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Cyclic Organosilicon Compounds. I. Preparation of Cyclic Silanes

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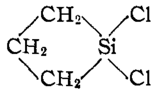
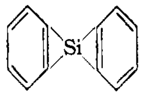
Twenty-one new cyclic compounds, containing silicon as the heterocyclic member in five-, six- and seven-membered rings have been prepared. The reaction of cyclopolymethylenedichlorosilanes with α,ω-polymethylenedilithium compounds has been shown to yield organosilicon spiranes. Attempts to prepare an aromatic-type ring compound containing silicon in the ring by catalytic hydrogenation have been unsuccessful.

The first report in the chemical literature of cyclic organosilicon compounds appeared as early as 1887, when Hart claimed to have prepared cyclotrimethylenedichlorosilane (I) and "o-diphenylenesilane" (IA), by sodium condensations from organic halides and silicon tetrachloride.[2]



I



IA

These compounds were only poorly characterized in his original paper. Widdowson, who carefully repeated Hart's work, was unable to isolate any traces of these organosilicon compounds. He concluded that Hart's compositions were mixtures and that compounds I and IA should be stricken from the literature.[3] The first authentic cyclic organosilicon compounds, therefore, were cyclopentamethylenedichlorosilane (IB) and its dimethyl (II) and diethyl derivatives, prepared by Bygden in 1915.[4,5] A patent on siloxane compositions derived from IB and similar intermediates has also been issued.[6]

Bygden introduced silicon into the six-membered ring by treating silicon tetrachloride with the Grignard reagent prepared from 1,5-dibromopentane. An improved modification of Bygden's method has been used in this investigation. Five-, six- and seven-membered silicon-containing rings were prepared from difunctional Grignard reagents of varying chain length; while the use of substituted chlorosilanes permitted the preparation of ring compounds with varying functionality at the silicon atom.

The yields of some of the compounds obtained in this way are given in Table I. Two generalizations can be drawn from the yield data: first, in each series the yield is highest for the six-membered ring, somewhat lower for the five-membered ring, and very much lower for the seven-membered ring. This result might be expected by analogy with many other well-known reactions involving ring closure. Second, the yield of cyclic product increases as the number of chlorine atoms on the silicon increases, in spite of the fact that the opportunity for polymer formation is greater when the functionality of the silicon is increased. The explanation may be that the additional chlorine atoms set up a stronger electrostatic field which facilitates the ring closure reaction.

TABLE I

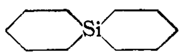
PER CENT. YIELDS OF CYCLIC SILANES

Grignard reagent	$SiCl_4$	CH_3SiCl_3	CH_3SiHCl_2
$BrMg(CH_2)_4MgBr$	51^a	47	40
$BrMg(CH_2)_5MgBr$	69^a	62^a	47
$BrMg(CH_2)_6MgBr$	11^a		4

[a] Average yield from several experiments.

Additional compounds were prepared by known synthesis methods from the cyclic silanes obtained by the Grignard reaction. The properties of all the cyclic compounds which were prepared are given in Table II. With the exception of IB and II, all are new compounds. All of the compounds are liquids at room temperature except cyclopentamethylenesilanediol (VIII). Structures were established by analysis and by the molar refraction data.[7] As an additional check on the assigned structures, several of the compounds were prepared by two or more routes, as indicated in the experimental section.

Although IB reacts only slowly with Grignard reagents, it is readily alkylated by the more reactive organolithium compounds. If alkyldilithium reagents[8] are used instead of the usual monofunctional lithium compounds, the product of the reaction is a spirane with silicon as the spiro atom.[9] Three such organosilicon spiranes have been prepared as the first members of a novel type of organosilicon compounds.[10] They are colorless oils with faint camphoraceous odors; their properties are summarized in Table III. Compared with typical organosilicon compounds, these spiranes have unusually high densities, refractive indices and melting and boiling points. These abnormal properties reach a maximum in bis-(cyclopentamethylene)-silane (XXIII). The boiling point of this compound, 227°, is about 45° higher than would be predicted judging from the boiling points of linear tetraalkylsilanes of comparable molecular weight. Cyclic compounds often boil at temperatures somewhat higher than the



XXIII

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[1] Department of Chemistry, Lehigh University, Bethlehem, Pa.

[2] W. B. Hart, *Rep. Brit. Assoc.*, 661 (1887).

[3] R. R. Widdowson, *J. Chem. Soc.*, 956 (1926).

[4] A. Bygden, *Ber.*, **48**, 1236 (1915).

[5] G. Gruttner and M. Wiernik, *ibid.*, **48**, 1474 (1915).

[6] J. M. Hersh, U. S. Patent 2,464,236 (March 15, 1944).

[7] R. O. Sauer, THIS JOURNAL, **68**, 954 (1946); E. L. Warrick, *ibid.*, **68**, 2455 (1946).

[8] R. West and E. G. Rochow, *J. Org. Chem.*, **18**, 1739 (1953).

[9] A preliminary note reporting the synthesis of such compounds has already appeared. See R. West and E. G. Rochow, *Naturwissenschaften*, **40**, 142 (1953).

[10] Spiro compounds based on siloxane bonds are known, however; see W. L. Roth and D. Harker, *Acta Cryst.*, **1**, 34 (1948).

TABLE II

PROPERTIES OF CYCLIC SILANES

Cpd. no.	Formula	B.p., °C.	$n^{25}D$	d^{25}_4	Analyses, % Carbon (or Cl) Calcd.	Carbon (or Cl) Found	Hydrogen Calcd.	Hydrogen Found	Mol. ref.[11] Calcd.	Mol. ref.[11] Found
IB[4]	$(CH_2)_5SiCl_2$	170	1.4679		41.9	41.3[a]				
II[4]	$(CH_2)_5Si(CH_3)_2$	133	1.4380	0.798	65.55	65.57	12.58	12.57	42.04	42.18
III	$(CH_2)_5Si(CH_3)Cl$	167	1.466	1.01	23.8	23.6[a]			41.67	40.9
IV	$(CH_2)_5SiH_2$	102	1.4533	0.818	59.93	60.31	12.08	12.23	33.30	33.13
V	$(CH_2)_5Si(CH_3)H$	118	1.4462	0.809	63.08	62.87	12.35	12.52	37.67	37.67
VI	$(CH_2)_5Si(H)Cl$	143	1.467	1.018	26.3	26.2[a]			37.30	36.70
VII	$(CH_2)_5Si(OCH_3)_2$	171	1.4309	0.958	52.45	52.67	10.06	10.02	43.56	43.31
VIII	$(CH_2)_5Si(OH)_2$				45.41	45.56	9.15	9.23		
IX	$[(CH_2)_5SiCH_3]_2O$	253	1.4640	0.927	59.45	59.42	10.79	10.65	72.44	72.15
X	$(CH_2)_4SiCl_2$	143	1.463	1.173	45.7	45.8[a]			36.67	36.40
XI	$(CH_2)_4Si(CH_3)_2$	107	1.4335	0.780	63.07	63.24	12.35	12.46	37.41	37.70
XII	$(CH_2)_4SiH_2$	71	1.444	0.80	55.72	56.10	11.69	11.74	28.67	28.6
XIII	$(CH_2)_4Si(CH_3)Cl$	132	1.453	0.981[c]	26.3	26.3[a]			37.0	36.8[c]
XIV	$(CH_2)_4Si(CH_3)H$	91.5	1.4390	0.798	59.91	59.76	12.07	12.06	33.04	33.04
XV	$(CH_2)_4Si(OCH_3)_2$	148.5	1.433	0.960	49.27	49.27	9.65	9.83	38.93	38.82
XVI	$[(CH_2)_4SiCH_3]_2O$	221	1.457	0.933	56.00	56.24	10.34	10.30	63.18	62.60
XVII	$(CH_2)_6SiCl_2$	201	1.452	1.065	38.7	38.6[a]			45.93	46.17
XVIII	$(CH_2)_6Si(CH_3)_2$	161	1.4335	0.780	67.51	67.66	12.75	12.79	46.67	47.45
XIX	$(CH_2)_6SiH_2$	135	1.459[d]	0.80[d]	63.06	63.9	12.35	11.92		
XX	$(CH_2)_6Si(CH_3)H$	144	1.423[d]		65.53	64.4	12.57	12.7		

[a] % Cl. [b] M.p. 130–132°. [c] d^{30}_4; mol. ref. found using estimated d^{25}_4 0.99. [d] Compound not obtained pure.

TABLE III

PROPERTIES OF ORGANOSILICON SPIRANES, $(CH_2)_nSi(CH_2)_m$

No.	n	m	B.p., °C.	M.p., °C.	$n^{25}D$	d^{25}_4	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found	Mol. ref.[11] Calcd.	Mol. ref.[11] Found
XXI	4	4	178.5	<-70	1.4860	0.899	68.48	68.3	11.50	11.2	44.54	44.80
XXII	4	5	203	-35	1.4860	0.899	70.06	70.2	11.57	11.8	49.17	49.27
XXIII	5	5	227	-18	1.4869	0.900	71.35	71.3	11.98	12.0	53.80	53.77

boiling points of their straight-chain analogs, but the effect is particularly large in this case. From this and from the other abnormal properties mentioned above it can be inferred that the organosilicon spiranes are considerably more associated in the condensed phases than are most alkylsilanes.

Attempts were made to prepare cyclic trienes by catalytic dehydrogenation of cyclopentamethylenesilane (IV) and cyclopentamethylenemethylsilane (V). The desired products would contain silicon–carbon double bonds, presumably stabilized by aromatic resonance; but no such compounds could be isolated. IV and V passed unchanged over platinum and palladium catalysts at temperatures up to about 500°. Above this temperature, some thermal cracking to hydrogen and mixed olefins took place. Over a chromia–alumina dehydrogenation catalyst,[12] both compounds were rapidly oxidized to siloxanes.

Experimental

Materials.—Silicon tetrachloride was obtained from the Stauffer Chemical Co., and trichlorosilane from the Anderson Chemical Co. The dichlorosilane was a gift of the Linde Air Products Co., while methyltrichlorosilane and methyldichlorosilane were donated by the General Electric Co. The organic reagents were all Eastman organic chemicals with the exception of 1,6-dibromohexane which was obtained from the Halogen Chemical Co.

Cyclopentamethylenedichlorosilane (I).—A Grignard reagent was prepared by adding 92 g. (0.40 mole) of 1,5-dibromopentane dissolved in 400 ml. of anhydrous ethyl ether to 22 g. (0.9 mole) of magnesium turnings. The resulting solution was transferred under a nitrogen atmosphere to a 600-ml. dropping funnel. The dropping funnel was then attached to one neck of a 2-l. three-necked flask which was also equipped with a reflux condenser and a Hershberg-type wire-wound stirrer. Both the reflux condenser and the dropping funnel were protected from the atmosphere by calcium chloride–soda lime tubes.

In the flask was placed 1 liter of anhydrous ether and 61 g. (0.36 mole) of silicon tetrachloride. Vigorous stirring was started and the (two-phased) Grignard reagent was added dropwise, causing refluxing of the ether and precipitation of magnesium halides. The yield does not appear to be dependent on the time taken for addition, which in different runs varied from 30 minutes to two hours. After completion of the addition the mixture was stirred for 30 minutes and then refluxed on the steam-bath for at least four hours.

The reaction mixture was then cooled and transferred to a nitrogen-filled dry-box. The precipitated magnesium salts were filtered from the ethereal solution containing the product on a büchner funnel, with the use of suction. The salts were washed well with ether and pressed dry. The ether was next distilled from the combined filtrate and washings in glass apparatus protected from atmospheric moisture. Heating on a steam-bath was continued until the distillation of ether became slow. The resulting sludge of ether, magnesium salts and higher-boiling products was diluted with twice its volume of petroleum ether (30–60°). The mixture was then again filtered with suction, and the magnesium salts were washed well with petroleum ether. The filtrate and washings were fractionally distilled through a column having an efficiency of about 12 theoretical plates. At 169–171°, I distilled as a colorless oil. Yields obtained in six such runs averaged 70%, while the yield reported by Bygden[4] was 49%.

This method was used with suitable variation of the dibromoalkane and chlorosilane reactants to prepare many other cyclic silanes (Tables I and II). Compounds not included in Table I but prepared by this method include IV (36% yield) and VI (59%).

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(11) Molecular refractions were calculated by the method of E. L. Warrick, THIS JOURNAL, **68**, 2445 (1946).

(12) M. Orchin, L. Reggel and R. A. Friedel, *ibid.*, **74**, 1094 (1952).

Cyclopentamethylenedimethylsilane (II).—A Grignard reagent was prepared from 28.5 g. (0.20 mole) of methyl iodide and the required quantity of magnesium in 150 ml. of ethyl ether. A solution of 14.8 g. (0.10 mole) of cyclopentamethylenemethylchlorosilane (III) in 50 ml. of ether was then added. The mixture was refluxed for 20 hours, then cooled and decomposed with ice and dilute HCl. The organic layer was separated, washed with water, and dried over calcium chloride. Fractional distillation of the solution gave 9.2 g. (72%) of stable colorless product boiling at 131–135°.

II can also be prepared, in lower yield, by similar Grignard methylation of I. The analogous five- and seven-membered rings (XI and XVIII) were also obtained by this method from the corresponding dihalides.

Cyclopentamethylenesilane (IV).—To a solution of 4 g. (0.1 mole) of lithium aluminum hydride in 150 ml. of anhydrous ethyl ether was added 30 g. (0.175 mole) of I, also dissolved in 100 ml. of ether. The mixture was refluxed for three hours. Ethyl acetate, followed by ethanol and water, were then added cautiously in order to decompose excess $LiAlH_4$. The ether layer was separated, washed well with water, dried and fractionally distilled. At 101–102°, 5.5 g. (31%) of IV was collected.

As noted above, IV also can be prepared by the ring-closure reaction using dichlorosilane. The analogous seven-membered ring, XIX, was prepared from XVII and $LiAlH_4$ by the above method in 27% yield.

Cyclopentamethylenemethylsilane (V).—This compound was prepared in three different ways: by $LiAlH_4$ reduction of III, by Grignard methylation of VI, and by the ring-closure reaction between pentamethylene Grignard reagent and methyldichlorosilane. The method of choice is the last of these since it gives the highest over-all yield (47%). Using appropriate Grignard reagents, the same method was utilized to prepare XIV and XX (Table I), although XX could not be obtained pure.

Cyclotetramethylenesilane (XII).—A solution of 5.0 g. (0.12 mole) of $LiAlH_4$ was made up in 100 ml. of di-*n*-propyl ether, and to this was added a solution of 23.0 g. (0.15 mole) of cyclotetramethylenedichlorosilane (X) in 50 ml. of the same solvent. The resulting mixture was refluxed for two hours, then transferred directly to a Todd Precision Fractionation Apparatus (50-plate column). The fractions boiling at 69–78° were combined and refractionated to give 6.0 g. (47%) of XII, boiling at 70–72°.

Cyclopentamethylenedimethoxysilane (VII).—Sodium (9.2 g., 0.40 mole) was dissolved in 200 ml. of methanol. Over a period of 90 minutes, 32 g. (0.19 mole) of I was added, followed by 30 ml. of ethyl ether. The mixture was then refluxed for an hour. After removal of the precipitated NaCl by vacuum filtration, the solution was fractionally distilled to give 21.6 g. (71%) of VII, a colorless oil with an irritating camphor-like odor, boiling at 171–173°. A similar method was used to prepare XV.

Cyclopentamethylenesilanediol (VIII).—The method used followed that described by Sommer.[13] A solution of 12 g. (0.71 mole) of I in 220 ml. of anhydrous ether was precooled to 0°, and then added over five minutes to a vigorously stirred solution of 5.7 g. (0.142 mole) of NaOH in 100 ml. of water, maintained at 0 to −5°. The ether layer was separated and the aqueous layer was extracted once with 100 ml. of ether. The combined ethereal extracts were first dried over K_2CO_3 and then concentrated to 75 ml. below room temperature. The addition of 300 ml. of petroleum ether (30–60°) then caused the crude silanediol to precipitate as glistening micaceous plates. The crude yield was 6.3 g. (67%), but this was reduced to 35% in the course of two recrystallizations, one from warm chloroform and one from ether–petroleum ether. The crude product dehydrates to siloxane polymers in a few hours if not recrystallized, but after recrystallization it is stable for months. Some decomposition also takes place during recrystallization, which must accordingly be done rapidly and at the lowest practicable temperature.

Attempts to Prepare Cyclotetramethylenesilanediol.—Careful hydrolysis of X, under the conditions described above, led only to oily siloxane polymers. Polymeric material was also obtained when cyclotetramethylenedimethoxysilane (XV) was hydrolyzed with boiling water[14] and usually when it was hydrolyzed with water at room temperature[15] following procedures which are successful for the preparation of the unstable compound dimethylsilanediol. A small amount of impure crystalline material was obtained when XV was hydrolyzed with distilled water at room temperature in quartz apparatus.

Bis-(cyclopentamethylenemethyl)-disiloxane (IX).—A solution of 20 g. (0.134 mole) of III in 200 ml. of anhydrous ether, cooled to 0°, was treated with 1 *M* NaOH added dropwise until the mixture was alkaline.[16] The ether layer was separated and dried over K_2CO_3. Crude cyclopentamethylenemethylsilanol was left behind when the ether was evaporated. This silanol decomposed when heated above 150° and so could not be distilled. The water resulting from the decomposition was then distilled out and the disiloxane formed in the condensation reaction then distilled at 248–258°. The yield was 13 g. (81%).

Bis-(cyclotetramethylenemethyl)-disiloxane (XVI).—The five-membered ring XIII was hydrolyzed with NaOH under the conditions described above for III. Cyclotetramethylenemethylsilanol was probably present in the resulting ethereal solution, but this silanol was dehydrated to the disiloxane (XV) as the ether was evaporated at room temperature. The oily residue was separated and distilled to give a 71% yield of XV.

Bis-(cyclopentamethylene)-silane (XXIII).—An organolithium reagent was prepared by the dropwise addition of 34.5 g. (0.15 mole) of 1,5-dibromopentane diluted with ether to 5 g. (0.7 mole) of lithium shot in 200 ml. of ether.[2] The reaction was carried out at −25° under an atmosphere of nitrogen, with vigorous stirring.[17] After the addition was completed, the mixture was warmed to 0° over a period of an hour, and then filtered under nitrogen pressure through glass wool into a dropping funnel. To form the spirane, the organolithium solution was then added dropwise to a stirred solution of 20.5 g. (0.12 mole) of I in 800 ml. of ether. After refluxing the mixture for several hours to complete the reaction, water was added to remove lithium salts, and the ether layer was separated and dried over $CaCl_2$. Fractional distillation of the dried ether solution gave 11 g. (54%) of XXIII boiling at 226–228°.

The two other spiranes (XXI and XXII, Table III) were prepared by the reaction of X and I, respectively, with the dilithium compound derived from 1,4-dibromobutane, under the conditions described above. The yield of XXI was 52% and that of XXII was 60%. The symmetrical spirane XXIII was also prepared in one step from 1,5-dibromopentane and silicon tetrachloride, also under conditions similar to those given above. The yield in the one-step preparation was much smaller (22%).

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(13) P. D. George, L. H. Sommer and F. C. Whitmore, THIS JOURNAL, **75**, 1585 (1953).

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