were studied by Steward and Rooksby[3] who state that the magnesium compound is slightly distorted from the cubic structure. We found no evidence to suggest that the nickel compound was distorted, perhaps because of the limits of resolution of our cameras. The Goldschmidt tolerance factor $t = (R_A + R_0)/\sqrt{2}(R_B + R_0)$, however, is 0.94 for the nickel and the magnesium compounds (using the observed ionic radii listed by Wyckoff.[6] On this ground the expected structure would be cubic. It is interesting to note that for the $Sr_xBa_{1-x}(Zn_{1/2}W_{1/2})O_3$ phase, using a weighted average of Sr^{+2} and Ba^{+2} radii for the A cation radius, the tolerance factor falls to 0.89 at $x = 0.4$. This represents the highest concentration of strontium for which a cubic structure was found experimentally.

Since the cubic structure can be described in terms of closest packing of oxide ions and A cations, it seems reasonable to attribute the tetragonal distortions to the unfavorable packing of the small strontium ions. The slight difference in magnetic susceptibility of the cubic and tetragonal nickel compounds indicates no difference in bonding in the two crystals. This conclusion is compatible with the supposition that the symmetry is determined by ionic packing.

STORRS, CONN.

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[6] R. W. G. Wyckoff, "Crystal Structures," Interscience Publishers, New York, N. Y., 1948, Section I.

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, DREXEL INSTITUTE OF TECHNOLOGY]

Cyclohexylhalosilanes. Reaction of Cyclohexylsilane with Silver Isocyanate and Isothiocyanate[1]

BY HERBERT H. ANDERSON

RECEIVED MARCH 25, 1959

This paper establishes the direct, partial replacement of hydrogen by halogenoid in certain alkylsilanes, with yields of 41-44%. In a new modification, gradual addition of AgX to excess cyclo-$C_6H_{11}SiH_3$ furnishes cyclo-$C_6H_{11}SiH_2X$ and some cyclo-$C_6H_{11}SiX_3$; X is the halogenoid NCO or NCS. Oxidation of excess cyclo-$C_6H_{11}SiH_3$ with $HgSO_4$ or HNO_3 furnishes polymeric (cyclo-$C_6H_{11}SiO)_2O$ rather than (cyclo-$C_6H_{11}SiH_2)_2O$. Three reactions of (cyclo-$C_6H_{11}SiH_2)_2O$ follow: with warm, concentrated hydrofluoric acid to give impure cyclo-$C_6H_{11}SiH_2F$ and some hydrogen; with hot gaseous HCl and P_4O_{10} to give a 25% yield of pure cyclo-$C_6H_{11}SiH_2Cl$; with a deficiency of warm iodine to give gaseous HI, cyclo-$C_6H_{11}SiH_2I$ and a viscous liquid probably (cyclo-$C_6H_{11}SiHO)_{3\text{ or }4}$. Shaking cyclo-$C_6H_{11}SiCl_3$ with excess aqueous hydrofluoric acid furnishes cyclo-$C_6H_{11}SiF_3$ easily. Table I lists the properties of 11 new compounds containing the cyclo-C_6H_{11}-Si linkage.

Introduction

Four earlier papers establish the use of halides of certain transitional elements and elements in regular groups for the replacement of hydrogen attached to tin[2a] in $(C_2H_5)_3SnH$, to germanium[2b] in $(C_2H_5)_3GeH$ or to silicon first[3] in $(C_2H_5)_3SiH$ and later[4] in n-$C_7H_{15}SiH_3$. Gradual addition of $HgCl_2$ or $HgBr_2$ to an excess of $(C_2H_5)_2SiH_2$ or n-$C_7H_{15}SiH_3$ allows straightforward preparation of $(C_2H_5)_2SiHCl$, $(C_2H_5)_2SiHBr$, n-$C_7H_{15}SiH_2Cl$ and n-$C_7H_{15}SiH_2Br$, respectively[3,4]; this is apparently a new modification for the preparation of organosilicon compounds containing both Si-H and Si-Cl or Si-Br. In these papers the two main explanations for the reaction of $(C_2H_5)_3SnH$, $(C_2H_5)_3GeH$ or $(C_2H_5)_3SiH$ with a given halide depend on heats of formation per equivalent of available halogen in the compounds and on the appropriate ionization potentials of the elements.

This paper, in turn, reports the reaction of cyclo-$C_6H_{11}SiH_3$ with AgNCO or AgNCS to give moderate yields of cyclo-$C_6H_{11}SiH_2NCO$ or cyclo-$C_6H_{11}SiH_2NCS$, respectively, together with some cyclo-$C_6H_{11}Si(NCO)_3$ or cyclo-$C_6H_{11}Si(NCS)_3$; this is apparently a new modification. This paper also studies the separate reactions of (cyclo-$C_6H_{11}SiH_2)_2O$ with aqueous HF, anhydrous HCl and iodine. Table I lists the properties of 11 new compounds—and also cyclohexylbromosilane, previously mentioned without data.[5]

Experimental Results

Table I lists the conditions of distillation, the boiling points, densities, refractive indices, molar refractions and the analyses of 11 new compounds and cyclohexylbromosilane. There is one complete series: $RSiH_3$, $RSiH_2I$, $RSiHI_2$ and $RSiI_3$. Table I lists cyclo-$C_6H_{11}SiH_2NCO$ and cyclo-$C_6H_{11}SiH_2NCS$, both prepared from cyclo-$C_6H_{11}SiH_3$ and AgNCO or AgNCS, respectively. Shaking cyclo-$C_6H_{11}SiCl_3$ with excess aqueous hydrofluoric acid yields cyclo-$C_6H_{11}SiF_3$ easily.

Experimental

Equipment for all reactions employed ground joints throughout. There were also micro-pycnometers, micropipets for the measurement of liquids and the subsequent titration of available acidity, transfer pipets and special equipment for determining H present as Si-H.

Cyclohexylsilane.—Although cyclohexylsilane is available in 38% yield through reaction[6] of cyclo-$C_6H_{11}MgCl$ with SiH_3Br, the preparation was via $LiAlH_4$[7] and commercial cyclo-$C_6H_{11}SiCl_3$. After dissolving 21 g. of $LiAlH_4$[7] in 300 ml. of diethyl ether, there followed addition of 122 g. of cyclo-

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[1] Presented at 136th National Meeting of the A. C. S., Atlantic City, N. J., September, 1959.

[2] (a) H. H. Anderson, THIS JOURNAL, **79**, 4913 (1957); (b) **79**, 326 (1957).

[3] H. H. Anderson, *ibid.*, **80**, 5083 (1958).

[4] H. H. Anderson and A. Hendifar, *ibid.*, **81**, 1027 (1959).

[5] W. S. Miller and others, *ibid.*, **79**, 5605 (1957).

[6] H. E. Opitz and others, *ibid.*, **78**, 293 (1956).

[7] A. E. Finholt and others, *ibid.*, **69**, 2692 (1947).

TABLE I

PROPERTIES OF NEW CYCLOHEXYLSILANE DERIVATIVES (EXCEPT 4TH)

Compound[a]	B.p.,[b] °C.	d^{20}_4	n^{20}[c]	Mol. refr. Calcd.	Mol. refr. Found	Silicon Calcd.	Silicon Found	Halogen(oid) Calcd.	Halogen(oid) Found	Distilled at °C.	Mm.
$C_6H_{11}SiF_3$	105.3	1.113	1.3717	34.36	34.33	16.70	...	33.9	33.6[d]	106.2–106.4	762
$C_6H_{11}SiH_2F$	118.1	0.925	1.4207	36.80	36.24	21.24	...	14.4	14.8[e]	118.5–119.0	777
$C_6H_{11}SiH_2Cl$	158.0	0.980	1.4655	41.96	42.00	18.89	18.7	23.8	23.8	96–97	90
$C_6H_{11}SiH_2Br$[f]	182.0	1.243	1.4932	44.93	45.17	14.55	14.3	41.4	41.3	88.5–89.0	32
$C_6H_{11}SiH_2I$	210	1.494	1.5370	50.67	50.21	11.69	11.8	52.8	52.5	101–102	21
$C_6H_{11}SiHI_2$	270	1.979	1.6047	63.32	63.68	7.67	7.79	69.3	69.1	126–127	6
$C_6H_{11}SiI_3$	337	2.437	1.6775	75.97	76.07	5.71	5.73	77.4	77.2	170–171	1
$C_6H_{11}SiH_2NCO$	163.7	0.990	1.4668	44.09	43.50	18.09	17.9	27.1	26.9[g]	82–83	29
$C_6H_{11}Si(NCO)_3$	253	1.208	1.4787	56.23	55.65	11.84	12.1	53.1	..[h]	109–110	1
$C_6H_{11}SiH_2NCS$	231	1.018	1.5336	52.38	52.28	16.40	16.4	33.9	33.8[i]	91.0–91.8	1
$C_6H_{11}Si(NCS)_3$	348	1.231	1.6179	81.10	81.22	9.84	9.92	61.1	60.8	172–173	1
$(C_6H_{11}SiH_2)_2O$	273	0.928	1.4730	73.30	73.31	23.17	23.2	..	..[j]	115–116	1

[a] All compounds are colorless. [b] Boiling points under 760 mm. pressure. [c] In white light. [d] Calcd.: mol. wt., 168.2. Found: mol. wt., 173. [e] Calcd.: mol. wt., 132.3. Found: mol. wt., 135. [f] Reported in reference 5 without data. [g] Titration within one minute with very fast mixing. Calcd.: H as Si–H, 1.30. Found: H as Si–H, 1.32. [h] Calcd.: mol. wt., 237.2. Found: mol. wt., 252. [i] Calcd.: H as Si–H, 1.18. Found: H as Si–H, 1.16. [j] Calcd.: H as Si–H, 1.66; mol. wt., 242.5. Found: H as Si–H, 1.62; mol. wt., 246.

$C_6H_{11}SiCl_3$ with reflux for 90 minutes. Then passage of 0.6 mole of dry HCl gas through the solution swept most of the ether away, maintaining an acidic condition. Washing with water and extraction with a little ether furnished 40 g. of cyclo-$C_6H_{11}SiH_3$ (a 63% yield), only 2.8 g. of (cyclo-$C_6H_{11}SiH_2)_2O$ and 4.7 g. of higher-boiling alkylsiloxanes. *Measurements furnished the following data for the known* cyclo-$C_6H_{11}SiH_3$: b.p. 119.0°, n^{20} 1.4495, d^{20}_4 0.805 and *MR* 38.08, all in reasonable agreement with published data.[6] Redistilled material served for all reactions of cyclohexylsilane herein.

Cyclohexylchlorosilane and Cyclohexylbromosilane.—Metallic mercury and gaseous HCl or HBr formed during one hour of gentle reflux, with electrical heating, of 4.82 g. of cyclo-$C_6H_{11}SiH_3$ with 9.0 g. of $HgCl_2$ or 10.0 g. of $HgBr_2$, each added in four lots. A preliminary distillation under 100 mm. pressure left the metallic mercury behind; fractional distillations showed the presence of 5.01 g. of cyclo-$C_6H_{11}SiH_2Cl$ or of 6.24 g. of cyclo-$C_6H_{11}SiH_2Br$, center fractions of which had the properties in Table I. Yields were approximately 79% based on silicon (the basis used in this paper). In the processing of crude cyclo-$C_6H_{11}SiH_2Br$ there were some occasional slight flashes when warm air mixed with the compound.

Cyclohexyliodosilanes.—Slow addition of 84 g. of iodine over a period of 4 hours of gentle reflux to 22.4 g. of cyclo-$C_6H_{11}SiH_3$, and later fractional distillation gave 12 g. of cyclo-$C_6H_{11}SiH_2I$, 36 g. of cyclo-$C_6H_{11}SiHI_2$ and 16 g. of cyclo-$C_6H_{11}SiI_3$. Similarly, 11.3 g. of cyclo-$C_6H_{11}SiH_3$ and 74 g. of iodine furnished 36 g. of purer cyclo-$C_6H_{11}SiI_3$. Fractional distillations with a little copper wire present gave center fractions with the properties listed in Table I.

Cyclohexylfluorosilane.—Heating 5.57 g. of cyclo-C_6H_{11}-SiH_2Br with 1.48 g. of powdered, freshly sublimedS bF_3 gave 2.96 g. of crude cyclo-$C_6H_{11}SiH_2F$, a yield of 80%; some *metallic antimony formed. Distillation from* KF *and then* fractional distillation gave 0.70 g. of low, then 1.60 g. of center-fraction cyclohexylfluorosilane listed in Table I; this compound had a very penetrating odor. In contrast, the 10-minute reaction at 60° of (cyclo-$C_6H_{11}SiH_2)_2O$ with double the volume of 48% HF gave some hydrogen and an impure cyclo-$C_6H_{11}SiH_2F$ with 17.5% F, d^{20}_4 0.948 and b.p. 1116.5°.

Cyclohexyltrifluorosilane.—Heating 19.5 g. of cyclo-$C_6H_{11}SiI_3$ with 9.8 g. of sublimed SbF_3 gave 6.3 g. of cyclo-$C_6H_{11}SiF_3$, a yield of 94%. Distillation from KF and copper wire followed; then fractional distillation gave a 2.4-g. center fraction listed in Table I. Cyclohexyltrifluorosilane has a penetrating and sharp odor. A shorter method consisted of shaking 4.8 g. of cyclo-$C_6H_{11}SiCl_3$ with 4.7 g. of 48% HF for 30 minutes at 65°, followed by cooling and extracting with 10 ml. of ether; 2.6 g. of cyclo-$C_6H_{11}SiF_3$ (70% yield) resulted, with b.p. 105.5° and n^{20} 1.3708.

***sym*-Bis-(cyclohexyl)-disiloxane.**—Shaking exactly 7 g. of cyclo-$C_6H_{11}SiH_2Br$ with 3 successive 6-ml. portions of water, separation of layers and drying over Na_2SO_4 and washing with a little CCl_4, and then distillation gave 3.30 g. of (cyclo-$C_6H_{11}SiH_2)_2O$ (85% yield), with n^{20} 1.4732 and d^{20}_4 0.926. This checks data in Table I obtained from (cyclo-C_6H_{11}-$SiH_2)_2O$ present as a contaminant of the original preparations of cyclohexylsilane. *sym*-Bis-(cyclohexyl)-disiloxane is a fairly mobile liquid with a slight, reasonably pleasant odor. This compound reacted violently with $HgSO_4$ in reflux; an equimolar 1.5-hr. reaction with gradually added $HgCl_2$ in reflux gave material of b.p. 155–220° containing at least cyclohexylchlorosilane and cyclohexyltrichlorosilane. Gradual addition of 0.95 g. of iodine to 0.92 g. of (cyclo-$C_6H_{11}SiH_2)_2O$ gave escaping HI gas, 0.53 g. of cyclo-C_6H_{11}-SiH_2I and a high-boiling residue perhaps (cyclo-$C_6H_{11}SiHO)_3$ on. Heating 4 g. of (cyclo-$C_6H_{11}SiH_2)_2O$ with HCl gas and a little P_4O_{10} gave 1.3 g. of cyclo-$C_6H_{11}SiH_2Cl$, b.p. 157° and n^{20} 1.4662; mechanical limitations cut the yield to 25%.

Cyclohexylisothiocyanatosilane and Cyclohexyltriisothiocyanatosilane.—Gradual addition of 5.6 g. of AgNCS in one hour to 9.67 g. of cyclohexylsilane in 15 ml. of CCl_4 at 35° and then 20 minutes of reflux, followed by filtration gave a solution containing 5.88 g. of cyclo-$C_6H_{11}SiH_2NCS$ (41% yield) and 3.6 g. of essentially pure cyclo-$C_6H_{11}Si(NCS)_3$. Redistillation gave center-fraction cyclo-$C_6H_1SiH_2NCS$ listed in Table I; the liquid tended to foam in distillation. One hour of reflux of 6.10 g. of cyclo-$C_6H_{11}SiCl_3$ in 10 ml. of CCl_4 and 18.5 g. of AgN CS, added in one lot, gave 7.30 g. of cyclo-$C_6H_{11}Si(NCS)_3$, a yield of 91%. Redistillation gave the center fraction listed in Table I; this cyclo-$C_6H_{11}Si$-$(NCS)_3$ was a liquid of high viscosity and little odor.

Cyclohexyl(iso)cyanatosilane and Cyclohexyltri(iso)cyanatosilane.—Gradual addition of 7.4 g. of AgNCO in one hour, with some cooling, to 8.24 g. of cyclohexylsilane in 4 ml. of CCl_4 and then 30 minutes of reflux, followed by filtration and washing of silver salts, and finally fractional distillation gave 5.00 g. of cyclo-$C_6H_{11}SiH_2NCO$ (44% yield) and 6. g. of higher-boiling residues. Two successive fractional distillations gave a final 1.7-g. center fraction of cyclo-$C_6H_{11}SiH_2NCO$ with the properties in Table I; the compound has a fairly penetrating odor and foams badly in reflux. Repeated fractional distillations of the 6 g. residue gave no pure compounds such as cyclo-$C_6H_{11}SiH(NCO)_2$, but some of the compound may have been present. Reflux of 7.35 g. of cyclo-$C_6H_{11}SiCl_3$ and 18.5 g. of AgNCO in 12 ml. of CCl_4 for one hour gave 7.0 g. of cyclo-$C_6H_{11}Si(NCO)_3$ (90% yield), the center fraction of which had the properties in Table I.

Other Reactions of Cyclohexylsilane.—Only polymeric (cyclo-$C_6H_{11}SiO)_2O$ resulted in the reaction of 0.80 g. of cyclohexylsilane with 0.90 g. of $HgSO_4$ or 0.70 g. of 15 *M* HNO_3, each added very gradually with cooling; no (cyclo-$C_6H_{11}SiH_2)_2O$ formed. Cyclohexylsilane and a slight deficiency of AgCl gave an 80% yield of cyclo-$C_6H_{11}SiH_2Cl$, while $PdCl_2$ gave a very low yield of cyclo-$C_6H_{11}SiH_2Cl$.

Discussion

Preparative Methods.—In a new modification, gradual addition of AgNCO or AgNCS to excess cyclo-$C_6H_{11}SiH_3$ furnishes cyclo-$C_6H_{11}SiH_2NCO$ and some cyclo-$C_6H_{11}Si(NCO)_3$, or cyclo-$C_6H_{11}SiH_2NCS$ and some cyclo-$C_6H_{11}Si(NCS)_3$, respectively. This partial reaction corresponds to the partial reaction with $HgCl_2$ or AgCl to obtain cyclo-$C_6H_{11}SiH_2Cl$. In these halogenoids of silicon there is evidence for an isothiocyanate structure[8] but the oxygen analog could be either an isocyanate or a cyanate.

Both cyclohexylfluorosilanes hydrolyze very slowly in pure water at 20°, while the other halides hydrolyze readily. Thus shaking of warm, concentrated HF with cyclo-$C_6H_{11}SiCl_3$ gives cyclo-$C_6H_{11}SiF_3$ easily in one step. A two-step method is more typical of earlier syntheses[9] $R_2SiCl_2 + 2R'OH = R_2Si(OR')_2 + 2HCl$ and then $R_2Si(OR')_2 + 2HF = R_2SiF_2 + 2R'OH$, although they also list $R_3SiCl + HF = R_3SiF + HCl$.

Preparation of cyclohexylsilane from cyclo-$C_6H_{11}SiCl_3$ and $LiAlH_4$ in ether appears more convenient than the successive preparations of SiH_4, then of SiH_3Br and finally of cyclo-$C_6H_{11}SiH_3$.[6]

Molar Refractions and Bond Refractions.—Excluding the value for less-pure cyclo-$C_6H_{11}SiH_2F$, Table I lists calculated molar refractions with an average error of 0.48%. These calculations include Vogel's values for C–H, C–C, Si–C, Si–Cl, Si–Br, Si–O and Si–H and for[10] Si–N, C=N and C=O. They include 1.95 for the Si–F bond refraction[4] and 17.53 for Si–NCS.[3]

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[8] H. H. Anderson, THIS JOURNAL, **69**, 3049 (1947).

[9] N. S. Marans and others, *ibid.*, **73**, 5127 (1951).

[10] A. I. Vogel and others, *J. Phys. Chem.*, **58**, 174 (1954); *J. Chem. Soc.*, 531 (1952).

PHILADELPHIA 4, PA.

[CONTRIBUTION FROM THE RESEARCH LABORATORY, OLIN MATHIESON CHEMICAL CORPORATION]

The Nature of Boron Hydride Solids[1]

BY I. SHAPIRO[2] AND ROBERT E. WILLIAMS

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The reaction of diborane and decaborane in the liquid phase results in the formation of non-volatile yellow solids; no intermediate boron hydride compounds could be detected by mass spectrometry. The ratio of hydrogen evolved to diborane consumed is four. By application of the isotopic boron technique the molar ratio of reactants has been found to be unity. Infrared analysis indicates loss of bridge hydrogens; diborane is pictured as completing the icosahedron structure of decaborane followed by polymerization and rearrangement. The solid loses about one-half of its hydrogen as a function of temperature up to 180–200°; much higher temperatures are required to remove the remainder of the hydrogen. Hydrolysis of the solid yields trace amounts of tetraborane and hexaborane.

From the classical works of Alfred Stock and his collaborators to present-day studies, the literature on boron hydrides is sprinkled with remarks about the formation of "yellow solids," but apparently no concerted effort to study these solids has been reported. One reason, of course, is the difficulty of obtaining a truly reproducible sample. The pyrolysis of diborane produces a number of volatile boron hydride products in addition to yellow solids.[3,4] Yellow solids also are formed from the decomposition of the unstable higher boron hydrides. The color of such solids has been ascribed as "light yellow," "dark yellow," "light brown," "dark brown" or even "black," depending upon the previous history of the solids. Stock[3] has reported that the average ratio of boron to hydrogen in the (unheated) yellow solids is approximately unity, and the formula $(BH)_x$ is commonly used.

From the structure of the various boron hydrides it was conceivable that the diborane molecule might complete the icosahedron structure of the decaborane molecule. Decaborane heated alone to 100°, *i.e.*, just above its melting point, is stable, and the rate of disappearance of diborane (alone) at this temperature is comparatively slow. However, when diborane is heated in the presence of liquid decaborane, the rate of disappearance of diborane is greatly accelerated; a liquid phase reaction takes place. A solid product, soluble in decaborane, remains after the decaborane is sublimed from the reactor. That the product is not formed by pyrolysis of the diborane alone is shown by the fact that no intermediate boron hydride products are detected in the mass spectrum; hydrogen is the only gaseous product. Although the non-volatile solid is colored yellow when prepared under normal conditions, the color approaches white under mild thermal conditions, *i.e.*, short reaction time at 100°.

Since this method for forming the yellow solid appeared to be reproducible, a detailed study was undertaken in order to gain an insight of the nature of the solid.

Experimental

Materials: Diborane.—Isotopically labeled diboranes were prepared in the conventional manner[5] and stored in the vapor phase at room temperature. The diborane was frac-

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[1] Presented at the 132nd Meeting of the American Chemical Society, New York, September, 1957.

[2] Hughes Tool Company, Aircraft Division, Culver City, California.

[3] A. Stock and W. Mathing, *Ber.*, **69**, 1469 (1936).

[4] A. B. Burg and H. I. Schlesinger, THIS JOURNAL, **55**, 4009 (1933).

[5] I. Shapiro, H. G. Weiss, M. Schmich, S. Skolnik and G. B. L. Smith, *ibid.*, **74**, 901 (1952).