

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

Some Diels–Alder Adducts of 1,1,2,3,4,5-Hexaphenyl-1-silacyclopentadiene^{1,2}

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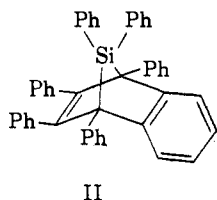
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1,1,2,3,4,5-Hexaphenyl-1-silacyclopentadiene (I) has been treated with benzyne, dimethyl acetylenedicarboxylate, and maleic anhydride to give the corresponding 1:1 Diels–Alder adducts. The benzyne adduct II was found to react readily with lithium aluminum hydride and with basic alumina. Pyrolysis of II in the presence of diphenylacetylene gave 1,2,3,4-tetraphenylnaphthalene and 1,1,2,3,4,4,5,5-octaphenyl-1,4-disilacyclohexadiene (III). The dimethyl acetylenedicarboxylate adduct (VI) was found to undergo an ethanol-induced rearrangement to give a solid yellow isomer. Theories concerning the nature of this facile isomerization are considered. The yellow isomer is believed to possess either a silacyclopropane or a silacycloheptatriene structure. A differentiation between these two possible structures does not seem to be possible at the present time in view of the formal analogy of this system to the norcaradiene \rightleftharpoons cycloheptatriene problem.

We have previously reported³ the preparation and reactions of some 7,7-dimethyl-7-silanorbornadiene derivatives. The unusual reactivity of these compounds and their possible utilization as an approach to divalent silicon compounds (silylenes) prompted a further investigation of the chemistry of this bicyclic system.

Treatment of 1,1,2,3,4,5-hexaphenyl-1-silacyclopentadiene (I)^{4a} with benzyne^{4b} gives a colorless crystalline adduct, which proved to be 1,4-dihydro-1,2,3,4,9,9-hexaphenyl-1,4-silanonaphthalene (II),⁵ m.p. 238–240°.

The assignment of structure II was based on the ease of ring opening of this adduct under relatively mild



conditions, and also on the identity of the resulting cleavage products.

Compound II undergoes the smooth pyrolytic decomposition previously reported³ for other 7-silanorbornadienes. Pyrolysis of II at 300° gives 1,2,3,4-tetraphenylnaphthalene (79%) and an amorphous diphenylsilyl polymer. When the pyrolysis of II is carried out in the presence of diphenylacetylene, 1,2,3,4-tetraphenylnaphthalene is obtained in a nearly quantitative yield. In addition to the naphthalene derivative, there is obtained a 63% yield of 1,1,2,3,4,4,5,6-octaphenyl-1,4-disilacyclohexadiene (III), m.p. 293.5–296°. The structure of this compound was formulated on the basis of the analysis, molecular weight determinations, infrared spectra, and by analogy with similar previously reported reactions.³

The diphenylsilyl polymer described above is stable under the pyrolysis conditions employed, eliminating

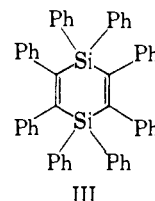
(1) Hexaphenylsilole is an alternate name for this silacyclopentadiene.

(2) The Preparation and Reactions of Some 7-Silanorbornadienes. Part II.

(3) For Part I of this series, see H. Gilman, S. G. Cottis, and W. H. Atwell, *J. Am. Chem. Soc.*, **86**, 1596 (1964).

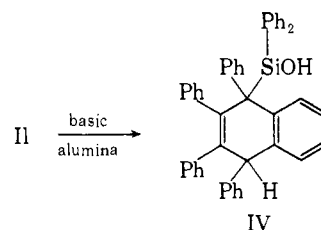
(4) (a) E. H. Braye, W. Hübel, and I. Caplier, *ibid.*, **83**, 4406 (1961); (b) L. Friedman and F. M. Logullo, *ibid.*, **85**, 1549 (1963).

(5) Although the structural similarity of II and the previously reported 7-silanorbornadienes³ is immediately obvious, the I.U.P.A.C. rules do not provide for the fusion type names with bicyclo ring names, but instead consider such systems to be bridged *ortho*-fused systems. Thus, the previously prepared 7,7-dimethyl analog of II³ is more correctly named as a 1,4-dihydro-1,4-silanonaphthalene derivative rather than as a benzenorbornadiene derivative. The nomenclature employed here is that recommended by *Chemical Abstracts*.



the possibility that III could be formed by reaction of this polymeric material with diphenylacetylene.

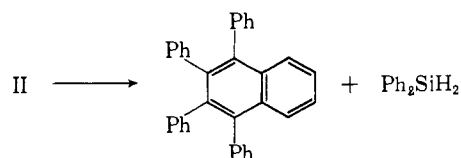
Attempts to chromatograph II on a basic alumina⁶ column resulted in ring opening with subsequent formation of (1,4-dihydro-1,2,3,4-tetraphenyl-1-naphthyl)-diphenylsilanol (IV).



The infrared spectrum of IV (carbon disulfide) contains a sharp band at 2.75 μ and a broad band at 12.05 μ indicative of the O–H and Si–O stretching vibrations respectively.⁷

The n.m.r. spectrum of IV shows a band at 5.47 τ assigned to the lone benzylic proton.⁸ A relatively sharp singlet due to the hydroxylic proton appears at 7.83 τ . The ratio of aromatic/nonaromatic protons was 17.0 (calcd. 17.0).

Compound II is readily cleaved by lithium aluminum hydride, and subsequent to acid hydrolysis a nearly quantitative yield of 1,2,3,4-tetraphenylnaphthalene is obtained. Diphenylsilane was identified as a com-



ponent of the reaction residue both by its characteristic odor and by comparison of the infrared spectrum with that of a known sample.

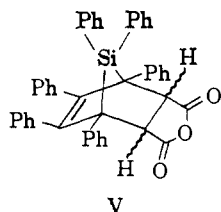
(6) The alumina employed was an activated grade F-20 made by Alcoa Chemicals.

(7) (a) K. Nakanishi, "Infrared Absorption Spectroscopy," Holden-Day, Inc., San Francisco, Calif., 1962; (b) A. L. Smith, *Spectrochim. Acta*, **16**, 87 (1960).

(8) The value of 6.0 τ has been reported for the benzylic protons in 1,4-dihydrohexaphenylbenzene; see R. Breslow and P. Dowd, *J. Am. Chem. Soc.*, **85**, 2729 (1963).

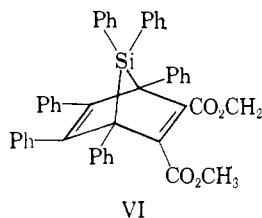
The reactivity of II with basic alumina and lithium aluminum hydride is similar to that observed for 1,1,2-triphenyl-1-silacyclobutane⁹ and 2:3-benzo-1,1-diphenyl-1-silacyclobut-2-ene¹⁰ with these reagents. These observations together with the observed ease of pyrolysis of the 7-silanorbornadienes illustrates that these bicyclic compounds are to be regarded as another class of strained organosilicon compounds.^{9,11}

The preparation of the first reported 7-silanorbornene derivative was accomplished by utilizing the reaction of I with an ethylenic dienophile. Reaction of I with maleic anhydride gives a white crystalline adduct designated as 1,4,5,6,7,7-hexaphenyl-7-silabicyclo[2.2.1]-hept-5-ene-2,3-dicarboxylic anhydride (V), m.p. 224–225.5°.¹²



The infrared spectrum of V shows the expected^{7a} anhydride bands at 5.39 and 5.60 μ . The n.m.r. spectrum of V contains a sharp singlet at 4.42 τ due to the two methinyl protons. The aromatic/aliphatic proton ratio was 7.43 (calcd. 7.50).

Reaction of I with dimethyl acetylenedicarboxylate gives dimethyl 1,4,5,6,7,7-hexaphenyl-7-silanorbornadiene-2,3-dicarboxylate (VI),¹³ m.p. 208–211° dec. (75%).



The reaction conditions needed for the preparation of VI were more stringent than those necessary for similar Diels–Alder reactions with 1,1-dimethyl-2,3,4,5-tetraphenyl-1-silacyclopentadiene.³ Thus, preliminary results indicate that smaller groups on silicon increase the reactivity of the silacyclopentadienes. Further evidence in support of this conclusion was the failure to obtain an adduct with I and phenylacetylene even under forcing conditions. A similar reaction with 1,1-dimethyl-2,3,4,5-tetraphenyl-1-silacyclopentadiene at 100° is complete within 11 hr.³

The n.m.r. spectrum of VI (CCl₄) exhibits a sharp singlet at 6.45 τ due to the two equivalent methoxy

(9) For a summary of the chemistry of silacyclobutanes, see H. Gilman and W. H. Atwell, *J. Am. Chem. Soc.*, **86**, 2687 (1964).

(10) H. Gilman and W. H. Atwell, unpublished studies.

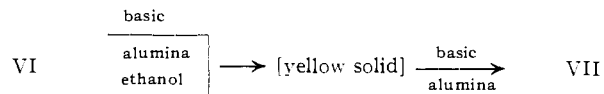
(11) (a) Heat of hydrogenation measurements on norbornadiene [R. B. Turner and W. R. Winkler, *J. Am. Chem. Soc.*, **79**, 4116 (1957)] indicate that a high degree of strain is associated with this compound, the heat of hydrogenation being about 68 kcal./mole (cyclohexene, 28 kcal./mole). (b) Recent correlation [C. S. Foote, *Tetrahedron Letters*, No. 9, 379 (1963)] of C¹³–H coupling constants of norbornadiene with those of other cyclic compounds also suggests a considerably strained system.

(12) A similar reaction employing pentaphenylphosphole and maleic anhydride has been reported¹⁴ to give a low yield of the desired adduct.

(13) The previously reported³ 7,7-dimethyl analog of VI is more correctly named as dimethyl 7,7-dimethyl-1,4,5,6-tetraphenyl-7-silanorbornadiene-2,3-dicarboxylate, in accord with the suggestions of *Chemical Abstracts*.

groups.³ The aromatic/aliphatic proton ratio was 4.80 (calcd. 5.00).

Adsorption of VI on a basic alumina⁶ column gives a brilliant yellow color which fades slowly. Eluates from the column provide a very high yield of dimethyl tetraphenylphthalate (VII). Addition of ethanol to a benzene solution of VI results in the formation of a



yellow solution. We have previously observed³ that dimethyl 7,7-dimethyl-1,4,5,6-tetraphenyl-7-silanorbornadiene-2,3-dicarboxylate behaves similarly upon treatment with ethanol, and attempts to purify the resulting yellow compound gave VII as the only isolable product. In the present work, however, evaporation of the yellow solution gave a bright yellow solid, m.p. 209–211°. The unusual and facile nature of this reaction prompted us to investigate the structure of this yellow solid.

The yellow solid is obtained most readily from I and dimethyl acetylenedicarboxylate using an ethanolic work-up, thereby eliminating the prior isolation and purification of VI. The pertinent analytical, spectral, and chemical information on this yellow solid is summarized: (1) The carbon, hydrogen, and silicon analyses of this solid indicate that it is isomeric with VI. (2) The infrared spectrum of this yellow compound shows two strong bands at 5.79 and 6.15 μ which appear to be due to the C=O group. Similar bands at 5.80 and 6.18 μ have been observed in the spectrum of the yellow solid obtained from the reaction of ethanol with the analogous 7,7-dimethyl-7-silanorbornadiene.³ (3) The ultraviolet spectrum (cyclohexane) of the yellow solid shows absorption in m μ (log ϵ) at: 273 (4.246), 285(sh) (4.210), 379 (3.782). (4) The n.m.r. spectrum (CCl₄) of this yellow isomer shows two bands at 6.05 (3 units) and 6.71 τ (3 units) due to two nonequivalent methoxy groups. The spectrum gave an aromatic/aliphatic proton ratio of 5.02 (calcd. 5.00), supporting the conclusion that the yellow compound is isomeric with VI. (5) The yellow isomer does not absorb hydrogen at atmospheric pressure in the presence of a platinum oxide catalyst. (6) The yellow solid reacts with basic alumina⁶ to give dimethyl tetraphenylphthalate. (7) Degradation of this yellow isomer with sodium methoxide gives dimethyl tetraphenylphthalate as the only recognizable product.

It seemed likely that a consideration of the possible modes of decomposition of VI by ethanol could give valuable information concerning the structure of the yellow isomer. The facile cleavage of β -oxygenated and β -halogenated alkyl groups from silicon (" β -effect") is well documented.^{14,15} In some instances the reaction conditions needed for such cleavages are extremely mild. For example, ethyl trimethylsilylacetate (VIII)¹⁶ and trimethylsilylacetone¹⁷ are cleaved

(14) C. Eaborn, "Organosilicon Compounds," Butterworths Scientific Publications, London, 1960.

(15) For a review of the preparation and properties of carbon-functional organosilicon compounds, see P. D. George, M. Prober, and J. R. Elliott, *Chem. Rev.*, **56**, 1065 (1956).

(16) J. R. Gold, L. H. Sommer, and F. C. Whitmore, *J. Am. Chem. Soc.*, **70**, 2874 (1948).

(17) C. R. Hauser and C. R. Hance, *ibid.*, **74**, 5091 (1952).

255 (3.45), and 249 (3.45). However, the similarity of the ultraviolet properties of the yellow isomer with previously prepared²⁶ heptaphenylcycloheptatrienes prevented the exclusion of XI as a structural possibility.

In the final analysis, we feel that neither the reactivity nor the spectral properties of the yellow isomer allows the rigorous elimination of either XI or XII as a structural candidate.

We are continuing work to elucidate the chemistry of the 7-silanorbornadienes, and the use of other "trapping" agents in the pyrolysis of these compounds is being actively pursued.

Experimental

The diphenylacetylene was purchased from Orgmet, Hamstead, N. H. The acidic and neutral alumina was made by Woelm and purchased from Alupharm Chemicals, New Orleans, La. Skellysolve B refers to the petroleum ether fraction b.p. 60–70°. 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. using a tetramethylsilane internal standard. Analyses were carried out by Ilse Beetz Mikroanalytisches Laboratorium, Kronach, Western Germany (formerly Dr. Ing. A. Schoeller). All the 7-silanorbornadienes prepared in this report and in previous work³ tended to give high carbon analyses. An unusually high analysis was obtained with the only 7-silanorbornene prepared.

Hexaphenylsilole (I).—To a tetrahydrofuran (THF)-ether solution of 1,4-dilithio-1,2,3,4-tetraphenylbutadiene³ made from 26.8 g. (0.15 mole) of diphenylacetylene and 1.04 g. (0.15 g.-atom) of lithium, was added dropwise, with vigorous stirring, 19 g. (0.075 mole) of dichlorodiphenylsilane in 60 ml. of THF. After the addition of the dichlorosilane Color Test I²⁷ was negative. If the color test was not negative at this time, small amounts of dichlorodiphenylsilane were added until a negative test was obtained.

The reaction mixture was evaporated to dryness and 300 ml. of cyclohexane added to the residue. After heating the mixture to boiling, filtering from salts, and allowing the filtrate to cool, 15 g. of I was obtained, m.p. 189–191°. Concentration of the filtrate gave an additional 7.5 g. of I, m.p. 186–190°. To the filtrate from the second crop was added 100 ml. of Skellysolve B, and the resulting solution chromatographed on a basic alumina⁸ column. Elution of the column with a large volume of Skellysolve B gave 5.1 g. of I, m.p. 188–191°. The total yield of good quality silole was 27.5 g. (68%) (lit.^{4a} m.p. 190°). The ultraviolet spectrum of this material in cyclohexane contained bands at 366 and 248 m μ in good agreement with those previously reported for I (lit.^{4a} $\lambda_{\text{max}}^{\text{cyclohexane}}$ 365, 249 m μ).

1,4-Dihydro-1,2,3,4,9,9-hexaphenyl-1,4-silanonaphthalene (II).—A solution containing 3.0 g. (5.5 mmoles) of I and 1.5 g. of isoamyl nitrite in 100 ml. of THF was heated to reflux. Over a period of 3 hr., 1.2 g. of anthranilic acid in 100 ml. of THF was added dropwise, with stirring, to the refluxing mixture. After the addition was completed, the solvent was completely removed and the red-orange residue was taken up in about 100 ml. of hot cyclohexane and filtered. About 20 ml. of Skellysolve B was added and the solution concentrated until crystals appeared. Upon cooling to room temperature, 2.5 g. of II was obtained. Recrystallization from Skellysolve B-cyclohexane (Norit) gave 2.2 g. (65%) of colorless, crystalline II which melted at 238–240°. Further crystallizations did not alter the melting point. The infrared spectrum (carbon tetrachloride) revealed major bands at 3.28, 6.23, 6.68, 6.86, 6.91, 9.00–9.09 (split), 9.28, 9.68, 10.27, 10.80, and 10.99 μ .

Anal. Calcd. for C₄₈H₄₄Si: C, 89.86; H, 5.57. Found: C, 90.42, 90.29; H, 5.34, 5.55.

Pyrolysis of II.—Four grams (6.64 mmoles) of II was heated at 300° for 3 hr. in a sealed, evacuated tube. After cooling, the resinous material was dissolved in 30 ml. of hot benzene. The solvent was then completely removed and replaced with a mini-

um amount of cyclohexane. After adsorbing the solution on a neutral alumina column, elution with carbon tetrachloride gave 1.9 g. (79.4%) of 1,2,3,4-tetraphenyl-naphthalene, m.p. 200–202° (m.m.p.). The silicon-containing material was eluted with benzene. After evaporation of the benzene, the residue was heated with Skellysolve B and allowed to cool. Filtration gave 0.75 g. of an amorphous, white powder which softened at 100–110°. The infrared spectrum of this material (KBr) was very similar to that of octaphenylcyclohexasilane^{28a} and decaphenylcyclopentasilane.²⁸ Most of the material was soluble in hot Skellysolve B, hot methanol, carbon tetrachloride, benzene, and carbon disulfide. Attempts to purify this diphenylsilyl polymer by sublimation or by recrystallization from Skellysolve B and methanol gave materials with melting point ranges from 100–220°.

Pyrolysis of II in the Presence of Diphenylacetylene.—A mixture of 2.0 g. (3.32 mmoles) of II and 1.0 g. of diphenylacetylene was heated at 300° for 3 hr. in a sealed, evacuated tube. The contents were dissolved in ca. 40 ml. of benzene and 60 ml. of Skellysolve B was added and the solution cooled. A white crystalline solid separated which was collected by filtration, washed with Skellysolve B, and dried; 0.5 g., m.p. 290–294°. A second crop, 0.35 g., m.p. 288–296°, was obtained by concentration of the filtrate. This material was crude 1,1,2,3,4,4,5,6-octaphenyl-1,4-disilacyclohexadiene (III).

The filtrate from the second crop was evaporated to dryness and the residue taken up in about 100 ml. of hot Skellysolve B. While warm, the solution was adsorbed on a neutral alumina column. Elution with the same solvent gave 0.15 g. of diphenylacetylene, m.p. 58–60°. A carbon tetrachloride fraction yielded 1.4 g. (100%) of 1,2,3,4-tetraphenyl-naphthalene, m.p. 198–201° (m.m.p.).

From the benzene eluent was isolated an additional 0.1 g. of III, m.p. 289–294°. The combined crude yield of III was 0.95 g. (80%). Recrystallization from Skellysolve B-benzene gave 0.8 g. (63%) of colorless monoclinic crystals, m.p. 293.5–296°. The infrared spectrum of III (Nujol) showed major bands at 3.27, 6.26, 6.35, 6.73, 6.98, 9.05, 9.35, 9.70, 10.13, 11.63, 12.55, 13.53, 13.87, 14.38, 14.93, and 15.25 μ .

Anal. Calcd. for C₆₂H₄₆Si₂: C, 86.62; H, 5.59; mol. wt., 721. Found: C, 86.89, 86.70; H, 5.66, 5.73; mol. wt., 709 (osmometer²⁹ in *o*-dichlorobenzene), 712 (osmometer in benzene).

Pyrolysis of the Diphenylsilyl Polymer in the Presence of Diphenylacetylene.—A mixture of 0.5 g. of the polymer and 1.0 g. of diphenylacetylene was heated at 300° for 3 hr. in a sealed, evacuated tube. The contents of the tube were dissolved in ca. 10 ml. of benzene. After adding 25 ml. of Skellysolve B and heating the mixture to boiling, no III could be obtained.

Reaction of II with Basic Alumina.⁸—A cyclohexane solution containing 0.5 g. (0.83 mmole) of III was placed on a basic alumina column. Upon elution with a 50:50 Skellysolve B-carbon tetrachloride solution, a band which fluoresced green in ultraviolet light was separated from a blue fluorescent band which remained on the column. This latter band was eluted with ethyl acetate and gave 0.4 g. (78%) of (1,4-dihydro-1,2,3,4-tetraphenyl-1-naphthyl)diphenylsilanol (IV), m.p. 185–200°. Recrystallization of this material from an ethanol-ether-acetic acid mixture gave 0.29 g. (56.5%) of fine colorless needles, m.p. 197–198°. The major bands in the infrared spectrum of IV (carbon tetrachloride) were located at 2.75, 3.24, 6.24, 6.67, 6.90, 6.97, 9.00, 9.32, 9.67, 11.10, and 11.50 μ .

Anal. Calcd. for C₄₈H₃₈O₂Si: C, 87.30; H, 5.73. Found: C, 87.53, 87.49; H, 5.49, 5.73.

Reaction of II with Lithium Aluminum Hydride.—A solution of 0.5 g. (0.83 mmole) of II in 25 ml. of THF was added dropwise, with stirring, to a mixture of 3.8 g. (0.1 mole) of lithium aluminum hydride and 30 ml. of ether. After all the THF solution was added, the reaction mixture was refluxed for 1 hr. The reaction mixture was acid hydrolyzed, extracted with ether, and the solvents removed with the aid of a rotary evaporator. The white resinous material obtained was dissolved in benzene and 10 volumes of Skellysolve B added. The resulting solution was concentrated to 5 ml., 10 ml. of Skellysolve B added, and the mixture

(26) Heptaphenylcycloheptatriene [M. A. Battiste, *Chem. Ind. (London)*, 550 (1961)] shows the following ultraviolet maxima in m μ (log ϵ): 266 (4.47), 306 (sh) (4.19). For the spectral properties of other heptaphenylcycloheptatrienes, see M. A. Battiste, *J. Am. Chem. Soc.*, **83**, 4101 (1961).

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

(28) (a) For a review of the chemistry of these cyclosilanes, see H. Gilman and G. L. Schwabke, "Organic Substituted Cyclosilanes," in F. G. A. Stone and R. West, "Advances in Organometallic Chemistry," Academic Press, Inc., New York, N. Y., 1964, pp. 89–141; (b) H. Gilman and G. L. Schwabke, *J. Am. Chem. Soc.*, **86**, 2693 (1964).

(29) The instrument used was a vapor pressure osmometer Model 301 A, manufactured by Mechrolab Inc., Mountain View, Calif.

was then allowed to cool overnight. Filtration gave 0.28 g. of 1,2,3,4-tetraphenylphthalene, m.p. 198.5–200.5°. A second crop weighing 0.07 g., m.p. 199–201°, was obtained from the filtrate. The combined crops of the naphthalene derivative represented a quantitative yield (m.m.p.).

From the reaction residue there was obtained a clear oil which was dried at 100° for 2 hr. The principal component of this oil was identified as diphenylsilane, Ph_2SiH_2 , by virtue of its characteristic odor and by comparison of the infrared spectrum with that of an authentic specimen.

1,4,5,6,7,7-Hexaphenyl-7-silabicyclo[2.2.1]hept-5-ene-2,3-dicarboxylic Anhydride (V).—A mixture of 2.0 g. (3.7 mmoles) of I and 8.2 g. of maleic anhydride was heated at 90° for 11 hr. After 3 hr. of heating, crystals appeared in the pale brown liquid. The cooled mixture was treated with a 75:25 Skellysolve B–benzene mixture and allowed to stand. Long needles, 1.9 g. of maleic anhydride (m.p. 50°), were obtained. Further dilution with Skellysolve B gave an additional 4.2 g. of recovered maleic anhydride. The filtrate was evaporated to dryness and the resulting residue treated with a mixture of benzene and cold methanol. Filtration gave 0.7 g. of crude V, m.p. 216–220° dec. Evaporation of the filtrate and addition of acetone gave an additional 0.4 g. of V. Recrystallization of the two crops from Skellysolve B–benzene gave 1.02 g. (43.5%) of V, m.p. 222–223°. An analytical sample, m.p. 224.5–225.5°, was obtained by an additional recrystallization from the same solvent mixture. It is of some interest to note that this compound first crystallized in the form of long needles, but upon standing at room temperature overnight in the presence of the mother liquor the needles had given way to the formation of rather large granular crystals. The infrared spectrum of V (carbon tetrachloride) showed major bands at 3.26, 5.39, 5.60, 6.25, 6.67, 6.75, 6.93, 7.00, 8.04, 8.25, 9.03–9.10 (split), 9.31, 9.45, 9.72, 10.45, 10.73, 10.95, 11.20, and 11.61 μ .

Anal. Calcd. for $\text{C}_{44}\text{H}_{32}\text{O}_3\text{Si}$: C, 82.99; H, 5.06; Si, 4.41. Found: C, 84.39, 84.39; H, 5.46, 5.25; Si, 4.16, 4.11.

Reaction of I with Phenylacetylene (Attempted).—When 2.0 g. (3.7 mmoles) of I and 2.5 g. of phenylacetylene were heated at 72° for 5 hr., no reaction occurred. Likewise, 1.2 g. (2.9 mmoles) of I and 2.5 g. of phenylacetylene at 100° for 11 hr. gave, subsequent to the usual work-up, 1.1 g. (73.5%) of recovered I.

Some reaction appeared to have occurred when 1.2 g. (2.9 mmoles) of I and 2.4 g. of phenylacetylene were heated at 120° for 24 hr. However, the dark orange reaction mixture could not be purified to yield any identifiable material. Since this procedure offered no advantage over the benzyne reaction, no further work was devoted to this reaction.

Dimethyl 1,4,5,6,7,7-Hexaphenyl-7-silanorbornadiene-2,3-dicarboxylate (VI).—Two grams (3.7 mmoles) of I and 2.0 g. of dimethyl acetylenedicarboxylate were heated at 75° for 11 hr. The reaction mixture was boiled in about 35 ml. of cyclohexane and Skellysolve B was added until the solution just became cloudy. After allowing the reaction mixture to cool to room temperature, the yellow solution was decanted from a yellow pasty precipitate. Concentration of the yellow solution was carried out until solid began to crystallize out. Subsequent to cooling, filtration gave 2.2 g. of pale yellow solid, m.p. 190–205°. Recrystallization from Skellysolve B–cyclohexane gave 1.89 g. (75%) of white solid, m.p. 208–211° dec. The infrared spectrum of VI (carbon tetrachloride) showed major bands at 3.28, 3.39, 5.80, 6.26, 6.70, 6.94, 7.00, 7.70, 8.15, 8.91, 9.04–9.11 (split), 9.21, 9.30, 9.45, 9.60, 9.76, 10.41, 11.00, 11.27, and 11.42 μ .

Anal. Calcd. for $\text{C}_{46}\text{H}_{36}\text{O}_4\text{Si}$: C, 81.15; H, 5.33. Found: C, 81.41, 81.63; H, 5.40, 5.40.

Reaction of VI with Basic Alumina.⁸—A solution of 0.5 g. (0.9 mmole) of VI in 30 ml. of cyclohexane was adsorbed on a basic alumina column. A yellow color appeared immediately. The color gradually faded and a band fluorescing blue in ultraviolet light developed. This band was eluted from the column with 150 ml. of benzene. After evaporation of the benzene, the residue was treated with hot Skellysolve B and cooled. Filtration gave 0.35 g. (96%) of dimethyl tetraphenylphthalate,⁹ m.p. 258–260° (m.m.p.).

Isomerization of VI with Ethanol.—One gram (1.8 mmoles) of VI was dissolved in 10 ml. of benzene. To this solution was added 40 ml. of ethanol. The solution was evaporated to dryness *in vacuo* at room temperature. The yellow residue was shaken with about 30 ml. of Skellysolve B and filtered to give 0.75 g. of a bright yellow solid, m.p. 202–206°. Recrystallization from Skellysolve B gave a crystalline yellow solid, m.p. 209–211°.

Anal. Calcd. for $\text{C}_{46}\text{H}_{36}\text{O}_4\text{Si}$: C, 81.15; H, 5.33; Si, 4.12. Found: C, 81.30; 81.53; H, 5.24, 4.99; Si, 4.16.

The infrared spectrum of this yellow isomer (carbon tetrachloride) showed major bands at 3.26, 3.38, 5.79, 6.15, 6.26, 6.70, 6.93, 6.99, 7.79, 7.85, 7.95, 8.17, 8.34, 8.52, 8.81, 8.97–9.05 (split), 9.35, 9.54, 9.60, 9.74, 10.49, 11.03, 11.35, 11.40, and 11.87 μ . In determining the spectrum in carbon tetrachloride it was observed that the yellow color of the solution disappeared when it was allowed to stand a few days. The spectrum of this colorless solution showed the major bands found in the spectrum of dimethyl tetraphenylphthalate.

Direct Preparation of the Yellow Isomer from I and Dimethyl Acetylenedicarboxylate.—Two grams (3.7 mmoles) of I and 2.6 g. of dimethyl acetylenedicarboxylate were heated at 70° for 16 hr. in a stoppered 10-ml. erlenmeyer flask immersed in an oil bath. A faint pink solution containing a yellowish colored precipitate formed during the course of the reaction. Upon shaking and cooling the reaction mixture solidified. The resulting solid mass was dissolved in 175 ml. of cyclohexane, concentrated, cooled, and *ca.* 50 ml. of ethanol added. The yellow solution obtained was evaporated *in vacuo* at room temperature until a yellow precipitate formed. Filtration gave 1.1 g. of yellow isomer, m.p. 197–206°. From the filtrate there was obtained an additional 0.9 g. of yellow solid, m.p. 195–205°. The combined crops represent a yield of 79%. Recrystallization from Skellysolve B gave the yellow isomer as a crystalline solid, m.p. 209–211°. A mixture melting point with the yellow solid obtained from the ethanol rearrangement showed no depression, and the infrared spectra were superimposable.

Reaction of the Yellow Isomer with Sodium Methoxide.—A solution of sodium methoxide was prepared by treating 0.2 g. (9.0 mg.-atoms) of sodium in 50 ml. of absolute methanol. To this solution was added 0.5 g. (0.9 mmole) of the yellow isomer and the mixture warmed slightly. The yellow solid dissolved rapidly forming a faint yellow-brown color. Evaporation of the solvent *in vacuo* at room temperature gave an orange-brown residue. This residue was treated with 30 ml. of benzene giving a yellow solution and a dark orange-brown precipitate. The solid phase was separated by decantation and the solution evaporated to dryness. The pale yellow residue was treated with 20 ml. of ethanol and filtered. Water was added to the filtrate until the solution became cloudy. Cooling and filtration gave 0.37 g. of solid, m.p. 255–260°. Recrystallization from ethanol gave 0.2 g. (41%) of dimethyl tetraphenylphthalate, m.p. 260–261° (m.m.p.).

Hydrogenolysis of the Yellow Isomer (Attempted).—A methanol solution containing 0.1045 g. (0.153 mmole) of the yellow isomer and a catalytic amount of platinum oxide was subjected to hydrogenation conditions at atmospheric pressure for 1.5 hr. No hydrogen uptake was observed. Evaporation of the solvent subsequent to filtration gave a bright yellow solid. The infrared spectrum (CCl_4) of this material was superimposable with that of a known sample of the yellow isomer (m.m.p.).

Hydrogenation of Dimethyl 1,4,5,6,7,7-Hexaphenyl-7-silanorbornadiene-2,3-dicarboxylate (VI) (Attempted).—A solution of 200 ml. of cyclohexane, 0.5 g. (0.74 mmole) of VI, and 0.1 g. (20% by weight) of 10% palladium-on-charcoal catalyst was placed in a Parr hydrogenation shaker.³⁰ The system was flushed several times with hydrogen. Finally, the pressure was adjusted to *ca.* 50 p.s.i.g., and the mixture was shaken for 18 hr. Subsequent to filtration and evaporation of the solvent, 0.45 g. (90%) of unchanged VI was recovered (m.m.p.).

Similarly, a cyclohexane solution of VI was not reduced in the presence of a platinum oxide catalyst (room temperature, 1 atm.).

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(30) The apparatus was manufactured by Paar Instrument Co., Moline, Ill., Hydrogenation Apparatus Model CA No. 314.