) W. C. Schumb and C. M. Saffer, *ibid.*, **63**, 93 (1941); L. H. Sommer and N. S. Marans, *ibid.*, **73**, 5135 (1951).

(5) There are a few exceptions to this statement. Halogen–metal exchange reactions between *n*-butyllithium and aromatic halides containing certain functional groups followed by coupling with a silicon halide are occasionally successful. See R. A. Benkeser and H. R. Krysiak, *J. Am. Chem. Soc.*, **76**, 599 (1954), where *o*-trimethylsilylbenzoic acid was prepared in this way.

(6) A. D. Petrov, G. I. Nikishin, N. P. Smetankina and Y. P. Egorov, *Bull. Acad. Sci. U.S.S.R., Div. Chem. Sci.*, 861 (1955) (English translation).

(7) The yield of product is apparently low, since we experienced difficulty in reproducing the experiment as described.

(8) Abstracts of the Fall Meeting of the American Chemical Society, Chicago, Ill., 1961, p. 31Q.

(9) R. Fessenden and F. J. Freenor, *J. Org. Chem.*, **26**, 2003 (1961).

(10) E. H. Braye, W. Hübel and I. Caplier, *J. Am. Chem. Soc.*, **83**, 4406 (1961).

(11) H. Gilman and R. D. Gorsich, *ibid.*, **80**, 3243 (1958).

(12) R. A. Benkeser, R. F. Grossman and G. M. Stanton, *ibid.*, **83**, 3716 (1961); **83**, 5029 (1961).

Presumably treatment of VIII with sulfuryl chloride and peroxide followed by thermal elimination of hydrogen chloride would yield 1,1-dichlorosilacyclopentadiene (IV). In reality this entire sequence, although presumably feasible, was never carried through to completion when it became apparent that the over-all yield of IV would be prohibitively low by this method.

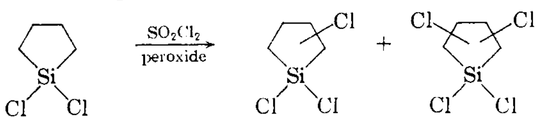
The synthesis of *cis*-1-trichlorosilyl-4-chloro-1-butene (VII) is worthy of some comment. Earlier work from this Laboratory[13] had shown that peroxide-catalyzed additions of trichlorosilane to substituted acetylenes produces predominantly *cis* products *via* a *trans* addition. Vapor phase chromatographic analysis of the product obtained from reaction 3 above disclosed two peaks in the ratio of 85/15, representing the *cis* and *trans* isomers, respectively. Such a ratio was quite in accord with our earlier findings.

The ring closure with magnesium (reaction 4 above) leading to 1,1-dichlorosila-2-cyclopentene (VIII) proved difficult and only a 28% yield of product was realized. Attempts to use diethyl ether as a solvent failed entirely, although Sommer[14] was successful in closing saturated silacyclic rings by this method. Likewise the use of sodium sand in toluene or distillation from zinc dust proved ineffective. However, the cyclization did proceed slowly upon prolonged reflux with magnesium in tetrahydrofuran.

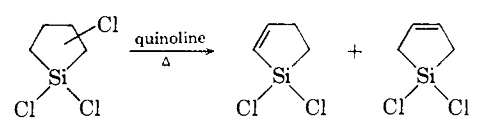
The infrared spectrum of VIII showed a $>C{=}C<$ band at 6.25 μ. This shift to longer wave lengths is probably the result of "conjugation" of the π-electron system of the olefin with the vacant 3d-orbitals of the silicon atom.[15] This band later proved very useful in detecting the presence of VIII in a mixture with 1,1-dichlorosila-3-cyclopentene ($>C{=}C<$ band at 6.1μ) and compound IV ($>C{=}C<$ band at 6.4 μ).

The synthesis which ultimately proved successful for silacyclopentadiene (III) employed 1,1-dichlorosilacyclopentane[16] (IX) as the starting material.

Treatment of IX with two equivalents of sulfuryl chloride and catalytic amounts of benzoyl peroxide yielded a monochlorination product (X) and a dichlorination product (XI). Products X and XI could be separated rather easily by fractionation since they differed in boiling points by about twenty degrees. A vapor phase chromatogram of X indicated that it was a mixture of both the α- and β-isomers in an approximate ratio of 1:9. The identity of these two isomers could be established by dehydrohalogenating the monochlorination mixture X with quinoline. Vapor phase chromatography disclosed that the olefinic product of this reaction was a two-component mixture. One of the components had a retention time identical to the authentic sample of 1,1-dichlorosila-2-cyclopentene (VIII) made previously and comprised 22% of the mixture. The other component, comprising 78% of the mixture, could only be 1,1-dichlorosila-3-cyclopentene (XII). An infrared spectrum of this mixture showed absorbance at 6.1 μ (medium) and 6.25 μ (weak). Since a sample of pure VIII was shown to absorb at 6.25 μ, the infrared data tended to substantiate the analytical results by V.P.C. Since compound XII (which comprises 78% of the dehydrohalogenation mixture) can arise only from the dehydrohalogenation of the β-isomer of X, while VIII (22%) could arise from ***both*** the α- and β-isomers of X, one must conclude that the chlorination of IX leads predominately to the β-isomer. From the vapor phase chromatographic analysis of X, it can be concluded, therefore, that the β- to α-chloro isomers are present in a 9:1 ratio. Recently[9] it was reported that photochlorination of 1,1-dimethylsilacyclopentane yields almost equal amounts of α- and β-isomers. Presumably, in our case, the electron-withdrawing (-I) inductive effect of the two chlorine atoms attached to silicon are of predominant importance in discouraging chlorine atom attack at the α-positions. Whitmore[17] and coworkers have reported that chlorination of ethyltrichlorosilane and *n*-propyltrichlorosilane gives a beta:alpha monochloro ratio of about 3:1 which is in rough agreement with our findings.

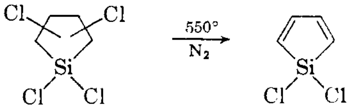


IX X XI



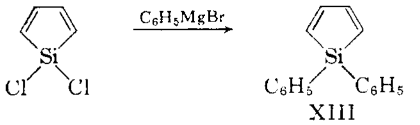
X VIII XII

Treatment of the dichlorination fraction XI (obtained in 48% yield) with quinoline yielded only silicon tetrachloride and tar. On the other hand, thermal dehydrochlorination at 550°, under nitrogen, yielded the desired 1,1-dichlorosilacyclopentadiene (IV) in yields of 60–70%.



XI IV

1,1-Diphenylsilacyclopentadiene.—1,1-Dichlorosilacyclopentadiene, like practically all chlorosilanes, undergoes facile displacement of its halogens by nucleophilic reagents. It reacts with the phenyl Grignard reagent to form 1,1-diphenylsilacyclopentadiene (XIII).



XIII

The structure of compound XIII was proved by reducing it with hydrogen over a platinum catalyst. It absorbed the theoretical amount of hydrogen and yielded 1,1-diphenylsilacyclopentane (XIV).

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[13] R. A. Benkeser, M. L. Burrous, L. E. Nelson and J. V. Swisher, *J. Am. Chem. Soc.*, **83**, 4385 (1961).

[14] L. H. Sommer and O. F. Bennett, *ibid.*, **81**, 251 (1959).

[15] For an excellent discussion of this point see "Organosilicon Compounds," by C. Eaborn, Butterworths Scientific Publications, London, Eng., 1960, p. 94.

[16] R. West, *J. Am. Chem. Soc.*, **76**, 6012 (1954).

[17] L. H. Sommer and F. C. Whitmore, *ibid.*, **68**, 485, 488 (1946).

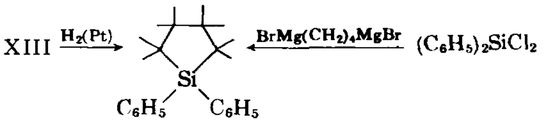
TABLE I

INFRARED SPECTRA OF SILACYCLIC DERIVATIVES[a,b]

Structure	
Silacyclopentane	3.4, 4.7, 6.8, 7.1, 8.0, 9.3, 10.5, 11.4
1,1-Dichlorosilacyclopentane	3.4, 6.8, 7.1, 7.9, 9.2, 11.6, 13.5
1,1-Dichlorosila-(x)-chlorocyclopentane	3.5, 6.9, 7.2, 8.0, 9.3, 11.6, 13.6, 14.2
1,1-Dichlorosila-(x)(x′)-dichlorocyclopentane	3.5, 6.9, 7.2, 8.0, 9.3, 11.7, 13.5, 14.2
1,1-Dichlorosila-2-cyclopentene	3.3, 3.4, 6.3, 6.8, 7.9, 9.2, 11.2, 13.6
1,1-Dichlorosila-3-cyclopentene[c]	3.3, 3.4, 6.1, 6.9, 7.1, 7.6, 9.1, 10.5, 11.2, 13.7
1,1-Dichlorosilacyclopentadiene	3.3, 6.4, 7.1, 7.9, 9..2, 11.9, 13.8
Silacyclopentadiene	3.4, 4.7, 6.4, 7.1, 7.9, 9.2, 10.7, 11.5
1,1-Diphenylsilacylcopentadiene	3.3, 6.4, 7.0, 8.0, 9.0, 12.4
1-Phenylsilacyclopentadiene[d]	3.3, 4.7, 6.4, 7.0, 7.8, 9.2, 10.2, 11.8
1,1-Diphenylsilacyclopentane	3.3, 3.4, 6.8, 7.0, 7.7, 9.3, 11.7
1-Phenylsilacyclopentane[d]	3.3, 3.5, 4.8, 6.8, 7.0, 8.0, 9.3, 9.5, 10.7, 11.8

[a] The wave length in microns of the principal bands are given. Certain obvious absorptions, like those characteristic of the phenyl ring, have not been included because of the limitations of space. [b] The data were obtained from a model 137 Infracord or a Perkin–Elmer model 221 spectrophotometer. [c] The spectrum was taken on a sample which contained 78% of the 3-olefin and 22% of the 2-olefin. [d] The synthesis of this compound is described in paper II of this series. The infrared data are included here for the sake of completeness.

The latter material proved identical in every respect with an authentic sample of the same compound prepared by reaction of diphenyldichlorosilane with the di-Grignard reagent of 1,4-dibromobutane.

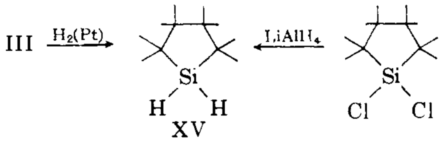


Compound XIII was found to form an adduct with hexachlorocyclopentadiene which melted at 41–42°.

1,1-Diphenylsilacyclopentadiene undergoes gradual decomposition upon exposure to the atmosphere. A sample which had been exposed to the air for several months no longer melted sharply. A small amount of maleic acid was identified as one of the decomposition products. While no detailed study of this decomposition was made, it seems certain to involve an oxidative degradation.

Of some interest was the observation[18] that the silacyclopentadienes exhibit a brilliant blue-white fluorescence when exposed to ultraviolet light. This property proved extremely useful in purifying such compounds by column chromatography. The path of these compounds could be traced very conveniently down the chromatographic column by their ultraviolet fluorescence.

Silacyclopentadiene.—1,1-Dichlorosilacyclopentadiene could be reduced with lithium aluminum hydride to silacyclopentadiene (III) in 54% yield. Compound III is a volatile liquid whose vapor phase chromatogram indicated a purity of about 95% immediately after its preparation. The principal impurity seems to be the 1,1-dichlorosila-3-cyclopentene arising from an imperfect fractionation of X from XI. Silacyclopentadiene undergoes rapid decomposition, upon exposure to air even at Dry Ice temperatures. Very likely an oxidative degradation is involved here also.



XV

To prove the structure of III, it was hydrogenated over platinum in a semi-micro catalytic hydrogenation apparatus to silacyclopentane (XV). The uptake of hydrogen was 98% of the theoretical amount and the product showed no trace of residual diene by either infrared or vapor phase chromatographic analysis. The silacyclopentane (XV) thus produced proved identical in every respect with an authentic sample prepared by the reduction of 1,1-dichlorosilacyclopentane with lithium aluminum hydride.

Silacyclopentadiene formed an adduct with hexachlorocyclopentadiene which melted at 35°. The structure of this material was not investigated.

Spectral Data.—Since the silacyclopentadienes represent a new class of organosilicon compounds, considerable effort was made to collect spectral data on the various compounds which were synthesized and characterized. Table I lists the principal infrared bands of twelve different silacyclic structures which are reported in this paper. Paper II of this series will list ultraviolet absorptions and the nuclear magnetic resonance spectra of these compounds.

Experimental

Hydrosilylation of 3-Chloro-1-butyne.—A solution composed of 44 g. (0.5 mole) of 3-chloro-1-butyne, 135 g. (1.0 mole) of trichlorosilane, 23.2 g. (0.09 mole) of benzoyl peroxide and 300 ml. of sodium-dried cyclohexane was refluxed for 72 hours. After the solvent was evaporated the residue was distilled. There was obtained 33.1 g. (30%) of 4-chloro-1-trichlorosilyl-1-butene boiling at 92–93° (10 mm.). An infrared spectrum of this product showed >C=C< stretch at 6.25 μ. Seven grams of the above trichlorosilyl product was added to an excess of methylmagnesium iodide in ether. Upon workup there was obtained 5.2 g. of 4-chloro-1-trimethylsilyl-1-butene boiling at 60–62° (10 mm.). Infrared showed >C=C< at 6.25 μ and Si-CH_3 at 8.0 μ.

Anal. Calcd. for $C_7H_{15}SiCl$: C, 51.66; H, 9.29; Cl, 21.79; Si, 17.26. Found: C, 51.38; H, 9.34; Cl, 21.56; Si, 16.80.

A vapor phase chromatogram of this methylated product disclosed two peaks (Carbowax column, 140°) in the ratio of 85:15, representing the *cis* and *trans* isomer, respectively.

1,1-Dichlorosila-2-cyclopentene.—To 2.4 g. (0.1 g. atom) of magnesium turnings in 200 ml. of dry tetrahydrofuran

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[18] Also reported by E. H. Braye and W. Hübel, *Chemistry & Industry*, 1250 (1959).

(distilled from lithium aluminum hydride) was added 22 g. (0.1 mole) of 4-chloro-1-trichlorosilyl-1-butene. The magnesium dissolved slowly during 20 hr. reflux. Dry pentane was added at this point to precipitate the magnesium chloride. After filtration and evaporation of the solvent the residue was distilled yielding 4.3 g. (28%) of product boiling at 138–140° (44–45° at 1 mm.). An infrared spectrum of this material disclosed olefin absorption at 6.25 μ.

Anal. Calcd. for $C_4H_6SiCl_2$: C, 31.35; H, 3.92; Cl, 46.30. Found: C, 31.28; H, 4.14; Cl, 45.95.

This reaction could not be made to proceed when diethyl ether was used as solvents. Likewise, sodium sand in toluene and distillation of the starting material from zinc dust were both ineffective.

Chlorination of 1,1-Dichlorosilacyclopentane.[16]—To 27 g. (0.2 mole) of sulfuryl chloride was added 1 g. of benzoyl peroxide and 30 g. (0.195 mole) of 1,1-dichlorosilacyclopentane. The resultant solution was warmed for five hours, and excess sulfuryl chloride was removed under vacuum. Fractionation (4-foot Vigreux column) yielded two major cuts boiling at 45–54° (2 mm.) and 62–70° (2 mm.), respectively. Elemental analysis indicated that the first fraction was monochlorinated product and the second was dichlorinated.

Anal. (First Cut) Calcd. for $C_4H_7SiCl_3$: C, 25.38; H, 3.73; Cl, 56.01. Found: C, 25.71; H, 4.07; Cl, 55.81. (Second Cut) Calcd. for $C_4H_6SiCl_4$: C, 21.42; H, 2.67; Cl, 63.39. Found: C, 21.64; H, 2.54; Cl, 63.33.

Isomeric 1,1-Dichlorosilacyclopentenes.—A 10-g. sample of the above monochlorination product was refluxed with 50 ml. of dry quinoline overnight. After filtration and distillation there was obtained 5.0 g. (75%) of olefinic product boiling at 138–140°. The infrared spectrum showed absorption at 6.1 μ (medium) and 6.25 μ (weak).

Anal. Calcd. for $C_4H_6SiCl_2$: C, 31.35; H, 3.92; Cl, 46.30. Found: C, 31.19; H, 3.98; Cl, 46.00.

Vapor phase chromatography disclosed two peaks: one, 22%, identical in shape and elution time with authentic 1,1-dichlorosila-2-cyclopentene (see above); the other, 78%, 1,1-dichlorosila-3-cyclopentene. Vapor phase chromatographic analysis of the monochlorinated product showed two closely spaced peaks also, in the ratio of 9:1. This represents the ratio of beta:alpha chlorination isomers.

Dichlorination of 1,1-Dichlorosilacyclopentane.—To 59 g. (0.44 mole) of sulfuryl chloride was added 2.5 g. (0.01 mole) of benzoyl peroxide and 30 g. (0.195 mole) of 1,1-dichlorosilacyclopentane. The mixture was refluxed for 20 hours, excess sulfuryl chloride removed under vacuum, and the residue distilled. There was obtained 4.5 g. (12%) of monochlorinated product (b.p. 42–58° at 2 mm.) and 19.5 g. (48%) of dichlorinated product (b.p. 62–70° at 2 mm.).

1,1-Dicylorosilacyclopentadiene.—A sample of 19 g. (0.085 mole) of the dichlorination fraction above was dropped slowly onto a 10-inch column of glass beads at 550° in a slow nitrogen stream. The pyrolysate was trapped in a Dry Ice–acetone-bath and redistilled. There was obtained 9.2 g. (65%) of a clear liquid boiling at 128–130°; $\lambda_{\max}^{\text{ether}}$ 228 mμ; log $\epsilon_{\max}$ 4.2. The infrared spectrum showed C=C absorption at 6.4 μ.

1,1-Diphenylsilacyclopentadiene.—Three grams (0.02 mole) of 1,1-dichlorosilacyclopentadiene was added to 0.1 mole of phenyl Grignard in 200 ml. of ether and stirred for several hours. After hydrolysis, the dried organic layer was evaporated under vacuum, taken up in dry pentane and chromatographed on alumina (Alcoa neutral). Bromobenzene and biphenyl were eluted with pentane, and the fluorescent layer of diene with ether. This was distilled to yield 1.5 g. (33%) of 1,1-diphenylsilacyclopentadiene, m.p. 54–55°, b.p. 128–130° (1 mm.); $\lambda_{\max}^{\text{ether}}$ 230 mμ, log $\epsilon_{\max}$ 4.0. The infrared spectrum showed C=C absorption at 6.4 μ.

Anal. Calcd. for $C_{16}H_{14}Si$: C, 82.00; H, 6.02; mol. wt., 234. Found: C, 81.91; 82.14; H, 5.99, 6.11; mol. wt. (Rast), 221.

This diene gave an adduct with hexachlorocyclopentadiene which melted at 41–42°.

Anal. Calcd. for $C_{21}H_{14}SiCl_6$: C, 49.70; H, 2.76; Cl, 42.01. Found: C, 49.67; H, 3.09; Cl, 42.20.

When a solution of 0.5 g. of 1,1-diphenylsilacyclopentadiene in 25 ml. of absolute ethanol was reduced at room temperature over platinum in a semi-micro catalytic hydrogenation apparatus at atmospheric pressure, it absorbed two equivalents of hydrogen. After filtration and evaporation of the solvent, the residual clear oil was distilled in a micro assembly. It boiled at 142° (2 mm.), n^{25}D 1.5850. These properties, as well as its infrared spectrum and retention time by V.P.C., agreed well with an authentic sample of 1,1-diphenylsilacyclopentane.[16]

A sample of 1,1-diphenylsilacyclopentadiene that had been exposed to air for several months no longer melted sharply. From this material it was possible, after repeated crystallizations from ethanol, to obtain a small amount of a pure compound melting at 130°. This was identified as maleic acid by comparison with an authentic sample.

Silacyclopentadiene.—Five grams (0.03 mole) of 1,1-dichlorosilacyclopentadiene was added dropwise with stirring to 3.8 g. (0.1 mole) of lithium aluminum hydride in 50 ml. of dry diglyme. The mixture was stirred for 2 hours at 0°, and then distilled at 30–40 ml. (pot temp. about 40°). The distillate, which was now free of diglyme, was collected in a Dry Ice trap. Upon redistillation of this material (b.p. 60–62°), 1.4 g. of product (54% yield) was obtained, n^{25}D 1.4265; $\lambda_{\max}^{\text{ether}}$ 232 mμ; log $\epsilon_{\max}$ 3.8. The infrared spectrum showed C=C absorption at 6.4 μ and Si–H at 4.7 μ.

Anal. Calcd. for C_4H_6Si: C, 58.46; H, 7.35. Found: C, 58.27; H, 7.61.

It was necessary to obtain the elemental analysis on a freshly prepared sample. Exposure to air, even for a relatively short period of time, caused rapid deterioration.

This compound formed an adduct with hexachlorocyclopentadiene in a bomb at 100°. It melted at 35–36°.

Anal. Calcd. for $C_9H_6SiCl_6$: C, 30.45; H, 1.70; Cl, 59.93. Found: C, 30.22; H, 1.89; Cl, 60.31.

Hydrogenation of Silacyclopentadiene.—A solution of 0.8 g. of silacyclopentadiene in 30 ml. of dry ether was hydrogenated over platinum in a semi-micro catalytic hydrogenation apparatus at room temperature and atmospheric pressure. The hydrogen uptake was 98% of theoretical as calculated for a diene (47.8 cc.). Removal of the ether and distillation of the residue yielded silacyclopentane, b.p. 70°, n^{25}D 1.4448.[19] When this compound was compared with an authentic sample prepared by reducing 1,1-dichlorosilacyclopentane with lithium aluminum hydride, the two compounds were identical in all respects (infrared spectrum, refractive index and retention time in V.P.C.).

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[19] The literature (see ref. 16) lists a b.p. of 71° and n^{25}D 1.444 for this compound.