

Small-Ring Organosilicon Compounds.

III. 1,1,2-Triphenyl-1-silacyclobut-2-ene and 1,1,2-Triphenyl-1-silacyclopent-2-ene

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The preparation of 2-bromo-1,1,2-triphenyl-1-silacyclobutane (V) and its conversion to the first reported silacyclobutene derivative, 1,1,2-triphenyl-1-silacyclobut-2-ene (I), is described. Detailed analyses of the n.m.r. spectra of I and V were carried out. The physical, spectral, and chemical properties of I are contrasted with those of its five-membered ring homolog, 1,1,2-triphenyl-1-silacyclopent-2-ene (II).

Introduction

In the first paper of this series we reported¹ a summary of the chemistry of the known silacyclobutanes. In addition, that report included a qualitative comparison of the relative reactivities of 1,1,2-triphenyl-1-silacyclobutane and 1,1,2-triphenyl-1-silacyclopentane toward a variety of reagents, together with a theoretical consideration of the factors contributing to the enhanced reactivity of silacyclobutanes. In a subsequent report² we described the preparation and properties of a pseudosilacyclobutene derivative, namely, 2:3-benzo-1,1-diphenyl-1-silacyclobut-2-ene.

At the present time no preparations or attempted preparations of silacyclobutenes have been reported. This report describes the methods employed in the preparation of the first known silacyclobutene, namely, 1,1,2-triphenyl-1-silacyclobut-2-ene (I). The reactivity of I is compared with that of its five-membered ring homolog, 1,1,2-triphenyl-1-silacyclopent-2-ene (II).

Results and Discussion

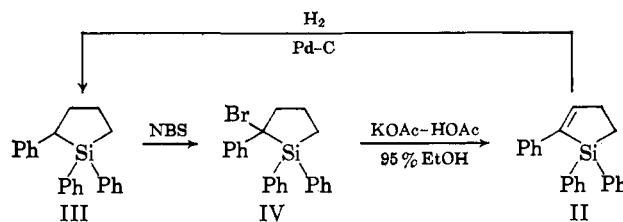
Preparation and Properties of 1,1,2-Triphenyl-1-silacyclopent-2-ene (II). Compound II was prepared by a two-step synthesis starting with the previously described¹ 1,1,2-triphenyl-1-silacyclopentane (III). Reaction of III with N-bromosuccinimide (NBS) gives 2-bromo-1,1,2-triphenyl-1-silacyclopentane (IV) in 79% yield.

The n.m.r. spectrum of IV (CCl₄) contains a multiplet centered at τ 8.65 assigned to the methylene protons adjacent to silicon. In addition to the low-field aromatic multiplet, the remainder of the spectrum shows a broad band centered at τ 7.60 due to the four remaining methylene protons. The ratio of aromatic/aliphatic protons was 2.50 (calcd. 2.50).

Treatment of IV with a potassium acetate-acetic acid mixture in refluxing ethanol gave the desired olefin II (77%). Compound II is a stable, colorless crystalline solid, m.p. 119–120°. This compound exhibits a light blue fluorescence in ultraviolet light in the solid state and shows the following ultraviolet absorption maximum: λ_{\max} 255 m μ (log ϵ 4.065).³

(1) H. Gilman and W. H. Atwell, *J. Am. Chem. Soc.*, **86**, 2687 (1964).

(2) H. Gilman and W. H. Atwell, *ibid.*, **86**, 5589 (1964).



The n.m.r. spectrum of II contains two multiplets at τ 8.73 and 7.22 assigned to the protons of the methylene group adjacent to silicon and the olefinic bound methylene group, respectively.⁴ The olefinic proton could not be observed in the spectrum and the aromatic/aliphatic proton ratio was in poor agreement with the theoretical value when the aromatic area was assumed to be equivalent to 15 protons. It appeared reasonable that the olefinic proton band could lie beneath the aromatic absorption since this latter band was quite broad and extended to τ 3.15. Indeed this appeared to be the case since a recalculation of the above ratio using an aromatic area based on 16 protons gave a value of 4.0 (calcd. 4.0). In addition, the olefin II was quite readily hydrogenated to give 1,1,2-triphenyl-1-silacyclopentane (II).

The infrared spectrum of II (CCl₄) is significantly different from that of the saturated material III. The spectrum of II shows a complete absence of the 9.60- μ band present in III.¹ Of particular interest is the fact that II shows three bands at 10.66 (m), 10.80 (s), and 11.02 (w) μ . At the present time these bands appear to be associated with the cyclic olefin system.⁵

Compound II does not react with ethanolic solutions of silver nitrate and is recovered quantitatively when chromatographed on acidic, neutral, and basic alumina.

Preparation and Properties of 2-Bromo-1,1,2-triphenyl-1-silacyclobutane (V). Reaction of 1,1,2-triphenyl-1-silacyclobutane (VI)¹ with NBS gives a monobromo compound (C₂₁H₁₉BrSi) which has been assigned structure V. The structural assignment was based on analytical, spectral, and chemical evidence.



(3) These results are in excellent agreement with those reported for 1-phenylcyclopentene: $\lambda_{\max}^{\text{EtOH}}$ 255 m μ (log ϵ 4.030); cf. W. H. Tallent, *J. Org. Chem.*, **21**, 862 (1956).

(4) These values are similar to those reported for the corresponding protons in 1,1-dichloro-1-silacyclopent-2-ene; see R. A. Benkeser, Y. Nagi, J. L. Noe, R. F. Cunico, and P. H. Gund, *J. Am. Chem. Soc.*, **86**, 2446 (1964).

(5) The infrared spectrum of 1-phenylcyclopentene contains only a single absorption in this region at 10.48 μ .³

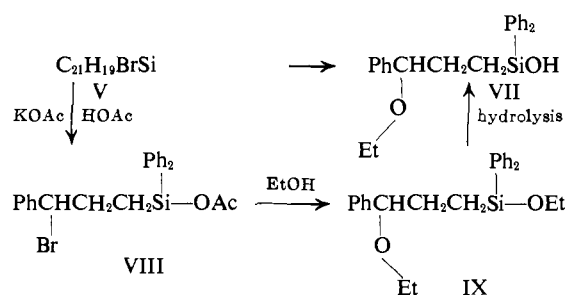
The unusual features of the n.m.r. spectrum of V prompted us to carry out a detailed analysis.⁶ An expansion of the aliphatic proton bands of the observed spectrum together with the calculated spectrum is given in Figure 1. The average deviation between the observed and the calculated frequency was 0.14 (only observed frequencies were included in this average). Bands with an intensity lower than 0.07 are not included in the calculated spectrum in Figure 1. The compatibility of the observed spectrum and the structural assignment is clearly indicated by an examination of Figure 1 and Table I.

Table I. N.m.r. Data for (3-Ethoxy-3-phenylpropyl)diphenylsilanol (VII)^{a,b}

Band position, τ values	Relative intensity	Band assignment
		O
5.83 (t) ^c	1	HCC-
6.32 (s) ^d	1	SiOH
6.74 (dq) ^e	2	-CCH ₂ O-
8.19 (m) ^f	2	-CCH ₂ C-
8.87 (m) ^f	5	CH ₂ C- and -CCH ₂ Si

^a Deuteriochloroform solvent. ^b Aromatic region excluded. ^c t = triplet, $J = 6.7$ c.p.s. ^d Broad singlet. ^e Double quartet separated by ca. 2.6 c.p.s. ($J = 6.7$ c.p.s.). ^f m = multiplet where the number of peaks could not be counted accurately.

In addition to the n.m.r. spectrum, strong chemical evidence was obtained which supports the conclusion that the monobromo compound is V. Reaction of the C₂₁H₁₉BrSi compound with a potassium acetate-acetic acid mixture in refluxing ethanol gives (3-ethoxy-3-phenylpropyl)diphenylsilanol (VII). The silanol VII is believed to result from (a) the cleavage of the silacyclobutane V by acetate ion⁸ giving VIII, (b) reaction



of VIII with ethanol to give the diethoxy compound IX, and finally (c) hydrolysis of the SiOEt to SiOH during work-up.⁹

The assignment of structure VII follows from an examination of the infrared (see Experimental section) and n.m.r. spectra. The pertinent n.m.r. spectral data for VII are listed in Table I. An interesting feature

(6) The authors are grateful to Dr. G. Morris and L. Rodewald for carrying out this n.m.r. analysis. A published⁷ iterative method for calculating accurate parameters from high-resolution spectra was adapted by L. Rodewald for use with the IBM 7074 computer.

(7) (a) C. A. Reilly and J. D. Swalen, *J. Chem. Phys.*, **32**, 1378 (1960); (b) *ibid.*, **34**, 980 (1961); (c) *ibid.*, **34**, 2122 (1961).

(8) The initial cleavage of V by acetate ion is consistent with the ring opening observed with other nucleophiles.¹

(9) In one experiment, the infrared spectrum (CCl₄) of the crude product from the reaction of V with KOAc-HOAc in ethanol contained bands at 8.65, 9.28, and 10.55 μ , indicative of the SiOEt linkage (in compound IX). No SiOH bands could be detected in the latter spectrum before chromatographic work-up.

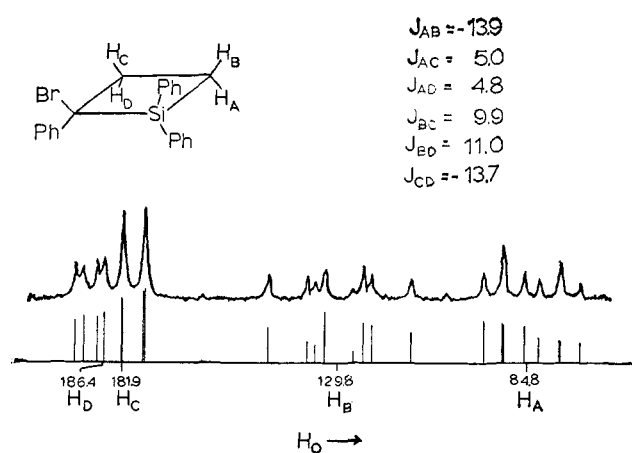
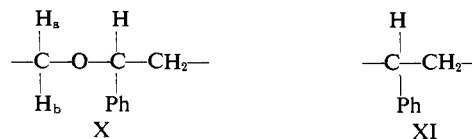


Figure 1. The observed aliphatic proton spectrum of 2-bromo-1,1,2-triphenyl-1-silacyclobutane together with that calculated from the parameters given in Table I. The chemical shift values are reported in c.p.s. downfield from tetramethylsilane. The coupling constants ($J =$ c.p.s.) are tabulated above the spectrum.

observed in this spectrum was the presence of a double quartet at τ 6.74 (see Table I, footnote e). It appears that the nonequivalence of the protons in the methylenoxy group results from an intrinsic internal asymmetry of the ether grouping X.¹⁰ To the protons H_a



and H_b of the methylenoxy group the attached group XI is asymmetric, and each proton experiences a different average environment. To what extent restricted rotation may be contributing to the nonequivalence was not studied.

The environment about the benzylic carbon atom was further confirmed by a double resonance¹¹ experiment. Irradiation of the methylene protons (PhCH(O-)₂CH₂-) 136 c.p.s. upfield from the benzylic proton triplet collapsed the latter to a sharp singlet. Finally it should be noted that the position of the ethoxy group in the silanol VII lends considerable support to the conclusion that the bromo substituent in V was located on the benzylic carbon.

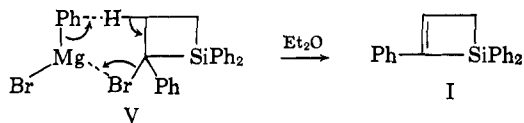
Preparation and Properties of 1,1,2-Triphenyl-1-silacyclobut-2-ene (I). The main difficulty involved in the preparation of a silacyclobutene derivative is the susceptibility of the four-membered silicon rings to nucleophilic ring opening.¹ Thus, a great majority of the known dehydrohalogenation techniques are of little use. The successful synthesis of I involved the treatment of 2-bromo-1,1,2-triphenyl-1-silacyclobutane (V) with an ethereal solution of phenylmagnesium bromide (1:1 ratio). By analogy with previously reported¹² dehydrohalogenations of this type we have suggested that this

(10) For a discussion of this subject, see (a) L. M. Jackman, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pergamon Press Inc., New York, N. Y., 1959, pp. 101-103; (b) J. A. Elvidge and R. G. Foster, *J. Chem. Soc.*, 981 (1964); (c) G. M. Whitesides, D. Holtz, and J. D. Roberts, *J. Am. Chem. Soc.*, **86**, 2628 (1964).

(11) R. Freeman, *Mol. Phys.*, **3**, 435 (1960).

(12) M. S. Kharasch and O. Reimuth "Grignard Reactions of Non-metallic Substances," Prentice-Hall Co., Inc., New York, N. Y., 1954, p. 1052.

bimolecular reaction proceeds through a cyclic mechanism.

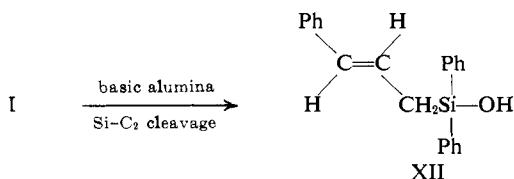


At the present time we attribute the successful synthesis of I to the stability of the silacyclobutane and silacyclobutene rings to phenylmagnesium bromide¹ and to steric conditions (in V) resulting in a slow "condensation" reaction.¹²

Compound I is a white, moderately stable solid, m.p. 54–55°, which can be distilled without apparent decomposition at low pressures (b.p. 149–150° at 0.005 mm.).¹³ The ultraviolet spectrum of I (ethanol) shows a maximum at 256 m μ (log ϵ 4.194). These values are in close agreement with those reported¹³ for 1-phenylcyclobutene, $\lambda_{\text{max}}^{\text{EtOH}}$ 251–255 m μ (log ϵ 4.138–4.146). The infrared spectrum of I (CCl₄) showed a complete absence of the 11.52- μ band previously reported¹ in the saturated precursor VI. In addition, the spectrum of I contains a trio of bands at 10.42 (m), 10.68 (m), and 11.02 (w) μ . While this latter pattern is similar to that observed in 1,1,2-triphenyl-1-silacyclopent-2-ene (II), a shifting of the position of the first two bands is apparent.

The n.m.r. spectrum of I contains a doublet centered at τ 8.10 ($J = 2.0$ c.p.s.). The magnitude of this coupling constant is of the order observed¹⁴ for cyclobutene derivatives. As in the case of the five-membered ring homolog II, the olefinic band was not apparent and the remainder of the spectrum consisted of a broad aromatic region extending to τ 3.10. Assuming an aromatic area of 16 protons (olefinic included in this area) gave an aromatic/aliphatic ratio of 8.0 (calcd. 8.0). In the case of I, it became desirable (for reasons which will become apparent later) to confirm the existence of the olefinic proton. This was readily accomplished by a double resonance¹¹ experiment. Irradiation of the aromatic multiplet 329 c.p.s. downfield from the methylene doublet collapsed the latter to a singlet (broad). From the above information the position of the olefinic proton was calculated as τ 2.72, well within the edge of the aromatic multiplet.

Compound I reduces an ethanolic solution of silver nitrate in agreement with previously reported^{1,15} silacyclobutane reactivity. Chromatography of I employing a basic alumina column results in ring opening. The infrared spectrum of the resulting product showed the presence of a SiOH group and a *trans* double bond,



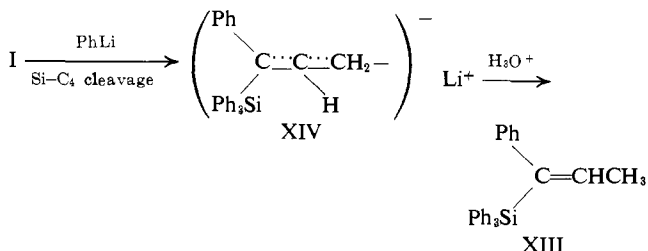
(13) Pure 1-phenylcyclobutene, an oil of styrene-like odor, sets to a gel (probably a polymer) on standing for several weeks; see J. W. Wilt and D. D. Roberts, *J. Org. Chem.*, **27**, 3430 (1962).

(14) (a) O. L. Chapman, *J. Am. Chem. Soc.*, **85**, 2014 (1963); (b) G. V. S. Smith and H. Kriloff, *ibid.*, **85**, 2016 (1963).

(15) For a discussion of the use of silver nitrate as a qualitative test for four-membered silicon-containing rings, see H. Gilman and W. H. Atwell, *J. Organometal. Chem.*, **2**, 277 (1964).

suggesting the formation of the silanol XII. The ultraviolet spectrum of XII contained a maximum at 259 m μ , giving further support to the proposed structure.

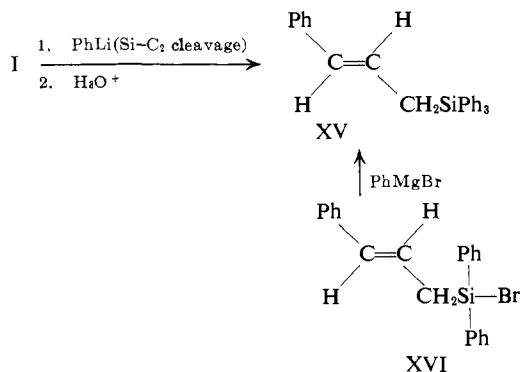
An alternate mode of ring opening of I was observed with phenyllithium. In this latter case the reaction product is 1-phenyl-1-(triphenylsilyl)propene-1 (XIII).



In view of the allylic nature of the intermediate organometallic compound XIV, it was not possible to ascertain the stereochemistry of the olefin XIII. The n.m.r. spectrum of XIII (CCl₄) shows, in addition to the aromatic multiplet, a doublet at τ 8.15 ($J = 6.5$ c.p.s.) and a quartet at τ 3.59 ($J = 6.5$ c.p.s.), assigned to the methyl and methinyl protons, respectively.

The ultraviolet spectrum of XIII shows no maximum above 220 m μ . An examination of a molecular model (Stuart models) of XIII revealed that the bulky triphenylsilyl group prevents coplanarity of the phenyl group and the ethylenic bond, thus rationalizing the observed spectrum. No (3-phenyl-2-propenyl)triphenylsilane (XV), the product which would result from Si-C₁₁ cleavage, could be isolated. A known sample of XV was prepared from bromo(3-phenyl-2-propenyl)diphenylsilane¹ (XVI) and phenylmagnesium bromide ($\text{H} > \text{C}=\text{C} < \text{H}$ at 10.45 μ , PhC=CH at 261 m μ).

One of the most unexpected properties of I was its inertness to $>\text{C}=\text{C}<$ hydrogenation. Although a variety of hydrogenation conditions were employed, I,



contrary to its five-membered ring homolog II, resisted hydrogen uptake (hence the necessity for the double resonance experiment). It seems a logical assumption that this resistance to hydrogenation can be attributed to steric conditions resulting in inadequate contact between I and the catalytic surface.¹⁶

Experimental

The alumina used was made by Woelm and purchased from Alupharm Chemicals, New Orleans, La. The n.m.r. spectra were measured with a Varian HR-60

(16) The same reasoning has been previously suggested to explain the inertness of dimethyl 1,4,5,6,7,7-hexaphenyl-7-silanorbornadiene-2,3-dicarboxylate (another strained organosilicon compound) to $>\text{C}=\text{C}<$ hydrogenation; see H. Gilman, S. G. Cottis, and W. H. Atwell, *J. Am. Chem. Soc.*, **86**, 5584 (1964).

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 melting points are uncorrected.

2-Bromo-1,1,2-triphenyl-1-silacyclopentane (IV). A mixture of 3.14 g. (0.01 mole) of 1,1,2-triphenyl-1-silacyclopentane¹ (III), 1.78 g. (0.01 mole) of N-bromosuccinimide (NBS), and a catalytic amount of benzoyl peroxide¹⁷ in 40 ml. of carbon tetrachloride was heated at reflux temperature. The reaction course was followed by observing the appearance of succinimide, and prolonged heating was avoided. Subsequent to cooling, filtration, and evaporation of the solvent, there was obtained 3.5 g. (90%) of white solid, m.p. 98–100° dec. Recrystallization from petroleum ether (b.p. 60–70°) raised the melting point to 101–103° dec. (79%).

Anal. Calcd. for C₂₂H₂₁BrSi: C, 67.18; H, 6.36; Si, 7.14. Found: C, 69.01, 69.00; H, 5.52, 5.71; Si, 7.21, 7.22.

Compound IV decomposed upon standing in a closed vial. The silicon analysis was carried out immediately after purification whereas the carbon-hydrogen analysis was carried out at a later date. In view of the ease of decomposition of IV, subsequent reactions employing this compound were carried out on the crude product immediately after preparation.

The infrared spectrum of this material was very similar to that of 1,1,2-triphenyl-1-silacyclopentane (III) except for the absence of the 9.60- μ band.

Table II. The Infrared Spectrum of II

Band position, μ	Intensity ^a	Characteristic ^{b,c,d}
3.27, 3.30	m-w	Aromatic CH
3.44, 3.52	m-w	Aliphatic CH
6.25, 6.69	w-m	C ₆ H ₅ -
6.35	w	Possibly Si=C ^e
6.93	m	Possibly -CH ₂ -
7.00	s	C ₆ H ₅ -
7.95, 8.42, 8.85	m-w-s	Possibly Si-alkyl
9.00	s	SiC ₆ H ₅
9.34, 9.72, 10.03	w-m-w	C ₆ H ₅ -
10.66, 10.80, 11.02	m-s-w	See Discussion section

^a Letters indicate the relative intensities of absorption bands: s, strong; m, medium; w, weak. ^b L. J. Bellamy, "The Infrared Spectra of Complex Molecules," Methuen and Co., Ltd., London, 1954. ^c A. L. Smith, *Spectrochim. Acta*, **16**, 87 (1960). ^d K. Nakanishi, "Infrared Absorption Spectroscopy," Holden-Day, Inc., San Francisco, Calif., 1962. ^e See ref. 4.

1,1,2-Triphenyl-1-silacyclopent-2-ene (II). The crude 2-bromo-1,1,2-triphenyl-1-silacyclopentane (IV) prepared (as described above) from 6.28 g. (0.02 mole) of 1,1,2-triphenyl-1-silacyclopentane (III) and 3.56 g. (0.02 mole) of NBS was dissolved in 70 ml. of ethanol. Four grams (0.04 mole) of potassium acetate and 6 ml. of glacial acetic acid were added and the mixture was refluxed for 12 hr. The resulting mixture was cooled and filtered to give 4.8 g. of II, m.p. 119–120° (76.5%). Recrystallization from absolute ethanol gave no change in melting point.

(17) In all the NBS reactions carried out in this work, an additional amount of peroxide was added if the reaction did not initiate within 20 min. In addition, equally good results were obtained when a General Electric sun lamp was used to initiate the NBS reactions.

Compound II was completely stable when chromatographed on a basic alumina column.

Anal. Calcd. for C₂₂H₂₀Si: C, 84.60; H, 6.41; Si, 9.00. Found: C, 84.48, 84.30; H, 6.47, 6.57; Si, 8.90, 9.10.

Hydrogenation of II. A mixture of 0.2 g. (0.637 mmole) of II and a catalytic amount of 10% palladium on charcoal in 15 ml. of cyclohexane was hydrogenated at 1 atm. At the end of 2 hr. approximately 1 equiv. of hydrogen uptake was observed. Filtration followed by evaporation of the solvent gave a viscous oil which crystallized upon addition of ethanol to give 0.15 g. (75%) of 1,1,2-triphenyl-1-silacyclopentane,¹ m.p. and m.m.p. 84–86°.

2-Bromo-1,1,2-triphenyl-1-silacyclobutane (VI). A mixture of 2 g. (0.0067 mole) of 1,1,2-triphenyl-1-silacyclobutane¹ and 1.2 g. (0.0067 mole) of NBS in 40 ml. of carbon tetrachloride was irradiated with a General Electric sun lamp for 10–15 min. Cooling followed by filtration gave 0.6 g. (91%) of succinimide, m.p. and m.m.p. 124–126°. Evaporation of the solvent under vacuum gave a light yellow oil. This oil was taken up in petroleum ether (b.p. 60–70°) and after standing for 6 days the reaction product crystallized. Filtration gave 2.4 g. of solid, m.p. 67–69°. Several recrystallizations from the same solvent raised the melting point to 69–70° (40%).

Anal. Calcd. for C₂₁H₁₉BrSi: Si, 7.41. Found: Si, 7.52, 7.56.

The infrared spectrum of V (CCl₄) was quite similar to that of 1,1,2-triphenyl-1-silacyclobutane (VI) except that in the former the 11.52- μ band was extremely weak. The n.m.r. spectrum of crude V (oil obtained upon evaporation of the carbon tetrachloride) was essentially identical with the spectrum of pure V (see Figure 1). This result indicates that the yield of V was essentially quantitative rather than the 40% isolated. Since V was observed to decompose rapidly upon standing in a closed vial, subsequent reactions were carried out using the crude product shortly after its preparation.

Preparation of (3-Ethoxy-3-phenylpropyl)diphenylsilanol (VII). The crude 2-bromo-1,1,2-triphenyl-1-silacyclobutane (V), prepared (as described above) from 4.0 g. (0.0134 mole) of 1,1,2-triphenyl-1-silacyclobutane (VI) and 2.37 g. (0.0134 mole) of NBS, was treated with 1.30 g. (0.0134 mole) of potassium acetate and 2–3 ml. of glacial acetic acid in 50 ml. of ethanol. An exothermic reaction ensued and the mixture was then refluxed for 4–5 hr. The reaction mixture was evaporated to dryness, petroleum ether (b.p. 60–70°) was added, and the mixture was filtered to give a trace of solid, m.p. 120–126°. The infrared spectrum of this material (CCl₄) contained bands at 8.65, 9.28, and 10.55 μ indicative of the SiOEt group. No SiOH bands could be detected. The filtrate was chromatographed on a basic alumina column. Ethyl acetate eluates gave 1.10 g. of product, m.p. 119–123° (22.2%). Recrystallization from carbon tetrachloride-petroleum ether (b.p. 60–70°) gave 0.90 g. of pure VII, m.p. 129–130° (18.4%).

Anal. Calcd. for C₂₃H₂₇O₂Si: C, 75.98; H, 7.49; Found: C, 75.88, 75.66; H, 7.05, 6.91.

The infrared spectrum of VII (CCl₄) contained bands at 2.70 and 2.92 μ characteristic of the free OH and hydrogen-bonded OH, respectively. A strong band at

9.05 μ indicative of the Si-phenyl linkage and a strong to medium intensity band at 9.20 μ (C-O-C linkage) are structurally important.

Preparation of 1,1,2-Triphenyl-1-silacyclobut-2-ene (I). Crude 2-bromo-1,1,2-triphenyl-1-silacyclobutane (V), prepared from 8.0 g. (0.027 mole) of 1,1,2-triphenyl-1-silacyclobutane and 4.76 g. (0.0268 mole) of NBS as described above, was dissolved in 100 ml. of ether. Phenylmagnesium bromide (0.027 mole) was added slowly to the ethereal solution of V so that little or no refluxing occurred. The separation of magnesium bromide was readily apparent during the reaction. The reaction mixture was hydrolyzed quickly with 5 *N* hydrochloric acid and extracted with ether and the extracts were dried over sodium sulfate. Subsequent to evaporation of solvent the residue was dissolved in petroleum ether (b.p. 60–70°) and chromatographed on an acidic alumina column. Elution with the same solvent gave 5.0 g. of viscous oil. Distillation of this oil gave, in addition to a small amount of biphenyl, 3.0 g. of I, b.p. 149–151° (0.005 mm.). This material solidified slowly upon treatment with a small amount of petroleum ether (b.p. 60–70°) m.p., 50–53° (37.5%). The purity of this material was sufficient for further reactions. An analytical sample was obtained by careful recrystallization from a large volume of absolute ethanol, m.p. 54–55°.

Anal. Calcd. for C₂₁H₁₈Si: C, 84.58; H, 6.03; Found: C, 84.36, 84.40; H, 6.26, 6.10.

An infrared spectrum of I (CCl₄ and BrCCl₃) showed the prominent bands listed in Table III.

Table III. The Infrared Spectrum of I

Band position, μ	Intensity ^a	Characteristic ^b
3.25, 3.30	s-m	Aromatic CH
3.40, 3.50	s-m	Aliphatic CH
6.26, 6.72, 7.0	w-m-s	C ₆ H ₅ -
6.38	w	Possibly SiC=C ^c
6.92	m	Possibly -CH ₂ -
7.95, 8.23, 8.43	m-m-w	Possibly Si-alkyl
9.0 (split)	s	SiC ₆ H ₅
9.37, 9.73, 10.04	m-m-w	C ₆ H ₅ -
10.42, 10.68, 11.02	m-m-w	See Discussion section

^a See footnote a, Table II. ^b See footnotes b, c, and d, Table II. ^c See ref. 4.

Reaction of I with Basic Alumina. A petroleum ether (b.p. 60–70°) solution of I (0.5 g.) was adsorbed on a basic alumina column (exothermic reaction). Elution with ethanol gave XII as a viscous oil (0.35 g., 70%). The infrared spectrum of this material (capillary cell) showed the absence of SiH and SiOSi absorption bands. The presence of bands at 3.0 and 12.0 μ characteristic of the OH and SiO stretch, respectively, indicated the presence of an SiOH group. A medium intensity band at 10.45 μ was indicative of the presence of a *trans* double bond. A weak band at 6.08 μ characteristic of the phenyl-conjugated double bond stretching vibrations was also present. The ultraviolet spectrum contained a typical styrene-type absorption band at 259 $m\mu$. In view of the anticipated high boiling point of this compound and the possibility of decomposition, no attempt was made to purify this material further.

Reaction of I with Phenyllithium. Compound I (0.25 g., 8.34 mmoles) was dissolved in 30 ml. of ether and added to 30 mmoles of phenyllithium (prepared in ether). Subsequent to 2 hr. of stirring the mixture was acid hydrolyzed. After the usual work-up, the reaction mixture was dissolved in petroleum ether (b.p. 60–70°) and chromatographed on an acidic alumina column. Elution with the same solvent gave 0.1 g. of slightly crude 1-phenyl-1-(triphenylsilyl)propene-1 (XIII), m.p. 161–164°. Recrystallization from ethanol raised the melting point to 166–168°.

Anal. Calcd. for C₂₇H₂₄Si: C, 86.13; H, 6.37; Found: C, 85.70, 85.82; H, 6.32, 6.22.

Preparation of (3-Phenyl-2-propenyl)triphenylsilane (XV). A THF solution of 1.0 g. (2.63 mmoles) of bromo-(3-phenyl-2-propenyl)diphenylsilane¹ (XVI) was added to an excess of phenylmagnesium bromide (10.0 mmoles). The mixture was refluxed for 2 hr., acid hydrolyzed, and extracted with ether, and the extracts were dried over sodium sulfate. Subsequent to removal of the solvents the residue was dissolved in petroleum ether (b.p. 60–70°) and chromatographed on basic alumina. Elution with the same solvent gave 0.4 g. of crude XV, m.p. 89–95° (40.4%). Recrystallization from petroleum ether (b.p. 60–70°)-ethanol raised the melting point to 96.5–97.5° (27%).

Anal. Calcd. for C₂₇H₂₄Si: C, 86.13; H, 6.37; Found: C, 86.31, 86.31; H, 6.35, 6.32.

The infrared spectrum of XV (CCl₄) contained a weak band at 6.08 μ characteristic of the phenyl-conjugated double bond and also a strong absorption at 10.44 μ indicative of a *trans* double bond. Thus compounds XII, XV, and XVI all show infrared properties characteristic of the phenyl-conjugated *trans* double bond.

The ultraviolet spectrum of XV contained a typical styrene-type absorption band at 261 $m\mu$.

Attempted Hydrogenation of I. A. In the presence of Pd-C or PtO at Room Temperature. A mixture of I (0.2 g., 0.67 mmole), 15 ml. of cyclohexane, and 0.1 g. of 10% palladium on charcoal was subjected to hydrogenation conditions (H₂, 1 atm.) for 1 hr., with little hydrogen uptake being observed. Filtration followed by evaporation of the solvent gave 0.18 g. (90%) of recovered I, m.p. and m.m.p. 53–55°.

When the above conditions were repeated using a platinum oxide catalyst, 85% of recovered starting material was obtained, m.p. 53–55°.

B. In the Presence of PtO at 40–50 P.s.i.g. and Room Temperature. Compound I (0.2 g., 0.67 mmole), 30 ml. of cyclohexane, and 0.1 g. of PtO were placed in a Parr hydrogenation shaker¹⁸ and the system was flushed several times with hydrogen. Finally, the pressure was adjusted to ca. 40–50 p.s.i.g. and the mixture was shaken for 2 hr. Filtration of the resulting mixture followed by removal of the solvent gave 0.18 g. (90%) of recovered I, m.p. and m.m.p. 53–55°.

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(18) The apparatus was manufactured by the Parr Instrument Co., Moline, Ill., hydrogenation apparatus Model C. A. No. 314.

