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Small-Ring Organosilicon Compounds. II. 2:3-Benzo-1,1-diphenyl-1-silacyclobut-2-ene[1]

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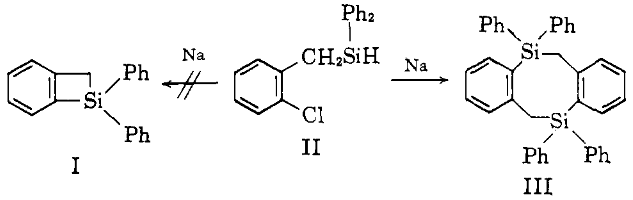
The first reported pseudo-silacyclobutene derivative, namely, 2:3-benzo-1,1-diphenyl-1-silacyclobut-2-ene (I), has been prepared by three independent synthetic methods. The physical and spectral properties of I are described, together with the observed chemical reactivity toward a variety of reagents. Compound I undergoes facile ring opening with bromine in carbon tetrachloride, ethanolic silver nitrate, basic alumina, phenyllithium, and lithium aluminum hydride (LAH). Reaction of I with LAH in refluxing tetrahydrofuran gives a dimeric product which has been shown to be 2:3,6:7-dibenzo-1,1,5,5-tetraphenyl-1,5-disilacycloocta-2,6-diene (III). The mechanism of formation of this dimeric product is considered.

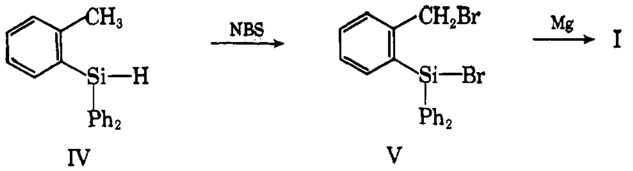
Only a relatively few silacyclobutane derivatives have been prepared,[1] and no silacyclobutene or pseudo-silacyclobutene compounds have been reported at the present time. In connection with a study of the preparation and chemistry of benzosilacycloalkenes,[2] an attempt was made[3] to prepare 2:3-benzo-1,1-diphenyl-1-silacyclobut-2-ene (I) by the condensation of *o*-chlorobenzyldiphenylsilane (II) with sodium. However, only low yields of a dimeric product believed to be 2:3,6:7-dibenzo-1,1,5,5-tetraphenyl-1,5-disilacycloocta-2,6-diene (III) could be isolated.[3] We wish to report the first successful synthesis of 2:3-benzo-1,1-diphenyl-1-silacyclobut-2-ene (I).



Results and Discussion

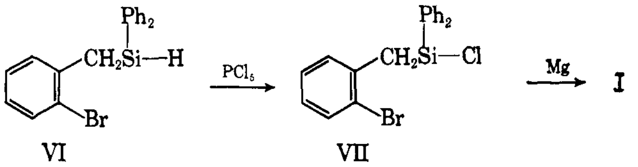
Preparation of I.—Compound I has been prepared by three independent synthetic methods. Treatment of diphenyl-*o*-tolylsilane (IV)[4] with N-bromosuccinimide (NBS)[5] (method A) gives (α-bromo-*o*-tolyl)bromodiphenylsilane (V). Reaction of V with magnesium in tetrahydrofuran (THF) affords compound I. The yields of I obtained by method A were quite low (4–5%) and highly dependent upon small changes in the reaction conditions.

Method A



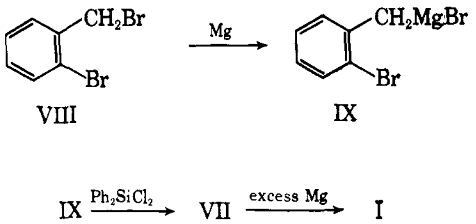
The yield of I is significantly improved by employing method B. *o*-Bromobenzyldiphenylsilane (VI)[3] is converted to *o*-bromobenzylchlorodiphenylsilane (VII) by the use of phosphorus pentachloride.[6] Reaction of this crude chlorosilane with magnesium in THF gives I (28%). Although method B enjoys the advantage that increased and consistent yields of I are obtained, it is somewhat unattractive because of the number of synthetic steps involved.

Method B



It seemed likely that the *in situ* formation of VII in the presence of excess magnesium should also yield compound I, and this constituted the basis for method C. *o*-Bromobenzyl bromide (VIII) has been reported[7] to react with magnesium in ether to give high yields of *o*-bromobenzylmagnesium bromide (IX). We observed that addition of dichlorodiphenylsilane to an *o*-bromobenzylmagnesium bromide–magnesium mixture gives 25–30% yields of I. Method C was further simplified by employing the simultaneous addition of VIII and dichlorodiphenylsilane to magnesium in ether, thereby eliminating the preparative step involving the prior formation of IX.

Method C



Physical and Spectral Properties of I.—Benzo silacyclobutene (I) is a crystalline solid, m.p. 75–76°, which can be readily distilled at low pressure without decomposition; b.p. 130–134° (0.06 mm.).

The infrared spectrum of I is quite similar to that of the previously described 2:3-benzo-1,1-diphenyl-1-silacyclopent-2-ene.[2,3] However, the spectrum of I contains a sharp band at 9.65 μ not present in the spectrum of the five-membered ring homolog. Since ring-opening of I results in the disappearance of this 9.65 μ band, it appears that this band is associated with the strained benzosilacyclobutene system.

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[1] For part I of this series, see H. Gilman and W. H. Atwell, *J. Am. Chem. Soc.*, **86**, 2687 (1964).

[2] H. Gilman and O. L. Marrs, *Chem. Ind.* (London), 208 (1961).

[3] H. Gilman and O. L. Marrs, *J. Org. Chem.*, in press.

[4] Diphenyl-*o*-tolylsilane has been reported [H. Gilman and H. G. Brooks, unpublished M.S. Thesis, Iowa State University, Ames, Iowa, 1958] to be a liquid, b.p. 138–140° (0.046 mm.), n^{20}_{D} 1.6113. However, a sample of this previously prepared material was found to contain small crystals and cooling caused this material to solidify, m.p. 43–45°.

[5] NBS has been similarly used in a previously reported synthesis of 1,1,2-triphenyl-1-silacyclobutane (see ref. 1).

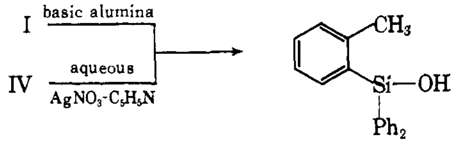
[6] An extensive investigation of the conversion of silicon hydrides to chlorosilanes using phosphorus pentachloride has been recently carried out: S. Cooper, G. R. Chainani, R. A. Tomasi, K. Y. Chang, and H. Gilman, unpublished studies.

[7] M. H. Beeby and F. G. Mann, *J. Chem. Soc.*, 411 (1951).

Compound I exhibits a light blue fluorescence in the solid state in the presence of ultraviolet light. The ultraviolet spectrum of I (ethanol) gives maxima in mμ (log ϵ) at: 263.5 (3.230), 269.5 (3.342), and 276.5 (3.243). These ultraviolet properties are quite similar to those reported[8] for benzocyclobutene, $\lambda_{\max}^{\text{EtOH}}$ (log ϵ): 260 (3.09), 265.5 (3.28), and 271.5 (3.27).

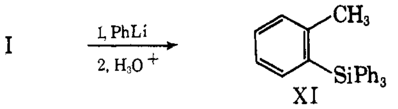
The n.m.r. spectrum of I (CCl_4) shows a sharp singlet centered at 7.54 τ due to the two equivalent benzylic protons[9] (aromatic/aliphatic proton ratio = 7.09, calcd. 7.00).

Chemical Reactivity of I.—Compound I exhibits the high degree of reactivity previously reported[10a] for other silacyclobutanes. Thus, I rapidly decolorizes solutions of bromine in carbon tetrachloride at room temperature, and reduces ethanolic solutions of silver nitrate,[10b] often with the formation of a silver mirror. Chromatography of I on a basic alumina column yields diphenyl-*o*-tolylsilanol (X). The assignment of structure X was based on analytical data and molecular weight determinations. In addition, the infrared spectrum of this material was found to be identical with that of an authentic specimen of X prepared by the reaction of diphenyl-*o*-tolylsilane (IV) with an aqueous silver nitrate–pyridine mixture.[11]



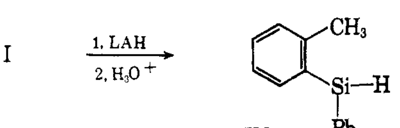
X

Compound I is readily cleaved by phenyllithium to give, subsequent to acid hydrolysis, *o*-tolyltriphenylsilane (XI).[12] None of the ring-opened product XI could be isolated from I and phenylmagnesium bromide at room temperature. Reaction under these conditions gives only recovered starting material.



XI

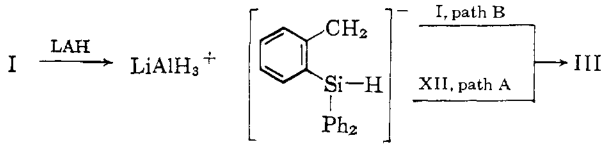
Cleavage of I with lithium aluminum hydride (LAH) in ether followed by acid hydrolysis gives the expected ring cleavage product, diphenyl-*o*-tolylsilane (IV).



IV

An unusual and unexpected dimerization was observed when compound I was added to LAH in refluxing tetrahydrofuran (THF). Under these conditions diphenyl-*o*-tolylsilane is obtained in 26% yield. In addition, a crystalline solid, m.p. 314-316°, is also obtained. This material was observed to be identical in all respects with the previously prepared[3] 2:3,6:7-dibenzo-1,1,5,5-tetraphenyl-1,5-disilacycloocta-2,6-diene (III).

It is quite reasonable to expect that the diphenyl-*o*-tolylsilane (IV) isolated in the above cleavage reactions is formed by acid hydrolysis of an initially formed complex of the type XII. The isolation of both III and IV under dimerization conditions suggested the possibility that XII is also an intermediate in the formation of III.



XII

Two distinct pathways can be envisioned for the formation of the dimer from XII. First, the reaction of XII in an intermolecular "head-to-tail" manner (path A) would yield the observed dimeric product III. Alternately, cleavage of I by XII (path B) would also be expected to give III. We feel that the most probable reaction mechanism is that outlined in path B. The evidence supporting our choice follows: (1) No increase in the yield of III is observed when the reaction time is doubled, indicating that III is not formed by a slow intermolecular condensation of XII. (2) Inverse addition (*i.e.*, addition of the LAH to I) results in the formation of comparable yields of III. Most important, however, no diphenyl-*o*-tolylsilane (IV) can be isolated under these conditions suggesting a rapid cleavage of I by XII. (3) Compounds of the type $LiAlR_4$ have been observed to have an initial reactivity comparable to that of organolithium compounds[13] and a reactivity greater than that of LAH would be expected for XII.[14] The ability of organolithium compounds to effect ring opening has been demonstrated in this and other work.[1] (4) Although path B (or path A) indicates that the dimerization could be achieved with a catalytic amount of LAH, inverse addition (see point 2 above) results in the formation of considerable amounts of polymer suggesting that intermolecular polymerization is more rapid than intermolecular cyclization to III.[15]

Examination of the eight-membered ring structure III using Stuart-Briegleb models shows that two nonplanar structures are possible for the unsubstituted basic ring system. Although a model of only one of the two possible conformations can be constructed with the tetraphenyl-substituted derivative, III is most likely inverting between the two possible forms. Further examination of these two conformations

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(8) M. P. Cava and D. R. Napier, *J. Am. Chem. Soc.*, **78**, 500 (1956).

(9) For comparison purposes, the benzylic protons of benzyltriphenylsilane fall at 7.20 τ.

(10) (a) For a summary of the chemistry of silacyclobutanes, see ref. 1. (b) For a brief discussion on the use of ethanolic silver salt solutions as a qualitative test for the silacyclobutane ring system, see H. Gilman and W. H. Atwell, *J. Organometal. Chem.*, **2**, 277 (1964).

(11) This reagent has been used in a qualitative test for mono-, di-, and trisubstituted silanes [H. Gilman, H. G. Brooks, Jr., and M. B. Hughes, *J. Org. Chem.*, **23**, 1398 (1958)], and it appears to be of considerable utility for preparative work.

(12) H. Gilman and G. N. Russell Smart, *ibid.*, **15** 720 (1950).

(13) (a) The chemistry of organoaluminum compounds has recently been reviewed: K. Ziegler, "Organo-aluminum Compounds," in H. Zeiss, Ed., "Organometallic Chemistry," Reinhold Publishing Corp., New York, N. Y., 1960, pp. 194–269; (b) G. E. Coates, "Organo-Metallic Compounds," 2nd Ed., John Wiley and Sons, Inc., New York, N. Y., 1960, pp. 126–144.

(14) Cleavage of 1,1,2-triphenyl-1-silacyclobutane with LAH has been reported[1] to give lower yields of the ring-opened product (3-phenylpropyl)-diphenylsilane if refluxing THF is used as reaction solvent, apparently owing to competitive cleavage of the silacyclobutane by the $LiAlH_3R$ complex.

(15) When *o*-bromobenzyldiphenylsilane (rather than *o*-chlorobenzyldiphenylsilane) is treated with sodium the yield of recovered starting material is decreased; however, the yield of III remains low (see ref. 3), supporting the conclusion that intermolecular polymerization is more favorable than intermolecular cyclization.

showed that the environments of the protons in a methylene group are nonequivalent, and the n.m.r. spectrum of III shows bands at 7.23 (2 units) and 7.40 τ (2 units)[16] due to the two pairs of nonequivalent methylene protons (aromatic/aliphatic proton ratio = 6.90; calcd. 7.00). The structure of the dimer III was further substantiated by molecular weight determination.

Benzocyclobutene and its derivatives have been reported[17] to undergo ring expansion with dienophiles such as maleic anhydride and N-phenylmaleimide. We observed no ring expansions of I with either maleic anhydride or dimethyl acetylenedicarboxylate.

We feel that the facile ring openings observed with I are readily explained in terms of the factors which have been previously described[1] as contributing to the enhanced reactivity of other silacyclobutanes.

Experimental

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. The basic alumina (80–200 mesh) was purchased from Chicago Apparatus Co., Chicago, Ill. The acidic and neutral alumina was manufactured by Woelm and purchased from Alupharm Chemicals, New Orleans, La. Reactions involving organometallic reagents were carried out under an atmosphere of dry, oxygen-free nitrogen. The tetrahydrofuran was freed from peroxides and moisture before use by refluxing over sodium, followed by distillation from lithium aluminum hydride immediately before use. The chlorosilanes were purchased from Dow-Corning Corp. and were used without further purification. All melting points are uncorrected.

***o*-Bromobenzyl Bromide (VIII).**[18]—N-Bromosuccinimide (NBS, 178 g., 1.0 mole), and 171 g. (1.0 mole) of *o*-bromotoluene in *ca.* 600 ml. of carbon tetrachloride was irradiated with a General Electric Sun Lamp. Refluxing occurred shortly thereafter as the exothermic reaction proceeded. The reaction mixture was cooled, filtered under nitrogen (CAUTION, LACHRYMATOR), and the solvent removed with the aid of a steam bath. Distillation of the residual oil gave 160 g. of product, b.p. 66–69° (0.2 mm.) (64%) (lit.[18] b.p. 136° (16 mm.)).

Diphenyl-*o*-tolylsilane (IV).[4]—The Grignard reagent prepared from 137 g. (0.8 mole) of *o*-bromotoluene and 24.32 g. (1.0 g.-atom) of magnesium in 350 ml. of ether was added to 166.2 g. (0.76 mole) of chlorodiphenylsilane in 150 ml. of the same solvent. Color Test I[19] was negative immediately after addition. Acid hydrolysis followed by the usual work-up gave a viscous oil. The oil was dissolved in ethanol and seeded with a known sample[4] of this material to give 179 g. (85.6%) of solid, m.p. 44–46°. This material was identified by mixture melting point and comparison of the infrared spectrum with that of a known sample.

The infrared spectrum of IV determined in both CCl_4 and CS_2 showed the absorption bands given in Table I.

(α-Bromo-*o*-tolyl)bromodiphenylsilane (V).—A mixture of 27.4 g. (0.1 mole) of diphenyl-*o*-tolylsilane, 35.6 g. (0.2 mole) of NBS, and 250 ml. of carbon tetrachloride was stirred in a 1-l., three-necked, round-bottomed flask. After an induction period, which varied slightly from run to run (20 min.), an exothermic reaction occurred and an orange color developed. When the initial heat of reaction had dissipated the mixture was irradiated with a General Electric sun lamp. The orange color faded and the final reaction mixture was yellow-white. Subsequent to cooling, filtration under nitrogen gave 21 g. (90.5%) of succinimide, m.p. 124–126° (m.m.p.). The solvent was completely evaporated from the filtrate to give a viscous oil which solidified upon treatment with sodium-dried petroleum ether (b.p. 60–70°). Recrystallization from the same solvent gave 37 g. (86%) of pure V, m.p. 93–94°. The infrared spectrum of this material (CCl_4) showed the absence of Si–H absorptions (see Table I) and was quite similar to that of *o*-tolyldiphenylsilane.

TABLE I

INFRARED SPECTRUM OF IV

Band position, μ	Intensity[a]	Characteristic[b,c]
3.26, 3.30	m, m	Aromatic C–H
3.42, 3.50	w, w	Aliphatic C–H
4.71	s	Si–H
6.31, 6.74, 6.81	w, w, w	Ph–
6.90	m	Possibly Si–alkyl
7.01, 7.81, 7.95	s, w, w	Ph–
8.33, 8.44, 8.65	w, w, w	Possibly Si–alkyl
Shoulder 8.90	s	. . .
9.00	s	Si–Ph
9.32, 9.74, 10.03	w, w, w	Ph–
12.20, 12.45, 12.67	s, s, s	Si–H
13.45	s	*o*-Disubstitution
13.70, 14.07, 14.38	s, s, s	Ph–

[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).

Anal. Calcd. for $C_{19}H_{16}Br_2Si$: Si, 6.50. Found: Si, 6.50, 6.71.

The purification of this readily hydrolyzable material was found to be tedious and generally unnecessary. In future reactions involving V the crude product was used immediately after its preparation.

***o*-Bromobenzyldiphenylsilane (VI).**—The Grignard reagent, *o*-bromobenzylmagnesium bromide,[7] prepared from 50 g. (0.2 mole) of *o*-bromobenzyl bromide and 9.72 g. (0.4 g.-atom) of magnesium in 200 ml. of ether (titration yield, 83%), was added to 36.2 g. (0.165 mole) of chlorodiphenylsilane in 200 ml. of ether. Color Test I[19] was negative immediately after addition. Acid hydrolysis followed by the usual work-up gave a viscous oil. Distillation of this residual oil gave 35.4 g. of light yellow liquid, b.p. 158–160° (0.05 mm.), n^{20}_D 1.6260 (lit.[3] b.p. 148–150° (0.002 mm.), n^{20}_D 1.6268). The infrared spectrum of this material was identical with that of a known sample.[3]

Diphenyl-*o*-tolylsilanol (X).—One gram (3.65 mmoles) of diphenyl-*o*-tolylsilane was added to an aqueous silver nitrate–pyridine solution.[12] Heat was evolved and a brown color developed. After stirring for 1 hr. the mixture was extracted with ether. Removal of the solvents gave an oil which was chromatographed on an alumina column. Elution with petroleum ether (b.p. 60–70°) gave 0.76 g. (66%) of solid, m.p. 123–125°. Recrystallization from the same solvent raised the melting point to 126–127° (50%). The infrared spectrum of X (in CCl_4) showed bands at 2.73 and 12.45 μ indicative of the O–H and Si–O stretch, respectively. The remainder of the spectrum was very similar to that of diphenyl-*o*-tolylsilane.

Anal. Calcd. for $C_{19}H_{18}OSi$: Si, 9.72; mol. wt., 290.3. Found: Si, 9.50, 9.58; mol. wt.,[20] 294.4.

Preparation of 2:3-Benzo-1-silacyclobut-2-ene (I). a. From (α-Bromo-*o*-tolyl)bromodiphenylsilane (V).—Th ecrude product V, prepared from 27.43 g. (0.1 mole) of diphenyl-*o*-tolylsilane and 35.6 g. (0.2 mole) of NBS, was dissolved in 200 ml. of tetrahydrofuran and added slowly to 6.0 g. (0.25 g.-atom) of magnesium. An exothermic reaction occurred as a dark brown color developed. The mixture was allowed to stir overnight and then hydrolyzed with 5 *N* hydrochloric acid. Subsequent to the usual work-up there was obtained a viscous oil which was extracted with petroleum ether (b.p. 60–70°). The petroleum ether extracts were distilled to give 3.0 g. of viscous oil, b.p. 135–150° (0.01 mm.). Addition of petroleum ether (b.p. 28–38°) to the distillate gave 0.75 g. of solid, m.p. 124–126°. The infrared spectrum of this material was identical with that of diphenyl-*o*-tolylsilanol (X) and a mixture melting point was not depressed (yield 2.6%).

The petroleum ether filtrate was concentrated and addition

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[16] The solvent used was carbon disulfide. In view of the insolubility of III in this and other (CCl_4, $DCCl_3$, and C_6H_{12}) solvents, further refinement of the fine splitting of these two bands was not possible.

[17] (a) F. R. Jensen, W. E. Coleman, and A. J. Berlin, *Tetrahedron Letters*, 1, 15 (1962); (b) F. R. Jensen and W. E. Coleman, *J. Am. Chem. Soc.*, **80**, 6149 (1958).

[18] The procedure described here is that given by R. D. Gorsich, unpublished Ph.D. Thesis, 1957, Library, Iowa State University, Ames, Iowa.

[19] H. Gilman and F. Schulze, *J. Am. Chem. Soc.*, **47**, 2002 (1925).

[20] The instrument used was a vapor pressure osmometer Model 301A; manufactured by Mechrolab Inc., Mountain View, Calif.

of ethanol gave 1.3 g. of 2:3-benzo-1,1-diphenyl-1-silacyclobut-2-ene (I), m.p. 75–76° (4.8%).

Anal. Calcd. for $C_{19}H_{16}Si$: C, 83.80; H, 5.87; Si, 10.32; mol. wt., 272.3. Found: C, 83.92, 83.70; H, 5.96; 6.09; Si, 10.16, 10.06; mol. wt.,[20] 274.3.

b. **From *o*-Bromobenzylchlorodiphenylsilane (VII).**—A mixture of 20.3 g. (0.0575 mole) of *o*-bromobenzyldiphenylsilane and 50 ml. of carbon tetrachloride was added slowly to 120 g. (0.576 mole) of phosphorus pentachloride in 75 ml. of the same solvent.[6] The reaction was heated for 2 hr. and the solvent removed under vacuum with the aid of a steam bath. The infrared spectrum of the residual oil determined as a capillary cell showed the absence of any Si–H absorption bands and was quite similar to that of *o*-bromobenzyldiphenylsilane.[3]

The crude VII was dissolved in 100 ml. of tetrahydrofuran and added to 2.43 g. (0.1 g.-atom) of magnesium in 25 ml. of the same solvent. The reaction mixture was heated gently for 3 hr. and hydrolyzed with 5 *N* hydrochloric acid. Subsequent to the usual work-up and evaporation of the solvents there was obtained a viscous residue. Distillation gave 4.4 g. (28.2%) of I, b.p. 130–134° (0.06 mm.), which solidified upon standing, m.p. 74–75°. A mixture melting point with a known sample of I was not depressed and the infrared spectra were superimposable. The infrared spectrum of I determined in both CCl_4 and CS_2 showed the absorption bands given in Table II.

TABLE II

INFRARED SPECTRUM OF I

Band position, μ	Intensity[a]	Characteristic[b]
3.25, 3.30	m, w	Aromatic C–H
3.42	w	Aliphatic C–H
6.31, 6.72, 6.89	w, w, w	Ph–
6.95	m	Possibly Si–alkyl
7.00	s	Ph–
7.16	w	. . .
7.80, 7.95	w, w	Ph–
8.43	w	Possibly Si–alkyl
8.99	s	Si–Ph
9.35, 9.73, 10.04	w, w, w	Ph–
9.62	m to s	See Discussion section
12.85	s	. . .
13.47	s	*o*-Substitution
13.64, 13.87, 14.40	s, s, s	Ph–

[a] See footnote *a* in Table I. [b] See footnotes *b* and *c* in Table I.

c. **From Dichlorodiphenylsilane, *o*-Bromobenzyl Bromide (VIII), and Magnesium in Ether.**—A solution of 25.0 g. (0.1 mole) of VIII diluted to 100 ml. with ether was slowly added to 9.27 g. (0.4 g.-atom) of magnesium in 20 ml. of the same solvent. When the formation of *o*-bromobenzylmagnesium bromide[7] was initiated, the simultaneous addition of 25.3 g. (0.1 mole) of dichlorodiphenylsilane was begun.[21] The reaction mixture was refluxed during the addition of the chlorosilane (2 hr.) and then for an additional 48–72 hr. At this time Color Test I[19] was negative and the formation of considerable amounts of inorganic salts was observed. Subsequent to acid hydrolysis and the usual work-up the dried ether layer was evaporated. Addition of 75 ml. of cyclohexane gave 7.2 g. of diphenylsilanediol, m.p. 160–162° dec. (33.3%). The filtrate was evaporated, taken up in petroleum ether (b.p. 60–70°), and chromatographed on an acidic alumina column. Elution with the same solvent gave 7.5 g. (27.2%, based on the *o*-bromobenzyl bromide employed) of I, m.p. 73–75° (m.m.p.). Compound I was observed to be entirely stable when chromatographed on either acidic or neutral alumina.

Although crude samples of I decomposed slowly upon standing, pure samples are very stable and show no change in melting point after 1 year in a closed vial.

Reaction of I with Basic Alumina.—A solution of 1.0 g. (3.67 mmoles) of I (m.p. 74–75°) in 5 ml. of petroleum ether (b.p. 60–70°) was chromatographed on a basic alumina column. Elution with the same solvent gave 0.4 g. of solid, m.p. 126–127° (38%). This material was identified as diphenyl-*o*-tolylsilanol (X) by mixture melting point and by comparison of the infrared spectrum with that of an authentic sample.

Reaction of I with Phenyllithium.—To a solution of 54 mmoles of phenyllithium (prepared in ether) was added 1.0 g. (3.67 mmoles) of I in 20 ml. of the same solvent. After stirring for 1 hr. the reddish brown reaction mixture was hydrolyzed with 5 *N* hydrochloric acid. Extraction with ether followed by the usual work-up gave a viscous oil. This oil solidified upon addition of ethanol to give 0.4 g. of solid, m.p. 170–180° (30%). Recrystallization from the same solvent gave 0.3 g. (22.5%) of pure product, m.p. 187–189°. A mixture melting point with a known sample of *o*-tolyltriphenylsilane[13] (XI) was not depressed and the infrared spectra were superimposable.

Reaction of I with Phenylmagnesium Bromide (Attempted).—A solution of 27 mmoles of phenylmagnesium bromide (prepared in tetrahydrofuran) was added rapidly to 1.0 g. (3.67 mmoles) of I in 20 ml. of ether. After stirring for 16 hr. the mixture was hydrolyzed with 5 *N* hydrochloric acid. The usual work-up followed by removal of the solvents gave a viscous oil. Addition of ethanol gave 0.85 g. (85%) of recovered starting material, m.p. 73–75°.

Reaction of I with Lithium Aluminum Hydride (LAH). a. In Ether at Room Temperature.—A solution of 1.0 g. (3.67 mmoles) of I in 35 ml. of ether was slowly added to 0.76 g. (20 mmoles) of LAH in 30 ml. of the same solvent. The solution was refluxed for 72 hr. and then hydrolyzed with 5 *N* hydrochloric acid. The usual work-up gave a viscous oil which was chromatographed on an acidic alumina column. Elution with petroleum ether (b.p. 60–70°) gave 0.20 g. (20%) of slightly impure diphenyl-*o*-tolylsilane (IV), m.p. 39–42° (m.m.p. and comparison of the infrared spectrum with that of a known sample). Further elution of the column gave 0.5 g. of very viscous oil which could not be induced to crystallize. The infrared spectrum (CCl_4) of this latter material was very similar to that of IV.

b. **In Refluxing Tetrahydrofuran (THF).**—A solution of 1.0 g. (3.67 mmoles) of I in 25 ml. of THF was slowly added to 0.76 g. (20 mmoles) of LAH in 30 ml. of refluxing THF. Subsequent to 24 hr. of reflux, the reaction mixture was acid hydrolyzed. The usual work-up gave a viscous oil. Addition of petroleum ether (b.p. 60–70°) gave 0.4 g. of solid, m.p. 295–310°. Recrystallization from benzene–petroleum ether (b.p. 60–70°) gave 0.12 g. (12%) of crystalline solid, m.p. 314–316°. This compound was identified as 2:3,6:7-dibenzo-1,1,5,5-tetraphenyl-1,5-disilacycloocta-2,6-diene (III) by mixture melting point and by comparison of the infrared spectrum with that of a known sample.[8] The infrared spectrum of III determined in CS_2 showed the absorption bands given in Table III.

TABLE III

INFRARED SPECTRUM OF III

Band position, μ	Intensity[a]	Characteristic[b]
3.27, 3.33	m, m	Aromatic C–H
3.46	w	Aliphatic C–H
7.93	w	Ph–
8.35, 8.70	w, m	Possibly Si–alkyl
9.05	s	Si–Ph
9.74	w	Ph–
12.14, 12.88	w, s	. . .
13.07, 13.18 (sh)	s, s	*o*-Disubstitution
13.56, 13.72, 14.35	s, s, s	Ph–

[a] See footnote *a* in Table I. [b] See footnotes *b* and *c* in Table I.

Anal. Calcd. for $C_{38}H_{32}Si_2$: mol. wt., 544.8. Found: mol. wt., 540.0 (osmometer[20] in benzene).

The filtrate was concentrated and chromatographed on an acidic alumina column. Elution with petroleum ether (b.p. 60–70°) gave IV as a viscous oil which solidified upon treatment with ethanol; 0.26 g. (26%), m.p. 41–43°.

When the reflux time was extended to 48 hr., the yields of III and IV were 10 and 20%, respectfully.

c. **In Refluxing THF (Inverse Addition).**—A solution of 0.76 g. (20 mmoles) of LAH in 60 ml. of THF was filtered under nitrogen to give a clear solution. This LAH solution was added dropwise to 2.0 g. (7.4 mmoles) of I in 25 ml. of refluxing THF. An orange color developed rapidly. Subsequent to 48 hr. of reflux the mixture was acid hydrolyzed. Extraction with ether and evaporation of the solvents gave a sticky solid mass which resisted all crystallization attempts. The residue was dissolved

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[21] In order to allow simultaneous addition of this type, a four-necked round-bottomed flask was used. The rate of addition of the dichlorodiphenylsilane was faster than that of the *o*-bromobenzyl bromide.

in carbon tetrachloride and chromatographed on a neutral alumina column. No IV was eluted with either petroleum ether (b.p. 60–70°) or cyclohexane. However, elution with a 50:50 carbon tetrachloride–benzene mixture gave 0.20 g. of solid, m.p. 300–310°. Recrystallization from a large volume of cyclohexane gave 0.15 g. (7.5%) of dimer III, m.p. 310–313° (m.m.p.).

Reaction of I with Maleic Anhydride. a. In Refluxing Carbon Tetrachloride (Attempted).—A solution of 1.0 g. (3.67 mmoles) of I and 0.36 g. (3.67 mmoles) of maleic anhydride in 25 ml. of carbon tetrachloride was refluxed for 48 hr. Evaporation of the solvent gave a semisolid mass. Addition of petroleum ether (b.p. 28–38°) gave 0.88 g. of recovered I, m.p. and m.m.p. 74–76° (88%).

b. In a Sealed Tube at *ca.* 150°.—One gram (3.67 mmoles) of I and 0.36 g. (3.67 mmoles) of maleic anhydride was heated in a sealed tube at 150–160° (0.5 mm.) for 3 hr. The resulting solid pellet was dissolved in hot benzene and chromatographed on an acidic alumina column. Elution of the column gave only a glass-like polymeric material which could not be induced to crystallize.

Reaction of I with Dimethyl Acetylenedicarboxylate (Attempted).—One gram (3.67 mmoles) of I and 1.0 g. (7.1 mmoles) of dimethyl acetylenedicarboxylate were heated at 100–110° (under a nitrogen atmosphere) for 18 hr. Cooling gave a yellow oil which resisted crystallization attempts. This oil was dissolved in petroleum ether (b.p. 60–70°) and chromatographed on an acidic alumina column. Elution with the same solvent gave 0.8 g. (80%) of recovered I, m.p. and m.m.p. 73–75°. Further elution gave only small amounts of yellow oil.

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[Contribution from the Department of Chemistry, Stanford University, Stanford, Calif.]

Olefinic Cyclizations. VI. Formolysis of Some Branched-Chain Alkenyl *p*-Nitrobenzenesulfonates[1]

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Formolysis of 5-methyl-5-hexenyl *p*-nitrobenzenesulfonate gave cyclized material in only 39% yield. The remainder of the product consisted mainly of compounds arising from attack by formic acid on the terminal olefinic bond of the substrate. The main course of the formolysis of 4-methyl-4-pentenyl *p*-nitrobenzenesulfonate involved rearrangement to the 4-methyl-3-pentenyl ester, followed by solvolysis of the homoallylic system. The formolysis of 6-methyl-5-heptenyl *p*-nitrobenzenesulfonate (I) at 75° proceeded about 20 times as fast as that of the *n*-hexyl ester. The products were mainly those of five-membered ring closure, namely substances II, III, IV, and V. In addition, 2,2-dimethylcyclohexanol (VI) was identified among the products. This last substance was formed in increasing amounts, at the expense of the five-membered ring products, as the reaction period was lengthened. 6-Methyl-6-heptenyl *p*-nitrobenzenesulfonate, on formolysis, gave essentially the same products as the 6-methyl-5-heptenyl ester, indicating an isomerization of the former to the latter prior to solvolysis. A trace of 1-methylcycloheptanol was produced.

In a previous study[2] we examined the formolysis of 4-pentenyl, 5-hexenyl, and 6-heptenyl *p*-nitrobenzenesulfonate. The present study was undertaken with the view to determining how methyl substituents on the olefinic bonds would affect the rate and course of the reaction.

The 5-Methyl-5-hexenyl System.—The solvolysis of 5-hexenyl *p*-nitrobenzenesulfonate at 75° in formic acid containing sodium formate has been shown[2] to proceed at a rate which is about twice that of the solvolysis of the hexyl ester. The participation of the olefinic bond in the formolysis was attended by production of cyclized material in over 70% yield. It was considered of interest to examine the formolysis of the 5-methyl-5-hexenyl ester which, because of the more reactive olefinic bond, was expected to proceed with even larger rate acceleration to give higher yields of cyclized products than in the case of the 5-hexenyl ester. 5-Methyl-5-hexenyl *p*-nitrobenzenesulfonate, m.p. 43–45°, was prepared from the known alcohol. After treatment with formic acid–sodium formate for 2 hr. at 75°, the solvolysis was only 65% complete, indicating a rate comparable to that obtained with the saturated hexyl ester (63% completed under the same conditions). That there was relatively little participation of the olefinic bond was confirmed by the low yields of cyclic material which was identified (after ester cleavage) as 1-methylcyclohexanol (29% yield) and 1-methylcyclohexene (10% yield). The explanation of the failure of this relatively reactive olefinic bond to participate as much as expected in the solvolysis was forthcoming from examination of the remainder of the solvolysis product which proved to be a mixture of 5-methyl-1,5-hexanediol (10% yield) and 5-methyl-4-hexenol (16% yield). (An authentic specimen of the diol, with a bis-*p*-nitrobenzoate melting at 130–131°, was prepared by treating 5-methyl-5-hexenol with formic acid, followed by cleavage of the formates with lithium aluminum hydride.) These two solvolysis products must have arisen from a rapid competing process involving attack by formic acid on the terminal olefinic bond of the substrate to produce 5-formyloxy-5-methylhexyl *p*-nitrobenzenesulfonate by an addition process, and 5-methyl-4-hexenyl *p*-nitrobenzenesulfonate by a proton abstraction process. These two modified *p*-nitrobenzenesulfonates would be expected to undergo solvolysis at rates comparable to, or slower than, that of the saturated ester to give, by direct displacement, the observed products. The 35% of unsolvolyzed material in the experiment described above must have consisted largely of these two *p*-nitrobenzenesulfonates.

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[1] Part V of this series: W. S. Johnson and J. K. Crandall, *J. Am. Chem. Soc.*, **86**, 2085 (1964).

[2] W. S. Johnson, D. M. Bailey, R. Owyang, R. A. Bell, B. Jaques, and J. K. Crandall, *ibid.*, **86**, 1959 (1964).