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n-Heptylhalosilanes and n-Heptylsilane

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Lithium aluminum hydride and n-$C_7H_{15}SiCl_3$ in diethyl ether yield n-$C_7H_{15}SiH_3$, b.p. 140.7°. In apparently the first formation of $RSiH_2Cl$ or $RSiH_2Br$ through the use of $HgCl_2$ or $HgBr_2$, a deficiency of $HgCl_2$ or $HgBr_2$ converts n-$C_7H_{15}SiH_3$ into n-$C_7H_{15}SiH_2Cl$ or n-$C_7H_{15}SiH_2Br$, respectively. Reaction with the proper amount of iodine converts n-$C_7H_{15}SiH_3$ either into n-$C_7H_{15}SiI_3$ or into a mixture of n-$C_7H_{15}SiH_2I$ and n-$C_7H_{15}SiHI_2$. Antimony trifluoride and n-$C_7H_{15}SiI_3$ furnish pure n-$C_7H_{15}SiF_3$; SbF_3 and n-$C_7H_{15}SiHI_2$ yield n-$C_7H_{15}SiHF_2$ with a small amount of n-$C_7H_{15}SiF_3$ evidently present while a little metallic antimony forms. Table I lists the properties of 12 new compounds containing the n-$C_{17}H_{15}$–Si bonding.

Introduction

Three earlier papers establish the use of halides of certain transitional elements and elements in regular groups in the replacement of hydrogen attached to tin[1] in $(C_2H_5)_3SnH$, to germanium[2] in $(C_2H_5)_3GeH$ or to silicon[3] in $(C_2H_5)_3SiH$.

Gradual addition of $HgCl_2$, AgCl, $CuCl_2$ or $HgBr_2$ to an excess of $(C_2H_5)_2SiH_2$ allows straightforward preparation[3] of $(C_2H_5)_2SiHCl$ or $(C_2H_5)_2SiHBr$. This gradual addition of certain inorganic chlorides and bromides to an excess of $(C_2H_5)_2SiH_2$ in the previous paper or to an excess of n-$C_7H_{15}SiH_3$ in this publication apparently is a new modification for preparation of compounds containing the bonds Si–C, Si–H and Si–Cl or Si–Br.

Other investigators of alkylsilanes with Si–H bonding use reagents which do not include halides of transitional elements.

This paper, in turn, reports the reactions of n-$C_7H_{15}SiH_3$ with $HgCl_2$, $HgBr_2$ and iodine, also the preparation of three n-heptylfluorosilanes and *sym*-bis-(n-heptyl)-disiloxane from other n-heptylhalosilanes.

Experimental Results

Table I lists the boiling points, densities, refractive indices, molar refractions and analyses of 12 new compounds containing a single n-heptyl group attached to silicon. There are two complete series: n-$C_7H_{15}SiH_3$, n-$C_7H_{15}SiH_2F$, n-$C_7H_{15}SiHF_2$ and n-$C_7H_{15}SiF_3$; also, n-$C_7H_{15}SiH_3$, n-$C_7H_{15}SiH_2I$, n-$C_7H_{15}SiHI_2$ and n-$C_7H_{15}SiI_3$.

Iodine and an excess of n-$C_7H_{15}SiH_3$ yield a mixture of n-$C_7H_{15}SiH_2I$ and n-$C_7H_{15}SiHI_2$; 3 moles of iodine and one mole of n-$C_7H_{15}SiH_3$ furnish n-$C_7H_{15}SiI_3$.

Evidently n-$C_7H_{15}SiH_2Br$ has a higher purity than have n-$C_7H_{15}SiH_2F$, n-$C_7H_{15}SiH_2Cl$ and n-$C_7H_{15}SiH_2I$. Different preparative methods in the future may yield purer center fractions of n-$C_7H_{15}SiBr_3$ and n-$C_7H_{15}SiHF_2$.

All three n-heptylfluorosilanes have especially penetrating odors and hydrolyze very slowly in pure water at 25°; in contrast, the n-heptyliodosilanes all hydrolyze very easily.

Experimental

Equipment for all reactions included units with ground joints, micro-pycnometers, a 0.02460-ml. micropipet for the measurement of liquids and the subsequent titration of available acidity, transfer pipets and also special equipment for determining H present as Si–H.

n-Heptyltrichlorosilane.—After addition of 2 liters of 1.8 *M* n-$C_7H_{15}MgCl$ in diethyl ether over a period of 3 hr. to 600 g. of $SiCl_4$ dissolved in 0.5 liter of ether, the mixture stood overnight. Next came filtration and washing of the $MgCl_2$ with CCl_4; fractional distillation furnished approximately 460 g. of crude n-$C_7H_{15}SiCl_3$, a 54% yield; the center fraction served for measurements and for other preparations.

n-Heptylsilane.—Two hours of reflux followed after addition of 350 g. of n-$C_7H_{15}SiCl_3$ over a period of 1 hr. to 56 g. of $LiAlH_4$ dissolved in 500 ml. of diethyl ether. Next came addition of water, then making slightly acidic with aqueous HCl, then separation of layers and washing of the ether layer with water. Distillation of the ether and then fractional distillation furnished 150 g. of n-$C_7H_{15}SiH_3$, a 77% yield, and 45 g. of higher-boiling contaminated $(n\text{-}C_7H_{15}SiH_2)_2O$. Redistillation gave pure n-$C_7H_{15}SiH_3$.

n-Heptylchlorosilane and n-Heptylbromosilane.—Metallic mercury and gaseous HCl or HBr formed during 2 hr. of gentle reflux of 6.65 g. of n-$C_7H_{15}SiH_3$ with 14.2 g. of $HgCl_2$ or 17.1 g. of $HgBr_2$, each added in four lots. Pipetting, centrifuging or a preliminary distillation removed liquid mercury. Either 7.5 g. of n-$C_7H_{15}SiH_2Cl$, an 89% yield, or 9.6 g. of n-$C_7H_{15}SiH_2Br$, a 97% yield, resulted. All yields herein depend on the starting material present in the lesser amount. After rejection of the lowest-boiling 60% of the n-$C_7H_{15}SiH_2Cl$, the next 25% was taken for study. The middle third of the n-$C_7H_{15}SiH_2Br$ served for study.

n-Heptyltribromosilane.—Seventeen g. of aniline and 5.05 g. of n-$C_7H_{15}SiCl_3$ in 100 ml. of CCl_4 stood overnight; next came filtration and washing of the precipitated anilinium chloride. Passage of excess dry HBr gas through the solution of n-$C_7H_{15}Si(HNC_6H_5)_3$ furnished soluble n-$C_7H_{15}SiBr_3$ and precipitated anilinium bromide, which was later filtered and washed. Distillation of CCl_4 and then fractional distillation of the n-$C_7H_{15}SiBr_3$ gave a center fraction of 2.1 g. out of a total of 5.3 g., or a 63% yield.

n-Heptyliodosilanes.—Addition of 40 g. of powdered iodine in small lots during 3 hr. of reflux to 14.9 g. of n-$C_7H_{15}SiH_3$ furnished 15.4 g. of n-$C_7H_{15}SiH_2I$ and 17.5 g. of n-$C_7H_{15}SiHI_2$, center fractions of which had the properties in Table I. Addition of 83 g. of powdered iodine in small lots during 2 hr. of reflux to 14.0 g. of n-$C_7H_{15}SiH_3$ furnished crude n-$C_7H_{15}SiI_3$. Fractional distillation with a little copper wire present gave 0.5–1.0 g. of solid SiI_4 and 48.6 g. of n-$C_7H_{15}SiI_3$, a yield of 89%, the highest-boiling 60% having the properties in Table I.

n-Heptylfluorosilane.—Crude n-$C_7H_{15}SiH_2F$ resulted through reaction of 4.3 g. of n-$C_7H_{15}SiH_2I$ with 30 g. of 48% aqueous HF in a polyethylene plastic container, with 1 hr. of intermittent shaking, then removal of the aqueous acid by pipetting, followed by a quick shaking with a small amount of pure water. After transfer to a glass vial containing some powdered dry KF, there followed pipetting and fractional distillation, with rejection of the lowest-boiling 0.3 g. and collection of the next, iodine-free, 0.63 g. for study. A residue of 0.83 g. remained; the yield was 70%. In contrast, 13.7% F was present in the less pure n-$C_7H_{15}SiH_2F$ obtained from SbF_3 and n-$C_7H_{15}SiH_2Br$.

n-Heptyltrifluorosilane.—Addition of 8 g. of resublimed SbF_3 to 14.8 g. of n-$C_7H_{15}SiI_3$ furnished orange-yellow SbI_3 and 4.95 g. of crude n-$C_7H_{15}SiF_3$, first distilled under 150 mm. pressure and later treated with dry powdered KF and copper wire and fractionally distilled taking a 2.0-g. center fraction with the properties in Table I. This is a yield of 92%.

***sym*-Bis-(n-heptyl)-disiloxane.**—Shaking of 7.66 g. of n-$C_7H_{15}SiH_2Br$ with 8 g. of water was followed by transfer of the resulting aqueous acid with a pipet; a second shaking with 8 g. of water and later pipetting followed. After drying over Na_2SO_4, 4.23 g. of $(n\text{-}C_7H_{15}SiH_2)_2O$ was present, a yield of 84%. Table I lists the properties of the 1.6-g. center fraction obtained in distillation.

Analytical.—Table I lists determinations of silicon through weighing SiO_2 after treating each compound with concentrated nitric and fuming sulfuric acids, lists halogen

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[1] H. H. Anderson, THIS JOURNAL, **79**, 4913 (1957).

[2] H. H. Anderson, *ibid.*, **79**, 326 (1957).

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

TABLE I

PROPERTIES OF NEW *n*-HEPTYLSILANE DERIVATIVES

Compound[a]	B.p.,[b] °C.	d^{20}_4	n^{20}[c]	Mol. refr.		Silicon		Halogen		Mol. wt.		Distilled at	
				Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found	°C.	Mm
n-$C_7H_{15}SiH_3$	140.7	0.737	1.4199	44.95	44.73	21.56	..[d]	..	...	130.3	139	140.7–140.9	760
n-$C_7H_{15}SiH_2Cl$	176.8	0.884	1.4354	48.89	48.67	17.05	16.8	21.5	21.65[e]	164.8	175	113–115	98
n-$C_7H_{15}SiCl_3$	212.4	1.095	1.4465	56.77	56.83	12.02	12.0	45.5	45.3	233.7	244	104–106	19
n-$C_7H_{15}SiH_2Br$	194.5	1.097	1.4571	51.86	51.95	13.43	13.37	38.2	38.2	209.2	229	131–132	98
n-$C_7H_{15}SiBr_3$	260.5	1.625	1.5027	65.68	66.74	7.65	7.40	65.3	65.65	367.0	382	146–148	18
n-$C_7H_{15}SiH_2I$	219.3	1.303	1.4945	57.60	57.30	10.96	10.8	49.5	49.3	256.2	258	110–112	15
n-$C_7H_{15}SiHI_2$	269	1.730	1.5503	70.25	70.39	7.35	7.53	66.4	66.4	382.1	392	110–112	1
n-$C_7H_{15}SiI_3$	326	2.118	1.6108	82.90	83.25	5.53	5.44	74.9	74.95	508.0	511	159–161	1
n-$C_7H_{15}SiH_2F$	138.1	0.828	1.3997	43.73	43.42	18.94	...	12.8	13.0	148.3	156	138–138.5	763
n-$C_7H_{15}SiHF_2$	132.6	.916	1.3759	42.51	41.65	16.89	...	22.8	23.4	166.3	182	133.3–133.5	768
n-$C_7H_{15}SiF_3$	127.0	.983	1.3601	41.29	41.39	15.24	...	30.9	30.8	184.3	193	126.5–127.5	760
$(n$-$C_7H_{15}SiH_2)_2O$	282	.827	1.4374	87.15	87.05	20.46	20.4	..	...[f]	274.6	262	126–128	1

[a] All compounds are colorless. [b] Boiling points under 760 mm. pressure. [c] In white light. Use of Si–F as 1.95 and Si–I as 15.82 in calculating mol. refractions. [d] Calcd.: C, 64.52; H, 13.92; H present as Si–H, 2.32. Found: C, 64.58; H, 13.70; H present as Si–H, 2.30. [e] All determinations are averages of two closely agreeing values. [f] Calcd.: H present as Si–H, 1.46. Found: H present as Si–H, 1.43, 1.43.

obtained by closely agreeing duplicate titrations of the individual compound with ethanolic NaOH, lists molecular weights obtained by lowering of freezing point of naphthalene solutions and also lists determinations of H present as Si–H, as well as a commercial analysis for carbon and hydrogen.

Discussion

Preparative Methods.—Gradual addition of a deficiency of $HgCl_2$ or $HgBr_2$ to excess n-$C_7H_{15}SiH_3$ yields n-$C_7H_{15}SiH_2Cl$ or n-$C_7H_{15}SiH_2Br$, respectively, plus metallic mercury. Fortunately, the formation of *liquid* mercury indicates the progress of the reaction, and this is an advantage over the possible use of AgCl or $CuCl_2$,both of which should react[3] with n-$C_7H_{15}SiH_3$ to produce n-$C_7H_{15}SiH_2Cl$.

Preparations of monoalkylsilanes appear to be most satisfactory through the straightforward use of $LiAlH_4$[4] and the proper alkyltrichlorosilane, rather than through the painstaking preparation first of SiH_4 and second of SiH_3Br from SiH_4 using HBr and $AlBr_3$,[5] followed by reaction of SiH_3Br and n-C_4H_9MgBr to yield n-$C_4H_9SiH_3$.[6]

Gradual addition of 1.39 moles of iodine to one mole of n-$C_7H_{15}SiH_3$ yields a mixture of n-$C_7H_{15}SiH_2I$ and n-$C_7H_{15}SiHI_2$; gradual addition of 3 moles of iodine to one mole of n-$C_7H_{15}SiH_3$ furnishes n-$C_7H_{15}SiI_3$. Here both the gradual addition and the stoichiometry are vital.

There are difficulties in preparing pure n-heptylfluorosilanes with Si–H bonding. Although SbF_3 and n-$C_7H_{15}SiI_3$ furnish rather pure n-$C_7H_{15}SiF_3$, yet SbF_3 and n-$C_7H_{15}SiHI_2$ yield less-pure n-$C_7H_{15}SiHF_2$, apparently containing a little n-$C_7H_{15}SiF_3$; a little metallic antimony forms in the reaction. This formation of antimony resembles that in the reaction[7] $3SiHCl_3 + 4SbF_3 = 3SiF_4 + 2Sb + 2SbCl_3 + 3HCl$, or that in the reaction[3] $6(C_2H_5)_3SiH + 2SbCl_3 = 6(C_2H_5)_3SiCl + 2Sb + 3H_2$. Similarly, SbF_3 and n-$C_7H_{15}SiH_2I$ furnish fairly impure n-$C_7H_{15}SiH_2F$ (Found: F, 13.7. Calcd.: F, 12.8). However, reaction of n-$C_7H_{15}SiH_2I$ with 48% aqueous HF yields fairly pure n-$C_7H_{15}SiH_2F$, as listed in Table I.

Preparation of n-$C_7H_{15}SiBr_3$ by the Ruff process[8,9] apparently gives a slightly impure product. In this process there is a possibility of obtaining a slightly contaminated n-$C_7H_{15}SiBr_3$ containing excessive bromine. In contrast, the reaction of n-$C_7H_{15}MgBr$ with $SiBr_4$ should yield a purer product.

Molar Refractions and Bond Refractions.—Some explanation is necessary for the calculated molar refractions in Table I. There is serious disagreement in published values of the Si–F bond refraction: 2.10 from SiF_4 gas,[10] 1.50 listed in 1946[11] and 1.7 listed in 1954.[12] For the time being, 1.95 appears to be a fair over-all average for the Si–F bond refraction, covering all fluorosilanes with one to four fluorine atoms present, and serving in the calculations in Table I. Vogel's bond refractions[12] for C–H, C–C, Si–C, Si–Cl, Si–Br, Si–O and Si–H serve in the calculations.

No bond refraction of Si–I is present in the early listings.[11,12] However, calculations based on the available data and Vogel's values furnish the following information: CH_3SiCl_2I, *MR* 37.53[13] and Si–I 15.76; CH_3SiClI_2, *MR* 46.39[13] and Si–I 15.81; $(C_2H_5)_2SiI_2$,[9] unpublished n^{20} 1.578_0[14] and thus *MR* 56 17, also Si–I 15.90. These three compounds, including only monoiodo and diiodo compounds, give an average value of 15.82 ± 0.06 for the bond refraction Si–I used in calculations in Table I. Later inclusion of triiodo compounds or tetraiodosilane may raise the value of the Si–I bond refraction slightly.

Excluding the molar refractions of slightly impure n-$C_7H_{15}SiHF_2$ and n-$C_7H_{15}SiBr_3$, the average error in calculated molar refractions in Table I is 0.3%.

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(4) A. E. Finholt and others, THIS JOURNAL, **69**, 2692 (1947).

(5) A. Stock and C. Somieski, *Ber.*, **50**, 1739 (1917); **51**, 989 (1918).

(6) H. E. Opitz and others, THIS JOURNAL, **78**, 292 (1956).

(7) O. Ruff and C. Albert, *Ber.*, **38**, 53 (1905).

(8) O. Ruff, *ibid.*, **41**, 3738 (1908).

(9) H. H. Anderson and others, THIS JOURNAL, **73**, 2144, 5802 (1951).

(10) W. Klemm and P. Henkel, *Z. anorg. Chem.*, **213**, 115 (1933).

(11) E. L. Warrick, THIS JOURNAL, **68**, 2455 (1946).

(12) A. I. Vogel and others, *J. Phys. Chem.*, **58**, 174 (1954).

(13) H. H. Anderson, THIS JOURNAL, **73**, 5804 (1951).

(14) Measurement by H. H. Anderson on May 2, 1950, not included in earlier paper, Reference 9.