[CONTRIBUTION FROM THE WHITMORE LABORATORY, THE PENNSYLVANIA STATE COLLEGE]

Silylindenes and Silylindans[1]

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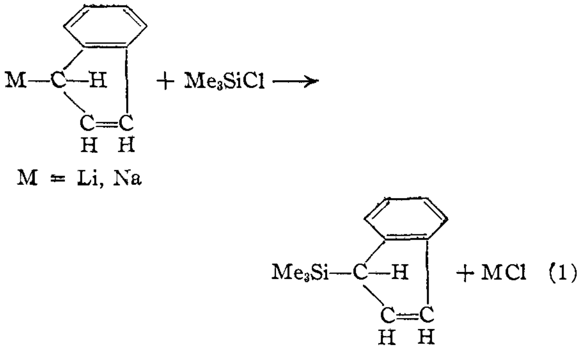
A series of silylindenes has been prepared by the reaction of (1) indenylsodium and (2) indenyllithium on alkylhalosilanes. Some reactions of the silylindenes have been studied for the purpose of further clarifying the effect of structure on the chemical behavior of the carbon–silicon bond in organosilicon compounds. A number of silylindans have been prepared by hydrogenation of the corresponding silylindenes.

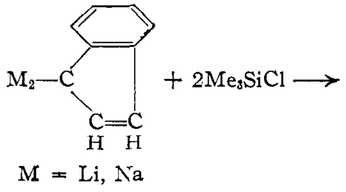
Open chain alkenylsilicon compounds have been reported in the literature and their reactions studied, *e.g.*, vinylsilanes[3,4] and allylsilanes.[5] The interesting cleavage reactions of the carbon to silicon bond in the latter compounds indicated the desirability of an analogous study on cycloalkenyl silicon compounds.

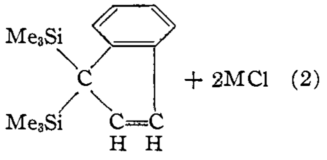
For this purpose the silylindenes were chosen. Compounds I-VIII (Table I) were prepared by the reaction of an organometallic compound and a chlorosilane. In method A, the appropriate chlorosilane was added to 1-indenylsodium[6] (not isolated) in boiling xylene and the silylindene compound isolated by fractionation. In method B, the appropriate chlorosilane was added to 1-indenyllithium (prepared by the metalation of indene with *n*-butyllithium but not isolated) in boiling xylene and the silylindene compound isolated by fractionation. For example, as shown in equation 1, Compound I was prepared from trimethylchlorosilane and 1-indenylsodium or 1-indenyllithium.



(I)

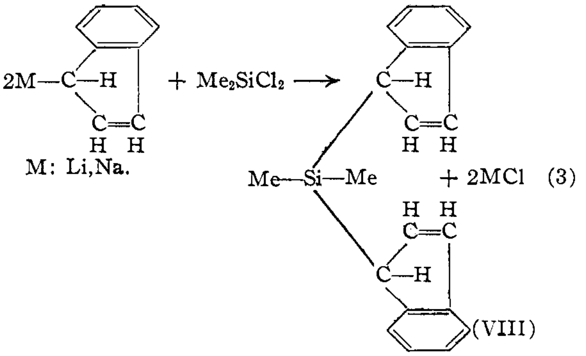
Compounds III and IV were prepared by the reaction of the appropriate chlorosilane and 1,1-indenyldisodium or 1,1-indenyldilithium (equation 2).





(III)

Compounds II, V and VI were synthesized in good yield through the use of reactions analogous to those shown in equations 1 and 2. Compounds VII and VIII resulted from reactions involving replacement of two chlorine atoms linked to the same silicon, as illustrated in equation 3.



It was found that 1-indenylsodium and 1-indenyllithium were equally effective in the preparation of Compounds I–IV. However, 1-indenyllithium gave better yields in the preparation of Compounds V and VI.

Compounds I–IV were selectively hydrogenated to the corresponding silylindans (Compounds XI–XIV) at 3 atmospheres pressure and 25°, using Raney nickel as a catalyst. The chlorosilylindenes, Compounds V and VI, were converted to the corresponding *n*-butoxysilylindenes, Compounds IX and X, by the use of *n*-butanol and pyridine, and then were hydrogenated to the corresponding *n*-butoxysilylindans, Compounds XV and XVI.

Experimental

Materials.—Indene from Koppers Co. was fractionally distilled to give material having a b.p. 79° (30 mm.), m.p. −1°, and $n^{20}\mathrm{D}$ 1.5738–1.5741. Pentane from Viking Distributing Co. was purified by stirring with three separate portions of concentrated sulfuric acid, washing with water, and subsequent careful fractionation. Dimethyldichlorosilane, methyltrichlorosilane, trimethylchlorosilane and trimethylethoxysilane, all from Dow Corning Corp., were used without further purification. *n*-Butyl chloride was prepared from *n*-butanol (Eastman Kodak Co. white label), hydrochloric acid, and zinc chloride[7] and on fractionation gave material b.p. 77° (734 mm.), $n^{20}\mathrm{D}$ 1.4013. Triethylchlorosilane, b.p. 144–145° (730 mm.), was prepared in two steps from the reaction of ethyl orthosilicate and ethylmag-

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[1] Paper 30 in a series on organosilicon chemistry. For Paper 29 see THIS JOURNAL, **73**, 5130 (1951).

[2] Taken in part from a thesis submitted by N. S. Marans in partial fulfillment of the requirements for the Ph.D. degree, February, 1949.

[3] D. T. Hurd, THIS JOURNAL, **67**, 1815 (1945).

[4] D. T. Hurd and G. F. Roedel, *Ind. Eng. Chem.*, **40**, 2078 (1948).

[5] L. H. Sommer, L. J. Tyler and F. C. Whitmore, THIS JOURNAL, **70**, 2872 (1948).

[6] R. Weissgerber, *Ber.*, **42**, 569 (1909).

[7] H. Gilman and A. H. Blatt, "Organic Syntheses," John Wiley and Sons, Inc., New York, N. Y., 1948, p. 142.

TABLE I

SILYLINDENES AND SILYLINDANS

Compound		Method[a]	Yield, %	d^{20}_4	n^{20}_D	B.p., °C.	B.p., mm.	Si, % Calcd.	Si, % Found	Cl, % Found	Cl, % Calcd.	Mol. wt.[b] Found	Mol. wt.[b] Calcd.	Molar refraction[c] Calcd.	Molar refraction[c] Found
1-(Trimethylsilyl)-indene	I	A	54.7	0.945	1.5423	87	4	14.9	15.0			188	189	62.6	62.7
		B	59	.945	1.5426	76	2								
1-(Triethylsilyl)-indene	II	A	49.3	.950	1.5412	121	3	12.2	12.0			230	228	76.5	76.2
		B	49.5	950	1.5420	113	2								
1,1-Bis(trimethylsilyl)-indene	III	A	17.7	930	1.5307	106	3	21.5	21.5			260	264	86.1	86.3
		B	15.4	930	1.5300	101	3								
1,1-Bis-(triethylsilyl)-indene	IV	A	27.1	.940	1.5335	190	6	16.3	16.1			344	349	113.9	113.9
		B	27.5	.939	1.5330	170	3								
1-(Dimethylchlorosilyl)-indene	V	A	14.5	1.071	1.5535	70	1	13.5	13.5	17.0	16.9			62.2	62.4
		B	64.2	1.076	1.5525	92	3				17.0				
1-(Methyldichlorosilyl)-indene	VI	A	27.8	1.200		84	2	12.2	12.1	30.9	30.8				
		B	73.6	1.201		92	3				30.7				
1-[(1-Indenyl)-methylchlorosilyl]-indene[d]	VII	A	11	1.131		179	2	9.10	9.01	11.5	11.6				
1-[(1-Indenyl)-dimethylsilyl]-indene	VIII	B	24	1.060	1.6110	155	4	9.73	9.67			288	298	94.9	94.4
1-(Methyldi-*n*-butoxysilyl)-indene	IX	C	53.5	0.976	1.5015	130	1.5	9.22	9.16			304	295	91.9	92.0
1-(Dimethyl-*n*-butoxysilyl)-indene	X	C	49.4	.964	1.5165	113	3	11.4	11.2			246	243	77.2	77.2
1-(Trimethylsilyl)-indan	XI	D	65	.930	1.5205	64	1.5	14.8	14.7			190	189	62.0	62.1
		E	61.9	.931	1.5205	76	3								
1-(Triethylsilyl)-indan	XII	D	76.3	.942	1.5250	120	3	12.1	12.0			232	241	75.9	75.5
		E	43.5	.942	1.5255	109	2								
1,1-Bis-(trimethylsilyl)-indan	XIII	E	24	.920	1.5135	94	2	21.6	21.6			262	266	85.5	85.6
1,1-Bis-(triethylsilyl)-indan	XIV	E	49	.941	1.5270	155	2	16.3	16.3			346	336	113.3	113.1
1-(Methyldi-*n*-butoxysilyl)-indan	XV	E	82	.952	1.5003	117	3	11.3	11.5			248	253	91.3	91.5
1-(Dimethyl-*n*-butoxysilyl)-indan	XVI	D	85.3	.963	1.4809	131	2	9.2	9.2			306	305	76.6	76.7

[a] Method A employs 1-indenylsodium, method B employs 1-indenyllithium, method C employes *n*-butanol and pyridine, method D employs ether as a solvent during hydrogenation, and method E employs ethanol as a solvent during hydrogenation. [b] All molecular weights obtained by freezing point depression of benzene solutions. [c] Calculated molar refractions were obtained by the summation of the average values of bond refractions for the indenyl to silicon bond (39.9) or indanyl to silicon bond (39.3) and the known bond refractions for the remainder of the molecule. [d] This is a side product in the preparation of Compound VI.

nesium bromide and treatment of the product with ammonium chloride and sulfuric acid.[8]

1-Indenylsodium.—A typical preparation of 1-indenylsodium is given. In a 1-liter three-necked flask equipped with a stirrer, Hopkins condenser, and dropping funnel or thermometer, there were placed 64 g., 0.55 mole, of indene and 27 g., 1.17 g. atoms, of sodium. The reaction mixture was stirred and heated to 140–150° with the formation of 1-indenylsodium evidenced by evolution of hydrogen and a temperature rise. 1,1-Indenyldisodium was prepared in smaller yields in the same manner by using more sodium. The crude mixture was used as described below.

Preparation of Silylindenes.—A typical preparation selected from the group listed in Table II is given for 1-(trimethylsilyl)-indene. Xylene, 200 cc., was added rapidly to the above indenylsodium at 80° and then with continued heating and stirring 115 g., 1.06 moles, of trimethylchlorosilane was added. After stirring and heating at 100° for 12 hours, the cooled mixture was poured into ice and water. The separated organic layer was dried over sodium sulfate. Fractionation gave 56.6 g., 0.301 mole, of 1-(trimethylsilyl)-indene, 54.7% yield based on indene.

TABLE II

SILYLINDENES FROM INDENYLSODIUM

Compound	Indene, moles	Sodium, g. atoms	Chlorosilane, moles	Yield, %
I	0.55	1.17	1.06	54.7[a,b]
II	1.54	1.22	1.12	49.3[c,d]
III	1.39	1.38	1.44	17.7[d,e]
IV	0.94	1.95	1.63	27.1[b,f]
V	.922	0.935	1.05	27.8[g]
VI	.474	0.543	0.539	14.5[g,h]

[a] 1,1-(Bis-trimethylsilyl)-indene was found in a 5.5% yield. [b] Yield is based on indene. [c] In the reaction 1,1-(bis-triethylsilyl)-indene was formed in an 11.5% yield. [d] Yield is based on sodium. [e] 1-(Trimethylsilyl)-indene was found in a 34.5% yield. [f] In this reaction 1-(triethylsilyl)-indene was formed in a 26.3% yield. [g] These compounds were fractionally distilled without hydrolyzing the reaction mixture. [h] 1-[(1-Indenyl)-methylchlorosilyl]-indene was found in an 11% yield.

Preparation of 1-Indenyllithium.—This is a typical preparation of indenyllithium. *n*-Butyllithium[9] was prepared in a 1-liter three-necked flask equipped with stirrer, dropping funnel, and condenser, from 11.0 g., 1.57 g. atoms of lithium, pounded into fine strips, 400 cc. of olefin-free pentane and 50 g., 0.55 mole, of *n*-butyl chloride.[10] The mixture was then heated under reflux for 12 hours under an atmosphere of nitrogen to give by titration a 96% yield of *n*-butyllithium. To the cool solution was added 400 cc. of xylene and 90 g., 0.77 mole, of indene. The metalation reaction was exothermic but to ensure completeness of reaction, the mixture was stirred and heated at 90° for 12 hours with no water cooling in the condenser. The latter procedure permitted removal of the pentane. Runs using a 2:1 molar ratio of *n*-butyllithium to indene gave the 1,1-indenyldilithium compound.

Preparation of 1-(Dimethylchlorosilyl)-indene.—This is a typical preparation of a silylindene compound from indenyllithium and is chosen from the group listed in Table III. To the cool reaction mixture containing 1-indenyllithium there was added with stirring 90 g., 0.703 mole, of dimethyldichlorosilane and the flask contents then stirred and heated at 100° for 24 hours. Fractionation gave 69.7 g., 0.334 mole, of 1-(dimethylchlorosilyl)-indene, 64.2% yield based on *n*-butyl chloride.

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(8) P. A. DiGiorgio, W. A. Strong, L. H. Sommer and F. C. Whitmore, THIS JOURNAL, **68**, 1380 (1946).

(9) H. Gilman, E. A. Zoellner and W. M. Selby, *ibid.*, **55**, 1252 (1933).

(10) An excess of lithium to *n*-butyl chloride was found to be necessary to insure complete reaction of the *n*-butyl chloride. Any remaining *n*-butyl chloride gave reaction with indenyllithium to form 1-*n*-butylindene, an impurity that could not be readily removed from either 1-(methyldichlorosilyl)-indene or 1-(dimethylchlorosilyl)-indene by fractionation.

TABLE III

SILYLINDENES FROM INDENYLLITHIUM

Compound	Lithium, g. atoms	*n*-Butyl chloride, mole	Indene, mole	Chlorosilane, mole	Yield, %
I	1.50	0.87	0.75	0.78	59[a]
II	0.93	.42	.52	.40	49.5[b]
III	1.50	.47	.23	.74	15.4[c]
IV	1.50	.68	.30	.66	27.5[d]
V	1.57	.54	.77	.70	64.2[a]
VI	1.23	.49	.60	.68	73.6[a]
VIII	1.64	.87	.82	.36	24[e,f]

[a] The yield is based on *n*-butyllithium. [b] The yield is based on triethylchlorosilane. [c] The yield is based on indene. [d] In addition 41.7% of 1-(trimethylsilyl)-indene was formed in the reaction. [e] The yield is based on indene. In addition 22.3% yield of 1-(triethylsilyl)-indene was formed in the reaction mixture. [f] Yield is based on dimethyldichlorosilane.

Reactions of Concentrated Sulfuric Acid with 1-(Trialkylsilyl)-indenes. (1) **1-(Trimethylsilyl)-indene.**—In a 500-cc. three-necked flask in an ice-bath and fitted with stirrer, dropping funnel, and Hopkins condenser, there was placed 100 cc. of concentrated sulfuric acid. To the flask with stirring there was added 40 g., 0.213 mole, of 1-(trimethylsilyl)-indene in one hour. After an additional 30 minutes of stirring, the reaction mixture was poured into ice and water. The organic layer was separated and the aqueous layer was extracted with three portions of ether. The combined organic material, after drying over sodium sulfate, gave on fractionation 11.5 g., 0.071 mole, of hexamethyldisiloxane,[11] b.p. 99° (730 mm.), $n^{20}\text{D}$ 1.3770, 67% yield.

(2) **1-(Triethylsilyl)-indene.**—The reaction was run in the same manner as above, using 65 cc. of concentrated sulfuric acid and 30.5 g., 0.132 mole, of 1-(triethylsilyl)-indene. Fractionation gave 14.1 g., 0.058 mole, of hexaethyldisiloxane,[12] 87.6% yield.

Reactions of Dilute Sulfuric Acid with Trialkylsilylindenes. (1) **1-(Trimethylsilyl)-indene.**—A solution of 170 cc. of 50% sulfuric acid was placed in a 500-cc. three-necked flask equipped with stirrer, Hopkins condenser, and dropping funnel. To this solution there was added over 15 minutes, 20.5 g., 0.109 mole, of 1-(trimethylsilyl)-indene and the mixture stirred and heated for 12 hours at 100°. The organic layer was separated and the aqueous layer extracted with three portions of ether. The combined organic material was dried over sodium sulfate. Fractionation of the organic product gave 4.0 g., 0.025 mole, of hexamethyldisiloxane,[11] b.p. 99° (729 mm.), $n^{20}\text{D}$ 1.3780, 46% yield and 7.5 g., 0.040 mole, of 1-(trimethylsilyl)-indene, b.p. 63° (2 mm.), $n^{20}\text{D}$ 1.5421, 36% recovery of starting material.

(2) **1-(Triethylsilyl)-indene.**—The procedure used was the same as in the above run of 1-(trimethylsilyl)-indene, using 56 cc. of 50% sulfuric acid and 12.5 g., 0.054 mole, of 1-(triethylsilyl)-indene. Fractionation gave 9.8 g., 0.043 mole, of 1-(triethylsilyl)-indene, b.p. 118°, (3 mm.), $n^{20}\text{D}$ 1.5413, 80% recovery of starting material.

Reaction of Sodium Hydroxide Solution and Trialkylsilylindenes. (1) **1-(Trimethylsilyl)-indene.**—In a 500-cc. three-necked flask, equipped with stirrer and Hopkins condenser there were placed 21 g., 0.111 mole, of 1-(trimethylsilyl)-indene and 100 cc. of 20% sodium hydroxide. The mixture was stirred and heated for 12 hours at 100°. The organic layer was separated and the aqueous layer extracted with three portions of ether. After drying the organic material over sodium sulfate, fractionation of the crude product gave (1) 3.5 g., 0.022 mole, of hexamethyldisiloxane,[11] b.p. 98° (729 mm.), $n^{20}\text{D}$ 1.3770, 40% yield, (2) 7.1 g., 0.061 mole, of indene, b.p. 73° (20 mm.), m.p. 0°, $n^{20}\text{D}$ 1.5745, 55% yield, and (3) 4.0 g., 0.021 mole, of 1-(trimethylsilyl)-indene, b.p. 120° (20 mm.), $n^{20}\text{D}$ 1.5415, 18.1% recovery.

(2) **1-(Triethylsilyl)-indene.**—In a manner similar to that above, 200 cc. of 20% sodium hydroxide and 18.4 g., 0.080 mole, of 1-(triethylsilyl)-indene were stirred and heated at 100° for 12 hours. Final fractionation gave 13.7 g., 0.060 mole, of 1-(triethylsilyl)-indene, b.p. 101° (1.5 mm.), $n^{20}\text{D}$ 1.5410, 75% recovery of starting material.

(3) **1,1-(Bis-trimethylsilyl)-indene.**—This reaction was run in the same manner as the preceding reaction using 10 g., 0.038 mole, of 1,1-(bis-trimethylsilyl)-indene and 100 cc. of 20% sodium hydroxide. Fractionation gave (1) 2.2 g., 0.0136 mole, of hexamethyldisiloxane,[11] b.p. 100° (730 mm.), $n^{20}\text{D}$ 1.3775, 35.8% yield based on other product being indene, (2) 2.2 g., 0.019 mole, of indene, b.p. 30° (2 mm.), $n^{20}\text{D}$ 1.5748, 59% yield, and (3) 0.6 g., 0.003 mole, of 1-(trimethylsilyl)-indene, b.p. 85° (4 mm.), $n^{20}\text{D}$ 1.5415, 8% yield.

Reactions of Bromine and Trialkylsilylindenes (1) **(Trimethylsilyl)-indene.**—In a 500-cc. three-necked flask equipped with stirrer, dropping funnel, and Hopkins condenser there was placed 20 g., 0.106 mole, of 1-(trimethylsilyl)-indene. To this was slowly added with stirring, 18 g., 0.113 mole, of bromine. Immediate fractionation of the reaction mixture gave 11.6 g., 0.076 mole, of trimethylbromosilane,[13] b.p. 78° (729 mm.), 72.1% yield.

Anal. Calcd. for C_3H_9SiBr: Br, 52.3. Found: Br, 51.3, 50.9.

(2) **1-(Triethylsilyl)-indene.**—This reaction run as above using 30 g., 0.13 mole, of 1-(triethylsilyl)-indene and 21 g., 0.132 mole, of bromine gave on fractionation 21.1 g., 0.108 mole, of triethylbromosilane,[14] b.p. 62° (23 mm.), 83.1% yield.

Anal. Calcd. for $C_6H_{15}SiBr$: Br, 40.9. Found: Br, 40.6, 40.3.

(3) **1,1-(Bis-trimethylsilyl)-indene.**—This reaction, run as above, using 13 g., 0.050 mole, of 1,1-(bis-trimethylsilyl)-indene and 16.5 g., 0.102 mole, of bromine, gave on fractionation 9.9 g., 0.063 mole, of trimethylbromosilane[13] b.p. 79° (730 mm.), 62.1% yield.

Anal. Calcd. for C_3H_9SiBr: Br, 52.5. Found: Br, 51.1.

Reactions of Ethanol with Trialkylsilylindenes (1) **1-(Trimethylsilyl)-indene.**—A solution of 22 g., 0.117 mole, of 1-(trimethylsilyl)-indene in 300 cc. of absolute ethanol was stirred for five hours at 25°. After the removal of the ethanol, fractionation gave 19.0 g., 0.101 mole, of 1-(trimethylsilyl)-indene, b.p. 63° (1.5 mm.), $n^{20}\text{D}$ 1.5425, 86.3% recovery of starting material.

(2) **1,1-(Bis-trimethylsilyl)-indene.**—A solution of 25 g., 0.097 mole, of 1,1-(bis-trimethyl)-silylindene in 150 cc. of absolute ethanol was stirred at 25° for six hours. Fractionation gave (1) 3.6 g., 0.019 mole, of 1-(trimethylsilyl)-indene, b.p. 79° (3 mm.), $n^{20}\text{D}$ 1.5420, 19.8% yield and (2) 13.4 g., 0.052 mole, of 1,1-(bis-trimethylsilyl)-indene, b.p. 91° (2 mm.), $n^{20}\text{D}$ 1.5310, 53.6% recovery of starting material.

(3) **1,1-(Bis-triethylsilyl)-indene.**—A solution of 18.0 g., 0.052 mole, of 1,1-(bis-triethylsilyl)-indene in 250 cc. of ethanol was stirred for six hours. Fractionation gave (1) 0.8 g., 0.004 mole, of impure 1-(triethylsilyl)-indene, b.p. 113° (2 mm.), $n^{20}\text{D}$ 1.5395, 7% yield, and (2) 12.2 g., 0.050 mole, of 1,1-(bis-triethylsilyl)-indene, b.p. 150° (2 mm.), $n^{20}\text{D}$ 1.5330, 68.5% recovery of starting material.

1-(Trimethylsilyl)-indene and Stannic Chloride.—A mixture of 28 g., 0.149 mole, of 1-(trimethylsilyl)-indene and 15.6 cc. of stannic chloride was heated to 100° (initial mixing gave an exothermic reaction) for 12 hours. The almost solid mixture gave on fractionation 4.8 g., 0.044 mole, of trimethylchlorosilane,[13] b.p. 56° (734 mm.), 29.8% yield.

Anal. Calcd. for C_3H_9SiCl: Cl, 32.7. Found: Cl, 32.4.

Reactions of 1-(Dimethylchlorosilyl)-indene (1) Aqueous Sodium Hydroxide.—In a 500-cc. three-necked flask fitted with stirrer, thermometer, and dropping funnel, there was placed a solution of 25 g., 0.121 mole, of 1-(dimethylchloro)-silylindene in 125 cc. of ether. The mixture was cooled to 0° in an ice-bath and over a period of one hour 100 cc. of 1.20 *N* NaOH was added with the temperature never exceeding 5°. The ethereal layer was separated and the faintly basic, aqueous layer was extracted with three portions of ether. Fractionation gave (1) 6.2 g., 0.054 mole, of indene, b.p. 31° (2 mm.), m.p. −1°, $n^{20}\text{D}$ 1.5735, 44.5% yield, (2) 2.7 g., b.p. 75–85° (2 mm.), $n^{20}\text{D}$ 1.5010–1.4765 and (3) 7.2 g. of high-boiling residue.

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[11] R. Sauer, THIS JOURNAL, **66**, 1707 (1944). The reported constants are b.p. 99–100°, $n^{20}\text{D}$ 1.3772.

[12] The constants for this compound are b.p. 233° (760 mm.), $n^{20}\text{D}$ 1.4340. *Cf.* reference 8.

[13] B. O. Pray, L. H. Sommer, G. M. Goldberg, G. T. Kerr, P. A. DiGiorgio and F. C. Whitmore, THIS JOURNAL, **70**, 433 (1948).

[14] Flood, *ibid.*, **55**, 1735 (1933).

(2) **Liquid Ammonia.**—In a 500-cc. three-necked flask in an ether–Dry Ice trap and fitted with dropping funnel, stirrer, and calcium chloride drying tube, there was placed 85 cc. of liquid ammonia. To this in 20 minutes was added a solution of 20 g., 0.096 mole, of 1-(dimethylchlorosilyl)-indene in 185 cc. of pentane. The reaction mixture was stirred for 12 hours while the temperature was permitted to reach 25°. Fractionation gave 2.8 g., 0.025 mole, of indene, b.p. 35° (2 mm.), n^{20}_D 1.5720, 26% yield.

(3) **Methylmagnesium Bromide.**—To methylmagnesium bromide, 0.49 mole, was added in five minutes 39.5 g., 0.189 mole, of 1-(dimethylchlorosilyl)-indene. After stirring and heating for two hours, the mixture was hydrolyzed by addition of an acetic acid, ice and water mixture. The organic layer was separated and the aqueous layer extracted with two portions of ether. The combined organic material after drying over sodium sulfate gave on fractionation 26.8 g., 0.143 mole, of 1-(trimethylsilyl)-indene, b.p. 79° (3 mm.), n^{20}_D 1.5420, d^{20}_4 0.945, 75% yield.

(4) ***n*-Butanol and Pyridine.**—To a solution of 7.6 g., 0.096 mole, of freshly distilled pyridine, and 8.0 g., 0.108 mole, of *n*-butanol, there was added 14.6 g., 0.070 mole, of 1-(dimethylchlorosilyl)-indene with a heavy precipitate being formed immediately with the evolution of heat. Xylene, 300 cc., was added to the cool reaction mixture and the contents of the flask filtered. Fractionation of the filtrate gave 8.5 g., 0.0346 mole, of 1-(dimethyl-*n*-butoxysilyl)-indene (Compound X), 49.4% yield.

Reactions of 1-(Methyldichlorosilyl)-indene (1) Aqueous Sodium Hydroxide.—In a three-necked flask in an ice-bath and equipped with a stirrer, dropping funnel and thermometer were placed 100 cc. of ether and 50 cc. of 1.20 *N* NaOH. To the mixture maintained at 0° was added slowly 5.7 g., 0.024 mole, of 1-(methyldichlorosilyl)-indene and then the mixture stirred for five minutes. The ethereal layer was separated and dried over potassium carbonate. No 1-(methyldihydroxysilyl)-indene was obtained but on distillation 1.2 g., 0.010 mole, of indene, b.p. 173–180° (730 mm.), m.p. −1°, n^{20}_D 1.5690, a 42% yield was obtained.

(2) **Water.**—In a 500-cc. three-necked flask in an ice-bath were mixed 16 cc. of *t*-amyl alcohol, 8 ml. of toluene and 66 ml. of water. To the reaction mixture maintained at 0° was added 23.0 g., 0.10 mole, of 1-(methyldichlorosilyl)-indene in 8 ml. of toluene. No solid separated at this point.[15] The organic layer was separated and dried over sodium sulfate. Fractionation gave 2.6 g., 0.023 mole, of indene, b.p. 76° (30 mm.), n^{20}_D 1.5713, 23% yield. The residue, 13.4 g., had the appearance of a solid polymer.

(3) **Methylmagnesium Bromide.**—To methylmagnesium bromide 0.64 mole, was added 1-(methyldichlorosilyl)-indene, 33.7 g., 0.148 mole. The remainder of the procedure was identical with that of the reaction of methylmagnesium bromide and 1-(dimethylchlorosilyl)-indene. Fractionation gave 20.7 g., 0.110 mole, of 1-(trimethylsilyl)-indene, b.p. 78° (3 mm.), n^{20}_D 1.5422, d^{20}_4 0.9451, 74.3% yield.

(4) ***n*-Butanol and Pyridine.**—To a solution of 60 g., 0.76 mole, of *n*-butanol there was added 63 g., 0.273 mole, of 1-(methyldichlorosilyl)-indene. The reaction was accompanied by considerable heat evolution and the precipitation of pyridine hydrochloride. After the addition of xylene, 300 cc., the cool reaction mixture was filtered. Fractionation gave 44.5 g., 0.146 mole, of 1-methyldi-*n*-butoxysilyl)-indene (Compound IX), 53.5% yield.

Reactions of Hydrogen with Silylindene Compounds: In Ether Solvent.—A typical reduction in ether, selected from the group in Table IV, is given. A solution of 42 g., 0.138 mole, of 1-(methyldi-*n*-butoxysilyl)-indene in 300 cc. of anhydrous ether, containing 2 g. of Raney nickel was shaken under *ca.* 3 atmospheres of hydrogen pressure at 25°. After the theoretical pressure drop, the crude product was fractionally distilled to give 36.2 g., 0.118 mole, of 1-(methyldi-*n*-butoxysilyl)-indan (Compound XV), 85.8% yield.

In Ethanol Solvent.—A typical preparation from among those listed in Table IV is given below. A solution of 27.0 g., 0.110 mole, of 1-(dimethyl-*n*-butoxysilyl)-indene in 300 cc. of ethanol was reduced under 3 atmospheres hydrogen pressure at 25° with Raney nickel. After the theoretical pressure drop, the reaction mixture was filtered. Fractionation gave 22.3 g., 0.090 mole, of 1-(dimethyl-*n*-butoxysilyl)-indan (Compound XVI), 82% yield.

Table IV

Hydrogenation of Silylindenes

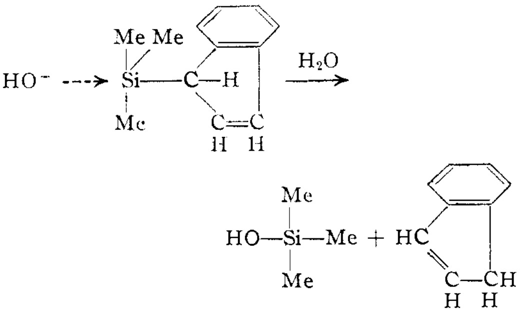
Compound	Method[a]	Silylindene Compound, mole	Time, hr.	Completion, %	Yield, %
XI	A	0.160	3.0	96	65[b]
	B	.150	5.5	102	61.9[b]
XII	A	.122	3.3	100	76.3[b]
	B	.147	9.5	100	43.5[b]
XIII	B	.084	24	104	24[b]
XIV	B	.061	14.5	89	49[b]
XV	A	.138	2.5	100	85.8
XVI	B	.110	5.0	111	82

[a] Method A employed ether as a solvent, method B employed ethanol as a solvent. [b] The crude material after hydrogenation was added to concentrated sulfuric acid to remove the silylindene compounds remaining and the organic layer then fractionated.

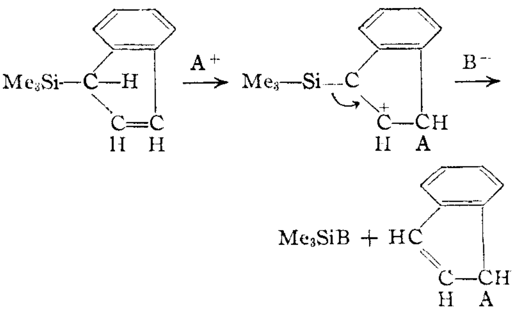
Reaction of 1-(Trimethylsilyl)-indan and Concentrated Sodium Hydroxide Solution.—A mixture of 11.0 g., 0.058 mole, of 1-(trimethylsilyl)-indan and 150 cc. of 20% sodium hydroxide was stirred and heated at 100° for 12 hours. The cool mixture was extracted with ether and the ethereal extracts dried over sodium sulfate. Fractionation gave 9.1 g., 0.048 mole of 1-(trimethylsilyl)-indan, b.p. (2 mm.), n^{20}_D 1.5208, 83% recovery.

Discussion

Allyltrimethylsilane[6] has been shown to undergo cleavage of the allyl to silicon bond by a variety of reagents such as bromine, concentrated sulfuric acid and potassium hydroxide in methanol solution. The mechanisms used in explaining the above cleavages by electrophilic and nucleophilic reagents may be applied to the rupture of the indenyl to silicon bond in silylindenes. The mode of attack by a nucleophilic reagent, sodium hydroxide, is illustrated by equation 4, and the mode of attack by an electrophilic reagent, bromine or sulfuric acid, is represented by equation 5.



(4)



(5)

State College, Penna. Received March 4, 1950

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[15] This procedure is that used in the preparation of diphenylsilanediol from diphenyldichlorosilane, *cf.* C. A. Burkhard, This Journal, **67**, 2173 (1945).