

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, IOWA STATE UNIVERSITY, AMES, IOWA]

# The Preparation and Reactions of Some 7-Silanorbornadienes. I. An Approach to Dimethylsilylene<sup>1</sup>

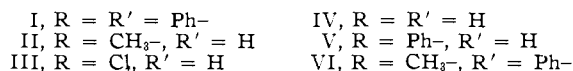
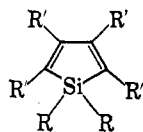
BY HENRY GILMAN, STEVE GUST COTTIS, AND WILLIAM H. ATWELL

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1,1-Dimethyl-2,3,4,5-tetraphenyl-1-silacyclopentadiene (VI) has been prepared. Compound VI has been shown to undergo Diels-Alder reactions to give 7-silanorbornadienes. The latter undergo smooth pyrolytic decomposition resulting in extrusion of the dimethylsilicon moiety with concomitant formation of the corresponding aromatic compounds. When the pyrolysis is carried out in the presence of diphenylacetylene, 1,1,4,4-tetramethyl-2,3,5,6-tetraphenyl-1,4-disilacyclohexadiene (X) is obtained, and the intermediate formation of dimethylsilylene is considered.

## Introduction

At the present time, only five silacyclopentadienes have been reported<sup>2-4</sup>; the properties of these compounds are given in Table I.



Compounds IV and V have been reported<sup>4</sup> to form 1:1 adducts with hexachlorocyclopentadiene. In addition, V was observed to give an adduct with tetracyanoethylene.<sup>4a</sup> However, to our knowledge neither the structures nor the chemical properties of these adducts have been investigated.

TABLE I

SILACYCLOPENTADIENES		Ref.
1-Silacyclopentadiene	Properties	
1,1,2,3,4,5-Hexaphenyl- (I) (hexaphenylsilole)	Greenish yellow solid, m.p. 191°	2
1,1-Dimethyl- (II)	Colorless liq., b.p. 83°	3a
1,1-Dichloro- (III)	Colorless liq., b.p. 128-130°	4
Silacyclopentadiene (IV)	Colorless liq., b.p. 60-62°	4
1,1-Diphenyl- (V)	Colorless solid, m.p. 54-55°	4

It seemed quite probable that the reaction of silacyclopentadienes under suitable Diels-Alder conditions could provide access to the 7-silanorbornadiene ring system.<sup>5</sup> In view of the unusual reactivity of norbornadienes in general, we felt that it would be of considerable interest to investigate the effects produced, if any, upon the introduction of silicon into this bicyclic system. In particular, it was of special interest to investigate the possibility of using the 7-silanorbornadienes as precursors to "divalent silicon" (silylene).<sup>6,7</sup>

(1) The term "silylene" (analogous to methylene) has been used to designate the "divalent silicon" species.

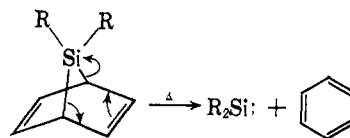
(2) (a) E. H. Braye and W. Hübel, *Chem. Ind. (London)*, 1250 (1959); (b) E. H. Braye, W. Hübel, and I. Caplier, *J. Am. Chem. Soc.*, **83**, 4406 (1961).

(3) (a) J. Groubeau, T. Kolmar, and H. Hofman, *Ann.*, **659**, 39 (1962); (b) O. M. Nefedov and M. N. Manakov, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 769 (1963) [*Chem. Abstr.*, **59**, 8781 (1963)].

(4) (a) R. A. Benkeser, R. F. Grossman, and G. M. Stanton, *J. Am. Chem. Soc.*, **83**, 3716 (1961); (b) *ibid.*, **84**, 4723 (1962). However, see R. A. Benkeser and G. M. Stanton, *ibid.*, **85**, 834 (1963).

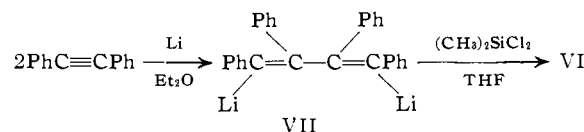
(5) An attempt to prepare the 7-phosphanorbornadiene ring system from the reaction of pentaphenylphosphole with dimethyl acetylenedicarboxylate gave dimethyl tetraphenylphthalate as the only isolable product.<sup>2b</sup>

(6) (a) An analogous approach was recently employed in the attempted synthesis of dimethoxycarbene: see J. Diekmann, *J. Org. Chem.*, **28**, 2880 (1963), and other references cited therein; (b) however, it appears that



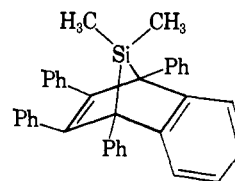
## Results and Discussion

The diene that was selected for use in our work was 1,1-dimethyl-2,3,4,5-tetraphenyl-1-silacyclopentadiene (VI) (1,1-dimethyltetraphenylsilole). Compound VI was prepared by the reaction of 1,4-dithio-1,2,3,4-tetra-phenylbutadiene (VII)<sup>2b</sup> with dichlorodimethylsilane



in tetrahydrofuran (THF). The silole VI is a stable yellow-green solid, m.p. 181-182°. This compound exhibits a strong blue fluorescence in ultraviolet light in the solid state and shows the ultraviolet absorption maxima in  $m\mu$  ( $\log \epsilon$ ) at 357 (3.999), 247 (4.413).<sup>8</sup>

Reaction of VI with benzyne<sup>9</sup> gave an adduct which, on the basis of its n.m.r. spectrum and chemical reactivity, is believed to be 2:3-benzo-7,7-dimethyl-1,4,5,6-tetraphenyl-7-silanorbornadiene (VIII), m.p. 233.5-234.5°.



VIII

The n.m.r. spectrum of VIII showed the presence of two different methyl groups with bands centered at

methylene is not formed in the pyrolysis of norbornadiene; see W. G. Woods, *ibid.*, **23**, 110 (1958).

(7) Only recently have there been proposals of divalent organosilicon compounds as reaction intermediates: (a) D. Wittenberg, M. V. George, and H. Gilman, *J. Am. Chem. Soc.*, **81**, 4812 (1959); (b) H. Gilman and G. D. Lichtenwalter, *J. Org. Chem.*, **24**, 1588 (1959); (c) see M. E. Vol'pin, Yu. D. Koreskov, V. G. Dulova, and D. N. Kursanov, *Tetrahedron*, **18**, 107 (1962), and references cited therein; (d) O. M. Nefedov, M. N. Manakov, and A. D. Petrov, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 1228 (1962); (e) see D. J. Peterson, "Trapping of Organometallic and Organometalloidal Radicals," unpublished Ph.D. thesis, Iowa State University, Ames, Iowa, 1962; (f) E. Wiberg, O. Stecher, H. J. Andrascheck, L. Kreuzbichler, and E. Staude, *Angew. Chem., Intern. Ed. Engl.*, **2**, 507 (1963).

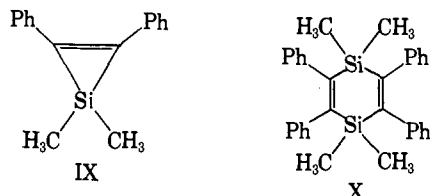
(8) These properties are in excellent agreement with those previously reported<sup>2b</sup> for hexaphenylsilole (I): 365 (3.915), 249 (4.435). The solvent used in our determination was also cyclohexane.

(9) The benzyne was generated by the splendid procedure recently reported by L. Friedman and F. M. Logullo, *J. Am. Chem. Soc.*, **85**, 1549 (1963).

9.29 and 10.02  $\tau$  in agreement with the proposed structure (see Experimental section). In addition, the aromatic/aliphatic proton ratio was found to be 4.0 (calcd. 4.0).

The most compelling evidence for the assignment of structure VIII was obtained from chemical reactivity. Pyrolysis of VIII at 300° gave 1,2,3,4-tetraphenyl-naphthalene<sup>10</sup> (88%) and an amorphous dimethylsilyl polymer  $[(CH_3)_2Si]_n$ ,<sup>11</sup> m.p. 300–315°. It seemed highly likely that dimethylsilylene could have been generated in this pyrolysis, and attempts to trap this possible intermediate were initiated.

Vol'pin has reported<sup>7c</sup> that pyrolysis of  $[(CH_3)_2Si]_{55}^{12}$  in the presence of diphenylacetylene yields 1,1-dimethyl-2,3-diphenylsilirene (IX, 6%), and formation of the "divalent silicon" species  $[(CH_3)_2Si:]$  was



postulated. Recently, a study by West and Bailey<sup>13</sup> has shown that the silicon compound reported<sup>7c</sup> to have the "silirene" structure IX is probably dimeric and structure X was proposed. Recent mass spectral studies<sup>14</sup> have confirmed the dimeric structure.

We have found that reaction of a dimethylsilyl polymer  $[(CH_3)_2Si]_n$ <sup>11b</sup> with diphenylacetylene at 280–290° for 8 hr. gave no 1,4-disilacyclohexadiene (X). Therefore, the reaction is not a general one for dimethylsilyl polymers. However, we have found that pyrolysis of adduct VIII at 300° in the presence of diphenylacetylene proceeds smoothly to give 1,2,3,4-tetraphenyl-naphthalene (72%) and a 50% yield of X,<sup>15</sup> m.p. 324–326°. The yield of X obtained represents a tenfold increase over that reported by previous workers.<sup>7c,13</sup> No material corresponding to the silirene IX, the expected "trapped" product, could be isolated in our pyrolysis reactions using VIII and diphenylacetylene. It is possible that IX, if formed, could dimerize under the pyrolysis conditions employed<sup>16</sup> to give XI followed by rearrangement to the observed 1,4-disilacyclohexadiene X. An intermediate similar to XI may be involved in the rearrangement of bis-triphenylcyclopropenyl to hexaphenylbenzene.<sup>17</sup> At the present time, our experimental evidence does not allow a distinction to be made between the above route

(10) We wish to express our appreciation to Dr. H. Zeiss for providing us with an authentic sample of this compound for identification purposes.

(11) Similar dimethylsilyl polymers have been obtained from the reaction of dichlorodimethylsilane with lithium in tetrahydrofuran: (a) O. M. Nefedov, M. N. Manakov, and A. D. Petrov, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 1717 (1961), m.p. 340–345°; (b) G. L. Schwebke, "Preparation and Stability of Perphenylated Cyclosilanes," unpublished Ph.D. thesis, Iowa State University, Ames, Iowa, 1964, m.p. 370–390° dec.

(12) This polymer was originally prepared [C. A. Burkhard, *J. Am. Chem. Soc.*, **71**, 963 (1949)] by the reaction of dichlorodimethylsilane with sodium in an autoclave, and the thermal properties of this material (unstable when heated in air at 200°) are considerably different from those of the other dimethylsilyl polymers mentioned in this report.

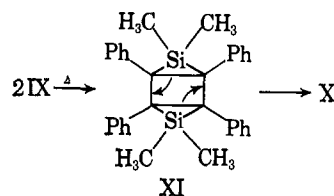
(13) R. West and R. E. Bailey, *J. Am. Chem. Soc.*, **85**, 2871 (1963).

(14) F. Johnson and R. S. Gohlke, unpublished results presented at the I.U.P.A.C. Meeting in London, July, 1963.

(15) We are grateful to Dr. R. West for providing us with a known sample of this compound.

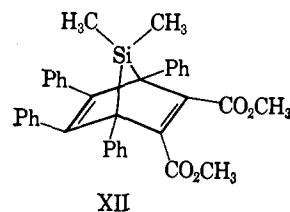
(16) Preliminary results indicate that pyrolysis temperatures greater than 275° (3 hr.) are required for decomposition of the Diels–Alder adducts.

(17) See R. Breslow and P. Gal, *J. Am. Chem. Soc.*, **81**, 4747 (1959).



and others (including some not involving dimethylsilylene) which may be written for the formation of X. However, the formal mechanistic scheme presented is consistent with the high yields of X obtained.

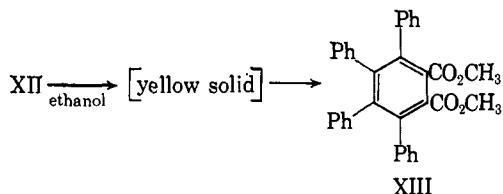
The yields of VIII obtained with benzyne varied somewhat from run to run (see Experimental section), and other dienophiles were investigated in an attempt to improve the yields of the Diels–Alder adducts. Reaction of VI with dimethyl acetylenedicarboxylate under mild conditions gave an 82% yield of 2,3-dicarbomethoxy-7,7-dimethyl-1,4,5,6-tetraphenyl-7-silanorborene (XII). Adduct XII is a white



solid which melts at 200° to a bright yellow oil which subsequently decomposes at 218–221°.

The n.m.r. spectrum of XII contained a sharp singlet centered at 6.37  $\tau$  (6 units) due to the two equivalent methoxy groups. The methyl groups on silicon appeared as a pair of singlets centered at 9.46 (3 units) and 9.56  $\tau$  (3 units). The aromatic/aliphatic proton ratio was 1.60 (calcd. 1.67).

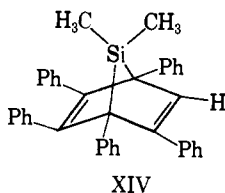
When XII was pyrolyzed in the presence of diphenylacetylene, none of the expected 1,4-disilacyclohexadiene X could be isolated. The unusual melting point behavior of XII suggested the thermal formation of a nonbenzenoid yellow intermediate. In addition, it was observed that treatment of a benzene solution of XII with ethanol resulted in the immediate formation of a bright yellow solution. Evaporation of the solvents gave a yellow solid. Attempts to purify this latter material resulted in slow decoloration and subsequent formation of dimethyl tetraphenylphthalate (XIII).<sup>18</sup>



At the present time, attempts to isolate this yellow intermediate have failed, and the identity and mode of decomposition of this material remain obscure.

Reaction of the silole VI with phenylacetylene gave 7,7-dimethyl-1,2,3,4,5-pentaphenyl-7-silanorborene (XIV), m.p. 148–150° (76%). The n.m.r. spectrum of XIV contained two methyl singlets centered at 9.38 (3 units) and 9.83  $\tau$  (3 units). The aromatic

(18) We wish to acknowledge the cooperation of Dr. W. Hübel in providing us with an authentic sample of XIII.



(olefinic proton included in this area)/aliphatic proton ratio was 4.41 (calcd. 4.33).

Adduct XIV was also found to undergo facile pyrolysis, and in the presence of diphenylacetylene there was obtained a 67% yield of the 1,4-disilacyclohexadiene X together with pentaphenylbenzene<sup>19</sup> (85%). Since the yield of the phenylacetylene adduct XIV was considerably better than that of the benzyne adduct VIII, the former appears to be the starting material most suitable for pyrolytic reactions of the type described herein. On the other hand, the behavior of the dicarbomethoxyacetylene adduct XII is anomalous (with respect to VIII and XIV) and appears to be of little value for the pyrolytic reactions. The unusual behavior of XII appears to be associated with the presence of the carbomethoxy groups, and the chemistry of this and other dicarbomethoxy-7-silanorbornadienes is under consideration.

The use of VIII, XIV, and other 7-silanorbornadienes as an approach to "divalent silicon" is currently under investigation in this laboratory. In addition, this investigation is being extended to include heteroatoms other than silicon.

### Experimental

The diphenylacetylene was purchased from Orgmet, Hampstead, N. H. The alumina used was made by Woelm and purchased from Alupharm Chemicals, New Orleans, La. The infrared spectra were determined using a Perkin-Elmer Model 21 spectrophotometer. The n.m.r. spectra were measured with a Varian HR-60 spectrometer operating at 60 Mc. Analyses were carried out by Ise Beetz Mikroanalytisches Laboratorium, Kronach, Western Germany (formerly Dr. Ing. A. Schoeller).

**1,4-Dilithio-1,2,3,4-tetraphenylbutadiene (VII).**—The apparatus consisted of a three-necked 1-l. round-bottomed flask equipped with a condenser and nitrogen inlet. A magnetic stirring bar was inserted into the flask. To the middle neck was placed a mechanical stirring device in such a manner that it would remain suspended above the level of the solution during magnetic stirring.

In a typical run, 1.04 g. (0.15 g.-atom; an excess of lithium should be carefully avoided) of finely cut lithium wire, 26.8 g. (0.15 mole) of diphenylacetylene, and 120 ml. of anhydrous ether were stirred gently by means of the magnetic stirring bar. After about 25 min. of continuous stirring the solution became red. The stirring was continued for *no longer than 16 hr.* During this time, the color of the solution deepened and a yellow solid separated. Fine pieces of lithium that may remain at this time can be removed mechanically, but it was not found necessary to do so. The mechanical stirrer was then lowered into the solution, and, with vigorous stirring, 450 ml. of anhydrous tetrahydrofuran (THF) was added at a moderate rate. After all the THF was added, a 10-ml. aliquot of the green solution was hydrolyzed with 30 ml. of anhydrous methanol. The 1,2,3,4-tetraphenylbutadiene, obtained in two crops, weighed 0.41 g. (87%) and melted at 183–185° (lit. value<sup>20</sup> 182.5–183°). The dark green solution gave a bright green Color Test I.<sup>21</sup>

**1,1-Dimethyl-2,3,4,5-tetraphenyl-1-silacyclopentadiene (VI).**—A mixture of 20 g. (0.11 mole) of diphenylacetylene and 0.78 g. (0.11 g.-atom) of cut lithium wire in 120 ml. of anhydrous ether was stirred for 16 hr. as described above. To this mixture was added 450 ml. of THF with mechanical stirring. While

stirring, 20 g. (0.155 mole) of dichlorodimethylsilane in 60 ml. of THF was added dropwise. Heat was evolved and the color of the solution became yellow near the end of the addition. Subsequent to cooling, 250 ml. of water was added slowly with stirring. After ether extraction, the ethereal solution was evaporated to dryness *in vacuo*. A slurry was made by treating the residue with petroleum ether (b.p. 60–70°) and the solid collected by filtration. The yellow-green product VI weighed 16.5 g. (72.5%) after drying and melted at 178–181°. In this form, the product was found to be suitable for further reactions. An analytical sample, m.p. 181–182°, was obtained by crystallization from petroleum ether (b.p. 60–70°) followed by crystallization from methanol. An infrared spectrum of VI in carbon disulfide showed absorption bands at 3.27, 3.31, 3.38, 7.74, 8.06, 9.22, 9.39, 9.75, 10.64, 11.00, 11.95, 12.60, 12.90, and 14.40  $\mu$ .

*Anal.* Calcd. for  $C_{30}H_{26}Si$ : C, 86.95; H, 6.31; Si, 6.77. Found: C, 87.11, 86.70; H, 6.28, 6.35; Si, 6.65.

**NOTE ADDED IN PROOF.**—In one repeat preparation of VIII, in which to the best of our knowledge the conditions employed were identical with those described above, a mixture of VIII and the 1,4-disilacyclohexadiene X was isolated. This mixture melted at 118–120°, and its infrared spectrum was similar to that of pure VIII. Separation of this mixture was readily accomplished by sublimation [100° (0.2 mm.)] to give 10.8% of pure X, m.p. 324–327°. The residue was VIII, m.p. 178–181° (44%).

**2:3-Benzo-7,7-dimethyl-1,4,5,6-tetraphenyl-7-silanorbornadiene (VIII).**—A solution of 4 g. (9.7 mmoles) of VI in 50 ml. of THF was heated to reflux. To this refluxing solution was added, dropwise and simultaneously, a solution of 4.8 g. of anthranilic acid in 90 ml. of THF and a solution of 6 g. of isoamyl nitrite in 60 ml. of the same solvent. The additions took approximately 4 hr. After allowing the reaction mixture to cool to room temperature, the solvents were removed under vacuum. The dark red-orange residue was treated with a hot cyclohexane–petroleum ether (b.p. 60–70°) mixture and chromatographed on a neutral alumina column. The product was eluted with cyclohexane. Upon concentration of the cyclohexane solution and addition of petroleum ether (b.p. 60–70°), yields ranging from 20–59.5% of the white crystalline adduct VI, m.p. 230–232°, were obtained. An analytical sample, m.p. 233.5–234.5°, was obtained by recrystallization from petroleum ether (b.p. 60–70°). The major bands in the infrared spectrum of this compound in carbon tetrachloride are located at 3.27, 3.30, 6.25, 6.70, 6.90, 6.94, 8.05, 8.65, 8.78, 9.30, 9.70, 10.82, 10.97, and 11.70  $\mu$ .

*Anal.* Calcd. for  $C_{36}H_{30}Si$ : C, 88.13; H, 6.16. Found: C, 88.56, 88.78; H, 6.09, 5.96.

An unequivocal assignment of the methyl bands in the n.m.r. spectrum of compound VIII was possible. The methyl group *syn* to the benzo ring would be expected to be influenced greatly by the diamagnetic shielding of this latter substituent.<sup>22</sup> Therefore, this methyl group was assigned the 10.02  $\tau$  position with the remaining 9.29  $\tau$  band being assigned to the methyl group *anti* to the site of benzo substitution.

**Pyrolysis of VIII.**—Two grams (4.1 mmoles) of VIII was heated in a sealed, evacuated tube at 300° for 3 hr. Subsequent to cooling the reaction mixture was dissolved in 25 ml. of hot benzene and allowed to cool to room temperature. An amorphous solid was collected by filtration and weighed 0.1 g. when dried, m.p. 300–315°. The infrared spectrum of this material showed bands characteristic of the silicon–methyl group and was quite similar to that of another dimethylsilyl polymer.<sup>11b</sup>

The filtrate was evaporated to dryness and then taken up in ca. 20 ml. of hot petroleum ether (b.p. 60–70°). Cooling of this mixture gave 1.55 g. (88%) of colorless 1,2,3,4-tetraphenyl-naphthalene, m.p. 198–200° (mixture melting point with an authentic sample<sup>19</sup> was not depressed).

**Pyrolysis of  $[(CH_3)_2Si]_n$ <sup>11b</sup> in the Presence of Diphenylacetylene.**—A mixture of diphenylacetylene (12.5 g., 0.07 mole) and 2.0 g. (0.0345 mole) of polymer<sup>11b</sup> was heated under nitrogen at 280–290° for 8 hr. Upon cooling, the green solution solidified. The solid mass was dissolved in benzene and filtered to give 1.8 g. (90%) of recovered polymer, m.p. 370–390° dec. (mixture melting point and comparison of infrared spectra).

The filtrate was evaporated to dryness and the light green residue dissolved in petroleum ether (b.p. 60–70°) and chromatographed on a basic alumina column. Elution with the same sol-

(19) An authentic sample of pentaphenylbenzene was obtained from Dr. E. I. Becker.

(20) L. I. Smith and H. H. Hoehn, *J. Am. Chem. Soc.*, **63**, 1184 (1941).

(21) H. Gilman and F. Schulze, *ibid.*, **47**, 2002 (1925).

(22) L. M. Jackman, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pergamon Press, New York, N. Y., 1959.

vent gave 9.5 g. (76%) of recovered diphenylacetylene, m.p. 59–61° (mixture melting point). Further elution with a variety of solvents gave only traces of green oil.

**Pyrolysis of VIII in the Presence of Diphenylacetylene.**—A mixture of 1.9 g. (3.9 mmoles) of VIII and 1.0 g. (5.5 mmoles) of diphenylacetylene was heated for 3 hr. at 300° in a sealed, evacuated tube. The dark green contents were dissolved in 35 ml. of benzene, and addition of petroleum ether (b.p. 60–70°) gave 0.4 g. of 1,4-disilacyclohexadiene X, m.p. 323–326°. The filtrate was evaporated to dryness, redissolved in 40 ml. of petroleum ether (b.p. 60–70°) and chromatographed on a neutral alumina column. Elution with the same solvent gave 0.3 g. of recovered diphenylacetylene. Elution with carbon tetrachloride gave 1.2 g. (72%) of tetraphenylphthalene, m.p. 199–203°. From the benzene eluent there was obtained an additional 0.12 g. of X, m.p. 317–322° (total crude yield was 0.52 g., 56.5%). Recrystallization of the crude material from a petroleum ether (b.p. 60–70°)-benzene mixture gave pure X as colorless needles, m.p. 324–327° (50%). A mixture melting point with an authentic sample<sup>15</sup> was not depressed and the infrared spectra were superimposable.

**2,3-Dicarbomethoxy-7,7-dimethyl-1,4,5,6-tetraphenyl-7-silanorbornadiene (XII).**—Two grams (4.8 mmoles) of VI and 2.4 g. of dimethyl acetylenedicarboxylate were heated at 70° by means of an oil bath. After a few minutes of heating a pink solution formed, followed by the gradual formation of a yellow solid. When the entire reaction mixture became a solid mass, 50 ml. of petroleum ether (b.p. 60–70°) was added and the resulting mixture refluxed for several minutes. After cooling to room temperature, the solid was collected by filtration; 2.55 g. (92.5%). This material melted to a yellow oil at about 200°, which in turn decomposed at 218–221°. Recrystallization gave colorless XII which had the same melting point characteristics as the initial crude product (82%). An analytical sample was obtained by further purification from petroleum ether (b.p. 60–70°) benzene, which also melted as described above. The infrared spectrum of XII (KBr) showed major bands at 3.30, 3.40, 5.80, 5.85, 6.25, 6.33, 6.38, 6.67, 6.94, 6.98, 7.75, 7.90, 7.97, 8.05, 8.10, 8.38, 8.75, 9.40, 11.75, 12.15, 12.57, and 14.25  $\mu$ . By analogy with the benzyne adduct VIII, the n.m.r. bands located at 9.46 and 9.56  $\tau$  were assigned to the silicon-methyl groups *anti* and *syn*, respectively, to the site of carbomethoxy-substitution.

*Anal.* Calcd. for C<sub>36</sub>H<sub>32</sub>O<sub>4</sub>Si: C, 77.68; H, 5.79. Found: C, 78.04, 78.20; H, 5.65, 5.85.

**Pyrolysis of XII in the Presence of Diphenylacetylene.**—A mixture of 1.15 g. (2.07 mmoles) of XII and 1.0 g. of diphenylacetylene was heated at 300° in an evacuated, sealed tube for 3 hr. After cooling, the reaction mixture was taken up in about 25 ml. of benzene, and 65 ml. of petroleum ether (b.p. 60–70°) was added. None of the desired 1,4-disilacyclohexadiene X was obtained upon cooling. The reaction mixture was evaporated to dryness, redissolved in petroleum ether (b.p. 60–70°) and chromatographed on a neutral alumina column. Elution of the column with a variety of solvents gave only oils which resisted further purification attempts by the usual methods.

**Rearrangement of XII with Ethanol.**—To a solution of 0.5 g. (0.9 mmole) of XII in *ca.* 25 ml. of benzene was added 25 ml. of ethanol. A brilliant yellow color developed, and the resulting solution was allowed to stand for several minutes. The solution was evaporated to dryness under vacuum, and the yellow residue

was taken up in petroleum ether (b.p. 60–70°). Concentration and cooling of this solution gave 0.11 g. of yellow solid which softened at 60–70°. From the filtrate, after concentration and cooling, there was obtained 0.3 g. of yellow crystalline solid which also melted as described above. The infrared spectrum of this yellow solid (carbon tetrachloride solution) was significantly different from that of XII, and contained bands at 3.30, 3.40, 5.80, 6.18, 6.26, 6.70, 6.94, 6.98, 7.50, 7.75, 8.20, 8.55, 8.80, 9.35, 9.51, 9.70, 10.40, 10.96, 11.32, and 11.75  $\mu$ . The bands at 5.80 and 6.18  $\mu$  appear to be due to the C=O grouping.

In an attempt to purify this yellow solid by recrystallization from petroleum ether (b.p. 60–70°), only a white crystalline solid was obtained which was identified as dimethyl tetraphenylphthalate, m.p. 259–261°.<sup>18</sup>

**7,7-Dimethyl-1,2,3,4,5-pentaphenyl-7-silanorbornadiene (XIV).**—A mixture of 4.0 g. (9.7 mmoles) of VI and 8.0 g. of phenylacetylene was heated at 100° for 11 hr. After cooling, the excess phenylacetylene was removed as completely as possible by evaporation. The resulting residue was dissolved in 15 ml. of petroleum ether (b.p. 60–70°) and cooled. The solid mass which formed was filtered and washed with several small portions of the crystallization solvent. After drying, the pale yellow powder weighed 4.0 g. and melted at 135–145°. A second crop of 0.5 g., m.p. 143–147°, was obtained from the filtrate. Recrystallization from the same solvent gave 3.8 g. (76%) of white solid, m.p. 148–150°. An analytical sample having the same melting point was obtained by additional recrystallizations from petroleum ether (b.p. 60–70°). The infrared spectrum (carbon tetrachloride) contained bands at 3.31, 3.41, 6.27, 6.73, 6.94, 8.05, 9.30, 9.70, 11.00, 11.35, and 11.85  $\mu$ . In the n.m.r. spectrum of XIV, the olefinic proton band was apparently buried beneath the broad aromatic absorption. This was verified to some extent by the excellent aromatic/aliphatic proton ratio obtained. By analogy with the other two adducts, the bands located at 9.38 and 9.83  $\tau$  were assigned to the silicon methyl groups *anti* and *syn*, respectively, to the unsymmetrically substituted site.

*Anal.* Calcd. for C<sub>38</sub>H<sub>32</sub>Si: C, 88.33; H, 6.24. Found: C, 88.39, 88.54; H, 6.12, 6.05.

**Pyrolysis of XIV in the Presence of Diphenylacetylene.**—A mixture of 2.0 g. (3.88 mmoles) of XIV and 1.0 g. of diphenylacetylene was heated at 300° for 3 hr. in a sealed, evacuated tube. Subsequent to cooling, the contents were dissolved in 50 ml. of hot benzene and filtered. Colorless needles slowly crystallized upon cooling. Filtration gave 0.61 g. of 1,4-disilacyclohexadiene X, m.p. 324–327° (67%).

The volume of the filtrate was adjusted to *ca.* 50 ml. by the addition of petroleum ether (b.p. 60–70°). After standing overnight at room temperature, filtration gave, in two crops, 1.75 g. of pentaphenylbenzene, m.p. 246–249° (98%). Recrystallization from petroleum ether (b.p. 60–70°)-benzene mixture gave 1.50 g. (84.3%) of pure product, m.p. 248–250°. A mixture melting point with a known sample was not depressed.<sup>19</sup>

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