triiodophenyl]-DL-alanine (XIII) was deacetylated without further purification. Paper chromatography of the precipitate obtained by acidification of the soluble fraction of the reaction mixture (see above) did not reveal the presence of the coupling product XIII. Deacetylation of XIII, carried out as described for that of VII, gave 23 mg. of XII, m.p. 209–211° dec. Although this melting point is slightly lower than that of the material prepared by method A, both substances had identical R_f values in paper chromatograms and gave identical infrared spectra.

Synthesis of 2:3-Benzo-1-silacycloalkenes. I

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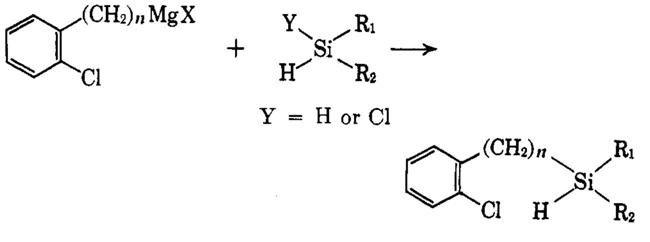
A new class of cyclic silanes, 2:3-benzo-1-silacycloalkenes, have been prepared by ring closure of (*o*-chlorophenyl)alkylsilanes with molten sodium. Two cyclic silicon hydrides were included. Attempts to effect ring closure of two benzyl derivatives were unsuccessful. Some n.m.r. and infrared data of the cyclic compounds are reported.

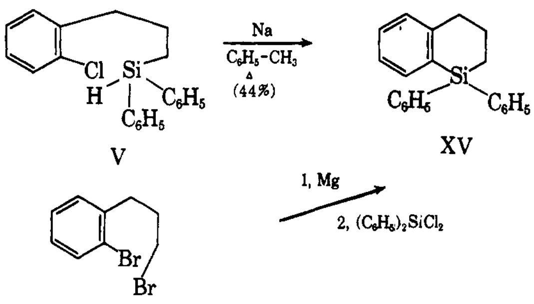
A class of compounds which may be of broad interest is that of the perhydro-1,2-cyclopentanophenanthrene ring system that has a silicon atom incorporated into the ring. Compounds which may serve as precursors to such derivatives are the benzosilacycloalkenes.

Only two compounds containing the benzosilacycloalkene nucleus, 2:3-benzo-1,1-diphenyl-1-silacyclohex-2-en-4-one (2,3-dihydro-1,1-diphenyl-4H-1-silanaphthalen-4-one)[1] and the seven-membered ring homolog have been reported.[2] These were prepared by an intramolecular acylation reaction of the acid chloride of triphenylsilyl-substituted carboxylic acids. Since this method is limited to the availability of the acid derivatives that were prepared from silylmetallic reagents, improved methods of preparation of these silanes were desirable. The first efforts were directed toward the preparation of the nonfunctional compound 2:3-benzo-1,1-diphenyl-1-silacyclohex-2-ene (XV). Attempts to prepare XV by ring closure of 3-triphenylsilylpropanol-1 and 3-triphenylsilylpropyl bromide using Lewis acid catalysts were unsuccessful.[2]

The method which appeared to be the most promising was an intramolecular cyclization reaction of (*o*-chlorophenyl)alkyl-substituted silicon hydrides with molten sodium in an inert solvent. Benkeser and Foster[3] have shown that silicon hydrides do not react with sodium, whereas phenylsodium reacts quantitatively with silicon hydrides to give the phenylated silicon compound. Also, Clark, *et al.*,[4] prepared *o*-phenylenebis(trimethylsilane) by coupling *o*-chlorophenyltrimethylsilane and chlorotrimethylsilane with molten sodium in refluxing toluene. Therefore, a series of (*o*-chlorophenyl)alkylsilanes was first prepared from the appropriate (*o*-chlorophenyl)alkylmagnesium halides and monochlorosilanes or silicon hydrides. The physical properties of these compounds are listed in Table I. These compounds were then added to molten sodium in refluxing toluene to give 2:3-benzo-1-silacycloalkenes (Table II). The Grignard reagents were prepared in good yields from the organic halides and were further characterized by carbonation to the corresponding (*o*-chlorophenyl)alkyl acids.



Thus, [3-(*o*-chlorophenyl)propyl]diphenylsilane (V), prepared from chlorodiphenylsilane and 3-(*o*-chlorophenyl)propylmagnesium bromide, was subsequently added to molten sodium in toluene to give 2:3-benzo-1,1-diphenyl-1-silacyclohex-2-ene (XV) in good yield.



An alternate synthesis of XV was realized by treating the di-Grignard reagent of 3-(*o*-bromophenyl)-propyl bromide with dichlorodiphenylsilane.

To illustrate the versatility of the ring closure with sodium and to make available other precursory benzosilacycloalkenes, the five- (XIII) and seven-membered (XVIII) ring compounds were prepared in good yields. The eight-membered ring homolog (XIX) was similarly synthesized, but in low yield.

By varying R_1 and R_2, the method proved to be applicable for the preparation of other functional and nonfunctional derivatives. For example, treatment of phenylsilane with 2-(*o*-chlorophenyl)ethylmagnesium bromide and 3-(*o*-chlorophenyl)propylmagnesium bromide and then effecting ring closure of the resulting [2-(*o*-chlorophenyl)ethyl]- and [3-(*o*-chlorophenyl)propyl]-phenylsilanes (III or VI) gave 2:3-benzo-1-phenyl-1-silacyclopent-2-ene (XII) and 2:3-benzo-1-phenyl-1-silacyclohex-2-ene (XIV), respectively. These Si–H-containing compounds were converted into the fully phenylated derivatives by reaction with phenyllithium.

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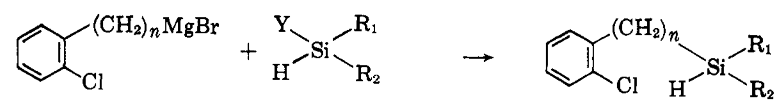
[1] The names and numbering system used herein are those recommended by the editorial staff of *Chemical Abstracts*.

[2] D. Wittenberg, P. B. Talukdar, and H. Gilman, *J. Am. Chem. Soc.*, **82**, 3608 (1960).

[3] R. A. Benkeser and D. J. Foster, *ibid.*, **74**, 5314 (1952).

[4] H. A. Clark, A. F. Gordon, C. W. Young, and M. J. Hunter, *ibid.*, **73**, 3798 (1951).

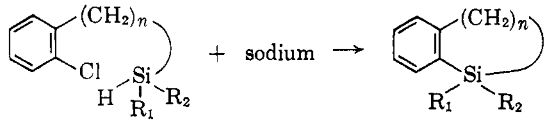
TABLE I



Compd.	n	R_1	R_2	Y	B.p., °C. (mm.)	$n^{20}D$	d^{20}_{20}	Yield, %	Formula	Silicon, % Calcd.	Silicon, % Found
I	1[a]	C_6H_5	C_6H_5	Cl	158–160 (0.012)	1.6141	1.133	73.9	$C_{19}H_{17}ClSi$	9.09	9.15, 8.95
II	2	C_6H_5	C_6H_5	Cl	161–163 (0.002)	1.6014	1.1136	53.4	$C_{20}H_{19}ClSi$	8.70	8.80, 8.73
III	2	C_6H_5	H	H	138–142 (0.6)	1.5756	1.0913	43.3	$C_{14}H_{15}ClSi$	11.38	10.7[b]
IV	2	$C_6H_5CH_2$	$C_6H_5CH_2$	H	166–168 (0.01)	1.5954	1.0965	52.4	$C_{22}H_{23}ClSi$	8.00	8.18, 8.18
V	3	C_6H_5	C_6H_5	Cl	162–168 (0.005)	1.5923	1.1055	82.7	$C_{21}H_{21}ClSi$	8.34	8.34, 8.18
VI	3	C_6H_5	H	H	163–165 (2.5)	1.5688	1.075	77.9	$C_{15}H_{17}ClSi$	10.77	10.48, 10.50
VII	3	C_6H_5	2-$CH_3C_6H_4$	H	177–180 (0.004)	1.5964	1.1008	63.4	$C_{22}H_{23}ClSi$	8.00	7.90, 7.87
VIII	3	C_6H_5	CH_3	Cl	123–125 (0.002)	1.5610	1.062	80.6	$C_{16}H_{19}ClSi$	10.22	10.03, 10.09
IX	3	$C_6H_5CH_2$	$C_6H_5CH_2$	H	206–211 (0.004)	1.5888	1.0849	25.2	$C_{23}H_{25}ClSi$	7.70	7.50, 7.56
X	4	C_6H_5	C_6H_5	Cl	174–176 (0.002)	1.5885		66.8	$C_{22}H_{23}ClSi$	8.00	7.87, 7.80
XI	5	C_6H_5	C_6H_5	Cl	173–179 (0.004)	1.5751		45.8	$C_{23}H_{25}ClSi$	c	

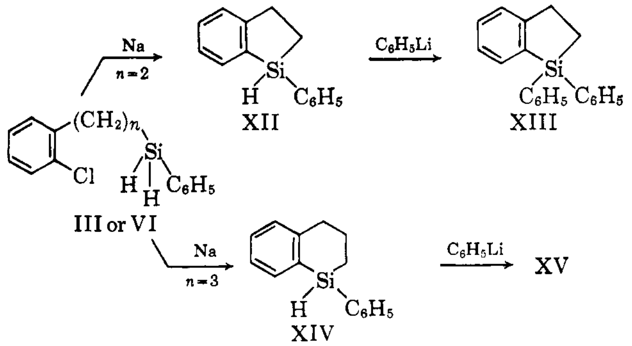
[a] o-Chlorobenzylmagnesium chloride. [b] *Anal.* Calcd.: C, 68.13; H, 6.13; MR, 75.22. Found: C, 68.71 and 68.69; H, 6.34 and 6.53; MR, 74.75. [c] *Anal.* Calcd.: C, 75.69; H, 6.90. Found: C, 75.35 and 74.68; H, 6.98 and 6.76.

TABLE II

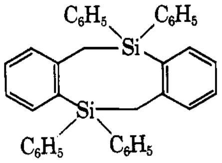


Compd.	n	R_1	R_2	Reflux time, hr.	Crystn. solvent[a]	M.p., °C.	Yield, %	Formula	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found	Silicon, % Calcd.	Silicon, % Found
XII	2	C_6H_5	H	7	B	b	54.3	$C_{14}H_{14}Si$	79.94	78.70, 78.68	6.71	6.83, 6.89		
XIII	2	C_6H_5	C_6H_5	9	A	62–63	62.1	$C_{20}H_{18}Si$					9.81	9.81, 9.63
XIV	3	C_6H_5	H	5		c	79.2	$C_{15}H_{16}Si$	80.29	79.98, 80.05	7.19	7.27, 7.38		
XV	3	C_6H_5	C_6H_5	4	A	76–77.5[d]	43.8	$C_{21}H_{20}Si$	83.94	84.09, 84.29	6.71	6.64, 6.82	9.35	9.28, 9.22[e]
XVI	3	C_6H_5	2-$CH_3C_6H_4$	11.5	A	85–87	62.7	$C_{22}H_{22}Si$					8.93	9.02, 8.88
XVII	3	C_6H_5	CH_3	6		f	23.9	$C_{16}H_{18}Si$	80.61	81.45, 81.30	7.61	7.91, 7.80		
XVIII	4	C_6H_5	C_6H_5	7		151–153	55.6	$C_{22}H_{22}Si$					8.93	8.96, 8.90
XIX	5	C_6H_5	C_6H_5	12		154.5–155.5	5.0	$C_{23}H_{24}Si$	84.09	84.00, 84.19	7.36	7.38, 7.28		

[a] A = absolute ethanol, B = petroleum ether (b.p. 60–70°)–ethanol mixture. [b] B.p. 125–126° (1.5 mm.), $n^{20}D$ 1.5998, d^{20}_{20} 1.0587. [c] B.p. 143–145.5° (2.5 mm.), $n^{18.5}D$ 1.6000, $d^{18.5}_{18.5}$ 1.0569. [d] B.p. 170–174° (0.006 mm.). [e] Found mol. wt. (benzene), 291. [f] B.p. 110–112° (0.002 mm.), $n^{20}D$ 1.5862, d^{20}_{20} 1.0362.



The simplest derivative in which ring closure was attempted was with o-chlorobenzyldiphenylsilane. The resulting cyclic compound, 2:3-benzo-1,1-diphenyl-1-silacyclobutene, should it have been formed, would have been of interest because of the inherent ring strain. However, o-chlorobenzyldiphenylsilane and sodium afforded a 55.5% recovery of starting material and a solid melting at 313–315°. The solid has been assigned the structure 2:3,6:7-dibenzo-1,1,5,5-tetraphenyl-1,5-disilacycloocta-2,6-diene (XX), based on its melting point, elemental analysis, and infrared spectrum. Molecular weight determinations gave erratic results, possibly due to the solid's insolubility, but the values obtained were in the range 481–778.



XX

Compound XX would result from an intermolecular cyclization reaction, and an analogous reaction has been utilized to prepare 5,10-dihydrosilanthrene derivatives from o-chlorophenylsilanes.[5]

To improve the yield of XX, o-bromobenzyldiphenylsilane was similarly treated with molten sodium. The yield of XX was still low, but the starting material was recovered in only a 15.5% yield. The reactions that appeared to be enhanced were the competing intermolecular polymerization reactions.

In an attempt to further broaden the scope of the reaction, dibenzyl[2-(o-chlorophenyl)ethyl]silane (IV) and dibenzyl[3-(o-chlorophenylpropyl)]silane(IX) were synthesized and allowed to react with molten sodium. However, there was no apparent reaction and the starting material was recovered in each case. To show that there had been no change in the starting material, IX

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(5) H. Gilman, E. A. Zuech, and W. Steudel, *J. Org. Chem.*, **27**, 1836 (1962).

TABLE III

N.M.R. DATA[a]

Compd.	Solvent	Si–H	$\mathrm{Si{-}}\overset{\mathrm{H}}{\overset{\vert}{\mathrm{C}}}$	C-4 H	C-5 H	C-6 H
XII	CCl_4	4.85 (3)		6.83 (3)	8.69 (m)	
XIII	CCl_4			6.85 (3)	8.57 (3)	
XIV	CCl_4	5.13 (3)		7.16 (3)	7.98 (6)	8.81 (7)
XV	$CDCl_3$			7.13 (3)	7.97 (m)	8.63 (m)
XVIII	$CDCl_3$			7.26 (3)	m	m
XIX	$CDCl_3$			7.23 (3)	m	m
Methyldiphenylsilane	CCl_4	5.10 (4)	9.41 (2)			
Ethyldiphenylsilane	CCl_4	5.21 (m)[b]	8.92 (1)			
Diphenyl-*n*-propylsilane	CCl_4	5.16 (3)	m			
Triphenylsilane	CCl_4	4.56 (1)				

[a] Values are given in τ-units relative to tetramethylsilane. Number in parenthesis represents peak multiplicity; m signifies a multiplet. [b] Broad signal.

was treated with phenyllithium to give dibenzyl[3-(*o*-chlorophenyl)propyl]phenylsilane. The reason for these anomalous results is, at present, unknown.

For the purpose of comparing the shielding values of the aliphatic protons and the proton attached to silicon (if present) of the various cyclic compounds prepared in this investigation, and to compare these values with those of the open-chained derivatives, the n.m.r. spectra of the benzosilacycloalkenes and their open-chained analogs were determined.[6] The resulting data are recorded in Table III. It is to be noted that the τ-value of the proton attached directly to silicon in the five-membered cyclic hydride XII is about 0.3 less than that of the six-membered homolog XIV. However, the shielding value of the six-membered derivative is about the same as that of the noncyclic compounds methyl-, ethyl-, and *n*-propyldiphenylsilane. Also, the shielding values of the C-4 protons, which are benzylic hydrogens, in the five-membered ring derivatives XII and XIII are about 0.3 of a τ-value less than that of the six-membered ring compounds XIV and XV, respectively, and about 0.4 less than the seven- or eight-membered ring homologs XVIII and XIX.

Ethyldiphenylsilane proved to be anomalous. Although the methyl group of methyldiphenylsilane exhibited the expected doublet, the protons of the ethyl group of ethyldiphenylsilane occurred as a single peak (two shoulders), rather than resolved methylene and methyl groups, commonly observed for ethyl derivatives. This appears to be related to the electronegativity of the group attached to the ethyl group and has also been observed with dichlorodiethylsilane[7] and tetraethyllead.[8]

Experimental[9]

2-(*o*-Chlorophenyl)ethanol-1.—*o*-Chlorophenylacetic acid, prepared by the carbonation of *o*-chlorobenzylmagnesium chloride,[10] was reduced with lithium aluminum hydride in the usual manner to afford the alcohol as a colorless liquid, b.p. 128–130° (12.5 mm.), n^{20}_{D} 1.5515, d^{20}_{20} 1.1904. The yields were 80–88%.

Anal. Calcd. for C_8H_9ClO: C, 61.35; H, 5.79; MR, 42.17. Found. C, 60.77 and 60.98; H, 5.61 and 5.77; MR, 42.01.

The 1-naphthylcarbamate of the alcohol melted at 121.5–123°, after recrystallization from absolute ethanol.

2-(*o*-Chlorophenyl)ethyl Bromide.—Phosphorus tribromide (54.14 g., 0.2 mole) was added to 62.6 g. (0.397 mole) of 2-(*o*-chlorophenyl)ethanol-1 cooled to 5°. The mixture was allowed to warm to room temperature, then heated at 100° for 1 hr. After cooling, ice was added and the aqueous layer was extracted with ether. The organic layer was washed neutral and dried. Removal of the solvent and distillation of the residue afforded 66.43 g. (76.2%) of the bromide, b.p. 110–112° (10 mm.), n^{20}_{D} 1.5710, lit.[11] b.p. 113–115° (10 mm.), prepared by bromination of the silver salt of 3-(*o*-chlorophenyl)propionic acid.

In some conversions of the alcohol to the bromide with phosphorus tribromide, the distillates became cloudy upon standing. In such cases, the material was dissolved in petroleum ether (b.p. 60–70°) and chromatographed on alumina. Distillation of the eluates afforded the pure product.

The bromide was readily converted to the acid, 3-(*o*-chlorophenyl)propionic acid, by reaction with magnesium in ether, followed by carbonation. The usual work-up gave a 35% yield of pure product, m.p. 96–98°, lit.[11] m.p. 96–97°.

3-(*o*-Chlorophenyl)propanol-1.—An ethereal solution of *o*-chlorobenzylmagnesium chloride, prepared from 161 g. (1 mole) of *o*-chlorobenzyl chloride and 26.75 g. (1.1 g.-atoms) of magnesium in 1000 ml. of ether, was cooled in an ice bath and a twofold excess of ethylene oxide in 100 ml. of ether was added at a moderate rate. A sticky solid slowly separated. Color Test I[12] was negative subsequent to complete addition. Dilute sulfuric acid was added and the layers were separated. The organic layer was dried over magnesium sulfate and concentrated. The oil was distilled at 65° (45 mm.) to remove the forerun, then at 151–154° (12 mm.) to give 119.0 g. (67%) of product, $n^{19.3}_{\mathrm{D}}$ 1.5440, $d^{19.3}_{19.3}$ 1.1569.

Anal. Calcd. for $C_9H_{11}ClO$: C, 63.33; H, 6.50; Cl, 20.77; MR, 46.80. Found: C, 62.92 and 62.73; H, 6.48 and 6.53; Cl, 20.41 and 20.45; MR, 45.56.

Treatment of a portion of the alcohol with 1-naphthyl isocyanate gave the 1-naphthylcarbamate, m.p. 105.5–107°, after two recrystallizations from petroleum ether.

3-(*o*-Chlorophenyl)propyl Bromide.—3-(*o*-Chlorophenyl)propanol-1 was allowed to react with phosphorus tribromide as described above for the ethyl derivative to give the bromide in yields of 67–80%, b.p. 84–88° (3.5 mm.), n^{20}_{D} 1.5612, d^{20}_{20} 1.4339.

Anal. Calcd. for $C_9H_{10}BrCl$: C, 46.29; H, 4.32; MR, 52.93. Found: C, 46.33 and 46.40; H, 4.36 and 4.20; MR, 52.88.

4-(*o*-Chlorophenyl)butyric Acid.—A Grignard reagent was prepared from 5.84 g. (0.025 mole) of 3-(*o*-chlorophenyl)propyl bromide and 0.73 g. (0.03 g.-atom) of magnesium in 50 ml. of ether and then carbonated. The usual work-up gave 3.25 g. (65.7%) of acid, m.p. 86–88°. Two recrystallizations from petroleum ether gave an analytical sample, m.p. 90–91°.

Anal. Calcd. for $C_{10}H_{11}ClO_2$: C, 60.46; H, 5.58. Found: C, 60.68 and 60.79; H, 5.60 and 5.64.

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(6) For correlations of some silicon hydrides with their carbon analogs, see D. E. Webster, *J. Chem. Soc.*, 5132 (1960).

(7) P. T. Narasimhan and M. T. Rogers, *J. Am. Chem. Soc.*, **82**, 5983 (1960).

(8) E. B. Baker, *J. Chem. Phys.*, **26**, 960 (1957).

(9) All melting points and boiling points are uncorrected. Reactions involving organometallic compounds were carried out under an atmosphere of dry, oxygen-free nitrogen.

(10) P. R. Austin and J. R. Johnson, *J. Am. Chem. Soc.*, **54**, 647 (1932).

(11) R. A. Barnes and M. D. Konort, *ibid.*, **75**, 303 (1953). The authors are grateful to Dr. Barnes for a sample of the bromide.

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

4-(*o*-Chlorophenyl)butanol-1.—*o*-Chlorobenzylmagnesium chloride (0.1 mole) was treated with 5.81 g. (0.1 mole) of trimethylene oxide dissolved in 100 ml. of ether while cooling the reaction flask in cold water. After stirring overnight, Color Test I was negative. Subsequent to acid hydrolysis and separation of the layers, the organic layer was dried and distilled to give 8.27 g. (44.7%) of pure product, b.p. 107–110.5° (3 mm.), n^{20}_{D} 1.5385, d^{20}_{20} 1.1282.

Anal. Calcd. for $C_{10}H_{13}ClO$: C, 65.04; H, 7.10; MR, 51.43. Found: C, 64.52 and 64.50; H, 7.08 and 7.08; MR, 51.24.

The 1-naphthylcarbamate of the alcohol melted at 91.5–93°, after successive recrystallizations from petroleum ether and ethanol.

4-(*o*-Chlorophenyl)butyl Bromide.—The bromide was prepared from the alcohol and phosphorus tribromide as described above for 2-(*o*-chlorophenyl)ethyl bromide. The yield was 68%, b.p. 122–124° (2 mm.), n^{20}_{D} 1.5550, d^{20}_{20} 1.3779.

Anal. Calcd. for $C_{10}H_{12}BrCl$: C, 48.51; H, 4.89; MR, 57.56. Found: C, 49.27 and 49.47; H, 4.86 and 5.02; MR, 57.67.

The bromide was converted into the known acid, 5-(*o*-chlorophenyl)pentanoic acid, by preparation of the Grignard reagent and carbonation. Recrystallization from petroleum ether gave a 60% yield of the acid, m.p. 46.5–48°, lit.[13] m.p. 46°.

5-(*o*-Chlorophenyl)pentanol-1.—To the Grignard reagent (0.151 mole) of 3-(*o*-chlorophenyl)propyl bromide was added an ethereal solution of ethylene oxide as described above for the preparation of 3-(*o*-chlorophenyl)propanol-1. The concentrated oil was distilled twice at reduced pressure to give 11.89 g. (44.5%) of pure product, b.p. 118–121° (0.4 mm.), n^{20}_{D} 1.5308, d^{20}_{20} 1.1076.

Anal. Calcd. for $C_{11}H_{15}ClO$: C, 66.49; H, 7.61; MR, 56.06. Found: C, 65.66 and 65.45; H, 7.47 and 7.31; MR, 55.51.

5-(*o*-Chlorophenyl)pentyl Bromide.—5-(*o*-Chlorophenyl)pentanol-1 (14.79 g., 0.075 mole) and phosphorus tribromide were mixed and treated as described previously. Reduced-pressure distillation gave 12.2 g. (62.5%) of a colorless liquid, b.p. 104–108° (0.2 mm.), n^{20}_{D} 1.5468, d^{20}_{20} 1.3383.

Anal. Calcd. for $C_{11}H_{14}BrCl$: C, 50.50; H, 5.39; MR, 62.19. Found: C, 49.26 and 50.75; H, 5.35 and 5.42; MR, 61.97.

Preparation of (*o*-Chlorophenyl)alkylsilanes (Table I). A. **[3-(*o*-Chlorophenyl)propyl]diphenylsilane (V).**—An ethereal solution of 21.9 g. (0.1 mole) of chlorodiphenylsilane was treated with 0.1 mole of 3-(*o*-chlorophenyl)propylmagnesium bromide, prepared in an 88% yield from 26.9 g. (0.115 mole) of 3-(*o*-chlorophenyl)propyl bromide and 3.9 g. (0.16 g.-atom) of magnesium turnings in 250 ml. of ether. After refluxing for 1 hr., Color Test I was negative. Subsequent to acid hydrolysis, separation, drying, and concentration of the organic layer, the reaction products were distilled to give 27.82 g. (82.7%) of V, b.p. 162–168° (0.005 mm.), n^{20}_{D} 1.5923, d^{20}_{20} 1.1055.

B. **[3-(*o*-Chlorophenyl)propyl]phenylsilane (VI).**—Phenyl silane (10.72 g., 0.099 mole) in 100 ml. of tetrahydrofuran (THF) was allowed to react for 24 hr. at room temperature with an ethereal solution containing 0.099 mole of 3-(*o*-chlorophenyl)propylmagnesium bromide.[14] The ether was then distilled and the resulting THF solution was refluxed for 1 hr. Hydrolysis was effected by pouring into an ice–sulfuric acid mixture. Ether was added and the layers were separated. The organic layer was dried and distilled to give 20.1 g. (77.9%) of the silane, b.p. 163–165° (2.5 mm.), n^{20}_{D} 1.5688, d^{20}_{20} 1.075.

2:3-Benzo-1-silacycloalkenes (Table II). A. **2:3-Benzo-1-phenyl-1-silacyclopent-2-ene (XII).**—Since the Si-H grouping readily reacts with base and because of the possible susceptibility of the five-membered ring toward cleavage by base, the work-up of the reaction mixtures for the preparation of compounds XII–XIV was modified slightly from that of the remaining compounds of Table II. The following procedure is illustrative of compounds XII and XIV. [2-(*o*-Chlorophenyl)ethyl]phenylsilane (20.65 g., 0.084 mole) in 100 ml. of dry toluene was added to a refluxing suspension of 3.86 g. (0.16 g.-atom) of sodium in 100 ml. of toluene. The mixture became purple in color soon after the addition was commenced. The addition was completed over a 1.5-hr. period. After refluxing for 3 hr., a 5-ml. aliquot was withdrawn and acid hydrolyzed. After the usual work-up, the infrared spectrum of the residual oil contained a strong absorption band at 12.2 μ, characteristic of an Ar_2RSiH system.[15] The band at 10.7 μ, characteristic of an $ArRSiH_2$ system, had almost disappeared. Therefore, the reaction mixture was refluxed an additional 2.5 hr. and then allowed to stand several hours at room temperature. The clear liquid was withdrawn by means of a pipet and poured into an ice–sulfuric mixture. The residual salt–sodium material in the flask was destroyed with ethanol.

The hydrolyzed portion was extracted with ether and the combined organic layer was dried. The concentrated oil was distilled at reduced pressure to give 9.57 g. (54.3%) of colorless liquid, b.p. 125–126° (1.5 mm.), n^{20}_{D} 1.5998, d^{20}_{20} 1.0587.

2:3-Benzo-1,1-diphenyl-1-silacyclopent-2-ene (XIII) was isolated by concentration of the dried organic layer and two recrystallizations of the crude product (m.p. 55–60°) from absolute ethanol. The pure material melted at 62–63°.

B. **2:3-Benzo-1,1-diphenyl-1-silacyclohept-2-ene (XVIII).**—The following procedure is representative of the preparation of compounds XV–XIX. A solution of [4-(*o*-chlorophenyl)butyl]-diphenylsilane (16.8 g., 0.048 mole) in 100 ml. of toluene was added to a refluxing suspension of 2.3 g. (0.1 g.-atom) of sodium in 100 ml. of toluene. After refluxing for 7 hr., the brown mixture was cooled and treated with ethanol. The solution was poured cautiously into an ammonium chloride solution and the layers were separated. The aqueous layer was extracted with ether and discarded. The organic layer was dried and distilled, to remove the solvents. Ethanol was added to the residue and then filtered to give 10.7 g. of solid, m.p. 148–151°. Recrystallization from ethanol and then petroleum ether afforded 8.38 g. (55.6%) of colorless crystals, m.p. 151–153°.

In some cases the desired cyclic compound was so contaminated by intermolecular reaction materials that it was impossible to crystallize directly. In such cases it was necessary to distil the reaction products at reduced pressure, and then treat the distillates with the recrystallization solvent.

2:3-Benzo-1,1-diphenyl-1-silacyclopent-2-ene (XIII) from 2:3-benzo-1-phenyl-1-silacyclopent-2-ene (XII).—Phenyllithium (0.0055 mole) was added to 1.07 g. (0.0051 mole) of XII in 5 ml. of ether and the mixture was refluxed for 18 hr. Dilute sulfuric acid was added and the layers were separated. The organic layer was dried and concentrated. The residual solid was recrystallized from absolute ethanol to afford 0.6 g. (41.1%) of colorless crystals, m.p. 62–63.5°, which was identified as 2:3-benzo-1,1-diphenyl-1-silacyclopent-2-ene by a mixture melting point determination.

2:3-Benzo-1,1-diphenyl-1-silacyclohex-2-ene (XV) from 2:3-Benzo-1-phenyl-1-silacyclohex-2-ene (XIV).—Compound XIV (0.94 g., 0.0042 mole) was allowed to react with phenyllithium (0.0043 mole) as described in the previous experiment. The yield of XV was 71.4% and the product melted at 77–79°. A mixture melting point with an authentic sample of 2:3-benzo-1,1-diphenyl-1-silacyclohex-2-ene was not depressed.

Alternate Synthesis of XV.—A di-Grignard reagent was made from 5.56 g. (0.02 mole) of 3-(*o*-bromophenyl)propyl bromide and 1.20 g. (0.05 g.-atom) of magnesium in 85 ml. of tetrahydrofuran (yield 82%); the filtered organomagnesium compound was added to 3.87 g. (0.0153 mole) of dichlorodiphenylsilane dissolved in 10 ml. of tetrahydrofuran. Color Test I was negative after refluxing for 1 hr. The reaction mixture was hydrolyzed with dilute hydrochloric acid and worked up in the usual manner. The organic layer was evaporated and petroleum ether was added to the residue. Filtration gave 0.61 g. (21%) of diphenylsilanediol, m.p. 162.5–163.8°, identified by mixture melting point and by comparison of the infrared spectra.

The silane was isolated without distillation by removal of the petroleum ether and addition of ethanol to the residual oil. The solid was filtered to give 3.66 g. of impure product, m.p. 70–74°. Recrystallization from ethanol afforded 2.29 g. (54.4%) of colorless crystals, m.p. 78–79.5°, which was identified as XV by mixture melting point and comparison of the infrared spectra.

***o*-Bromobenzyldiphenylsilane.**—*o*-Bromobenzylmagnesium bromide (0.047 mole) was added to an ethereal solution of chlorodiphenylsilane (10.28 g., 0.047 mole) dissolved in 15 ml. of ether. When the addition was complete, Color Test I was negative. The reaction mixture was poured into dilute sulfuric acid and worked up in the usual manner. The concentrated oil was distilled under reduced pressure to give 17.61 g. of a pale yellow liquid, boiling over the range 143–152° (0.004 mm.), which was taken up in petroleum ether and chromatographed over alumina. The petroleum ether and cyclohexane eluates were distilled to give 1.35 g. (44.5%) of product, b.p. 148–150° (0.002 mm.), n^{20}_{D} 1.6268, d^{20}_{20} 1.2814.

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(13) R. Granger, H. Orzales, and A. Muratelle, *Compt. rend.*, **252**, 1478 (1961).

(14) For a study of the reactions of Grignard reagents with silicon hydrides, see H. Gilman and E. A. Zuech, *J. Am. Chem. Soc.*, **81**, 5925 (1959).

(15) R. N. Kniseley, V. A. Fassel, and E. E. Conrad, *Spectrochim. Acta*, **13**, 651 (1959).

Anal. Calcd. for $C_{19}H_{17}BrSi$: Si, 7.95; MR, 97.62. Found: Si, 7.88 and 7.87; MR, 97.72.

Reaction of *o*-Chlorobenzyldiphenylsilane with Sodium.—To a refluxing suspension of 6.0 g. (0.26 g.-atom) of sodium in 100 ml. of toluene, there was added 29.84 g. (0.13 mole) of *o*-chlorobenzyldiphenylsilane in 100 ml. of toluene. The mixture was refluxed for 24 hr. and then allowed to stand for several hours at room temperature. The clear liquid was removed by means of a pipet and poured cautiously onto iced sulfuric acid. The residual sodium-salt mixture was washed twice with 25-ml. portions of toluene; the washings were removed and hydrolyzed after allowing the solid to settle. The sodium was then destroyed with ethanol.

Ether was added to the hydrolyzed portion and the organic layers were separated and dried. Evaporation of the solvents and distillation of the oil under reduced pressure gave 16.55 g. (55.5%) of unreacted starting material, confirmed by comparison of the refractive indices and infrared spectra.

The distillation residue was treated with petroleum ether to give 0.6 g. of solid, m.p. 280–295°. Recrystallization from a benzene–petroleum ether mixture afforded 0.28 g. of colorless crystals, m.p. 313–315°. The infrared spectrum of the compound in carbon disulfide showed prominent absorption bands at 3.27, 3.46, 9.05, and 13.07 μ, indicative of aromatic C–H, aliphatic C–H, the silicon–phenyl linkage, and *ortho* disubstitution, respectively. As a carbon tetrachloride solution, the characteristic Si–H absorption band was absent. The compound has been assigned the structure 2:3,6:7-dibenzo-1,1,5,5-tetraphenyl-1,5-disilacycloocta-2,6-diene (XX).

Anal. Calcd. for $C_{38}H_{32}Si_2$: C, 83.76; H, 5.92. Found: C, 83.78 and 83.99; H, 6.10 and 6.17.

For the purpose of improving the yield of XX, *o*-bromobenzyldiphenylsilane was similarly allowed to react with molten sodium in toluene. However, the yield of XX remained low (4.5%) but unreacted *o*-bromobenzyldiphenylsilane was recovered in only a 15.5% yield.

The infrared spectrum of the viscous distillation residue contained a strong Si–H absorption band at 4.76 μ.

2:3-Benzo-1,1-dibenzyl-1-silacyclopent-2-ene (Attempted).—A mixture of 7.81 g. (0.0223 mole) of dibenzyl[2-(*o*-chlorophenyl-ethyl]silane and 1.15 g. (0.05 g.-atom) of sodium in 100 ml. of toluene was refluxed for 48 hr. There was no evidence of a reaction. The solid was allowed to settle and then the clear liquid was withdrawn by means of a pipet and hydrolyzed by pouring into dilute sulfuric acid. The usual work-up of the organic layer gave a 74.6% recovery of starting material, confirmed by comparison of the infrared spectra.

2:3-Benzo-1,1-dibenzyl-1-silacyclohex-2-ene (Attempted).—Dibenzyl[3-(*o*-chlorophenyl)propyl]silane (21.06 g., 0.0577 mole) was similarly refluxed with sodium in 250 ml. of toluene for 48 hr. After the work-up as described in the previous experiment, the starting material was recovered in a 76.4% yield.

A repeat run was carried out, but the cyclization reaction could not be initiated and a 79.1% recovery of the starting material was realized.

Dibenzyl[3-(*o*-chlorophenyl)propyl]phenylsilane.—An ethereal solution of phenyllithium (0.033 mole) was added to 5.1 g. (0.014 mole) of the recovered dibenzyl[3-(*o*-chlorophenyl)propyl]silane dissolved in 10 ml. of ether. The mixture was refluxed for 24 hr. and then hydrolyzed. The organic layer was separated and dried. The ether was distilled and resulting oil was distilled at reduced pressure to give 3.9 g. (63.2%) of a pale yellow, viscous liquid, b.p. 196–198° (0.004 mm.), $n^{20}D$ 1.6065.

Anal. Calcd. for $C_{29}H_{29}ClSi$: Si, 6.37. Found: Si, 6.47 and 6.35.

Ethyldiphenylsilane.—To an ethereal solution of 10.28 g. (0.047 mole) of chlorodiphenylsilane was added 0.047 mole of ethylmagnesium bromide. Subsequent to complete addition, Color Test I was negative. Hydrolysis and the usual work-up afforded 6.66 g. (66.7%) of a colorless liquid, b.p. 122–122.5° (2.5 mm.), $n^{20}D$ 1.5677, d^{20}_{20} 0.9894, lit.[16] $n^{20}D$ 1.5674.

Since the n.m.r. spectrum of this compound was anomalous, a portion of the silane was treated with phenyllithium to give ethyltriphenylsilane, m.p. 74–76°, identified by mixture melting point and by comparison of the infrared spectra.

Diphenyl-*n*-propylsilane.—A mixture of *n*-propylmagnesium bromide (0.06 mole) and chlorodiphenylsilane (13.13 g., 0.06 mole) was stirred for 30 min. at room temperature and then worked up in the usual manner to give 8.89 g. (65.4%) of pure product, b.p. 126–128° (2.5 mm.), $n^{20}D$ 1.5608, d^{20}_{20} 0.9786.

Anal. Calcd. for $C_{15}H_{18}Si$: C, 79.57; H, 8.01; MR, 74.81. Found: C, 80.15 and 79.91; H, 7.79 and 7.84, MR, 74.89.

Infrared Spectra of the Benzosilacycloalkenes.—The infrared absorption spectra of the cyclic derivatives were determined on a Perkin-Elmer, Model 21, spectrophotometer and showed the expected aromatic and aliphatic C–H, *ortho* disubstitution and, when present, Si–H and Si–CH_3 absorption bands. However, the band characteristic of the silicon–phenyl linkage differed between the various ring sizes. The five-membered ring compounds contained a strong peak at 8.99 μ, whereas the six-membered ring homologs with at least one phenyl group attached to the silicon atom *consistently* showed two medium to strong bands at *ca.* 8.8 and 8.9 μ and a strong band at 9.05 μ. The data for some of the cyclic derivatives are shown in Table IV. The three bands at 8.8, 8.9, and 9.05 μ appear to be characteristic of the benzosilacycloalkene nucleus.

TABLE IV

Compd.	Medium	Infrared bands in the 8.7–9.1-μ region
XII	Liq.	8.98 (s)[a]
XIII	CS_2	8.99 (s)
XIV	Liq.	8.80 (s), 8.92 (s), 9.03 (s)
XV	CS_2	8.81 (s), 8.92 (s), 9.07 (s)
XVIII	CS_2	8.80 (w), 8.89 (m), 9.04 (s)
XIX	CS_2	8.75 (w), 8.99 (m), 9.06 (s)
Ethyldiphenylsilane	Liq.	9.05 (s)[b]

[a] s = strong, m = medium, and w = weak. [b] Slightly split.

N.m.r. Spectra.—The spectra were determined using a Varian Associates high resolution spectrometer, Model HR-60, operated at 60 Mc., and tetramethylsilane was the internal standard. The data are recorded in Table III.

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