n-Heptylsilicon Derivatives

HERBERT H. ANDERSON[1] AND ABDOLAH HENDIFAR

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This paper is an extension of our earlier publication of *n*-heptylhalosilanes and *n*-heptylsilane.[2] Previous articles on organosilicon esters[3-5] and on organosilicon halogenoids[6,7] also have a close relationship to this paper.

Nine new compounds in this paper include the following: *n*-heptyldibromosilane, *n*-heptylcyanosilane, *n*-heptylisothiocyanatosilane, *n*-heptyltriisothiocyanatosilane, *n*-heptyltriisocyanatosilane, *n*-heptyltris(trifluoroacetoxy)silane, *n*-heptyltris(pentafluoropropionoxy)silane, *n*-heptyltris(heptafluoro-*n*-butyroxy)silane, and *n*-heptyltriacetoxysilane. All these compounds hydrolyze quite easily and all except *n*-heptyltriisothiocyanatosilane and *n*-heptyltriisocyanatosilane show some decomposition at the normal boiling point.

Table I presents the properties and analyses of the nine new compounds, all of which have normal boiling points over 200°. On the whole the agreement between calculated and observed molar refractions[2,3] and between calculated and observed percentages of silicon, halogenoid, halide, or ester is surprisingly good for such difficultly volatile and easily hydrolyzed compounds.

TABLE I

PROPERTIES OF NEW *n*-HEPTYLSILICON HALOGENOIDS AND ESTERS

Compound	B.P.	d_4^{20}	n^{20b}	Mol. Refr.		Silicon[a]		Halogen(oid) or Ester		Distilled at	
				Calcd.	Found	Calcd.	Found	Calcd.	Found	°C.	Mm.
n-$C_7H_{15}SiHBr_2$	235[c]	1.413	1.4937	58.77	59.32	9.75	9.72	55.5	56.1	66–68	1
n-$C_7H_{15}SiH_2CN$	204[c]	0.830	1.4349	49.12	48.82	18.1	18.0	16.8	—[d]	81–83	8
n-$C_7H_{15}SiH_2NCS$	235[c]	0.921	1.4939	59.31	59.22	15.0	15.2[e]	31.0	31.3	75–77	1
n-$C_7H_{15}Si(NCS)_3$	347	1.129	1.5739	88.03	88.11	9.32	9.23	57.8	57.7	174–175	1
n-$C_7H_{15}Si(NCO)_3$	258	1.077	1.4516	63.31	63.41	11.1	11.2	49.8	—[f]	111–113	1
n-$C_7H_{15}Si(OCOCF_3)_3$	210[c]	1.310	1.3510	76.31	76.80	6.02	5.95	72.7	72.4	124.8–125.0	34
n-$C_7H_{15}Si(OCOC_2F_5)_3$	222[c]	1.398	1.3361	91.30	91.46	4.55	4.46	79.3	79.2	89–91	1
n-$C_7H_{15}Si(OCO$-n-$C_3F_7)_3$	260[c]	1.480	1.3324	106.29	106.33	3.67	3.47	83.4	83.2	113–114	1
n-$C_7H_{15}Si(OCOCH_3)_3$	—[c]	1.051	1.4227	74.75	73.71	9.23	8.93	58.2	57.8	144–146	1

[a] Weight as silicon dioxide after use of concentrated nitric and sulfuric acids. [b] In white light. All compounds are colorless. [c] With some decomposition. [d] Calcd.: H as Si—H, 1.29. Found: H as Si—H, 1.27. [e] Calcd.: H as Si—H, 1.07. Found: H as Si—H, 1.06. [f] Calcd.: mol. wt., 253.3. Found: mol. wt. (naphthalene), 274.

EXPERIMENTAL

Starting materials included the appropriate silver salts and the *n*-heptylsilane and *n*-heptyltrichlorosilane from our earlier paper.[2] Earlier publications cover the equipment, the calculations of molar refractions, and the analytical methods.[2,3,8]

***n*-Heptyldibromosilane.** Continuous slow addition of 20.8 g. of bromine to 7.37 g. of *n*-heptylsilane in very weak daylight over 2 hr. with agitation furnished hydrogen bromide and 11.3 g. of crude product boiling at 128–150° under 64 mm. Upon the fourth redistillation under 1 mm. pressure there was obtained a 3.2-g. center fraction of *n*-heptyldibromosilane for measurements. This compound decomposed slowly at the normal boiling point and some redistribution may have occurred under reduced pressure.

***n*-Heptylcyanosilane.** Gradual addition of 9.6 g. of mercuric cyanide over 1 hr., with addition of 0.8 g. every 5 min., to 4.8 g. of *n*-heptylsilane furnished gaseous hydrogen cyanide, mercury, and an organosilicon mixture. Fractional

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(1) Kindly address communications to this author.

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distillation under reduced pressure separated 2.4 g. of excess *n*-heptylsilane from 2.5 g. (44% yield) of crude *n*-heptylcyanosilane, later redistilled to obtain a 1.36 g. center cut for measurements.

n-Heptylisothiocyanatosilane. Gradual addition of 11.5 g. of mercuric thiocyanate over 2 hr., with addition of 0.5 g. every 5 min., to 4.8 g. of *n*-heptylsilane in 15 g. of carbon tetrachloride and then 20 min. of reflux gave mercury, thiocyanic acid later polymerized to thiocyanuric acid and an organosilicon mixture. Filtration and washing of the thiocyanuric acid with carbon tetrachloride and then fractional distillation separated the solvent and then the excess *n*-heptylsilane from approximately 3.3 g. (48% yield) of crude *n*-heptylisothiocyanatosilane; redistillation gave a 1.5-g. center cut for measurements.

n-Heptyltriisothiocyanatosilane. One-hour reflux of 5.5 g. of *n*-heptyltrichlorosilane and 16 g. of silver thiocyanate in 20 g. of carbon tetrachloride, and the usual process[6,7] with fractional distillation under reduced pressure, furnished 6.1 g. (87% yield) of crude *n*-heptyltriisothiocyanatosilane; redistillation gave a 2.8-g. center cut.

n-Heptyltriisocyanatosilane. One-hour reflux of 6.57 g. of *n*-heptyltrichlorosilane and 18 g. of silver cyanate in 16 g. of carbon tetrachloride, and the usual process[6,7] with distillation under low pressure, furnished 5.8 g. (80% yield) of *n*-heptyltriisocyanatosilane. The 1.6-g. center cut served for measurements.

n-Heptylsilicon esters. Typically, 70-min. reflux of 3.95 g. of *n*-heptyltrichlorosilane and 14.6 g. (a 30% excess) of silver trifluoroacetate in 16 g. of carbon tetrachloride, and then filtration and washing of silver salts and distillation under low pressure, furnished 1.43 g. of slightly low *n*-heptyltris(trifluoroacetoxy)silane, then 3.28 g. of center cut ester for measurements, and lastly 1.57 g. of slightly higher boiling ester. All these esters hydrolyzed quite rapidly in air of 50% relative humidity at 20°. All the yields of fluoroesters were 70% or better. Similarly, 4.27 g. of *n*-heptyltrichlorosilane and 12.5 g. of silver acetate in 16 g. of carbon tetrachloride after a 45-min. reflux furnished 0.8 g. of low fraction and then 1.7 g. of center cut *n*-heptyltriacetoxysilane for measurements; 2.6 g. of dark colored undistilled residue remained. Excessive decomposition evidently reduced the yield to 46% and also prevented the measurement of the normal boiling point.

CHEMISTRY DEPARTMENT
DREXEL INSTITUTE OF TECHNOLOGY
PHILADELPHIA 4, PA.

The Triphenylsilyltriphenylborate Anion and Its Germanium Analog

DIETMAR SEYFERTH, GUNTER RAAB, AND SAMUEL O. GRIM

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Our recent synthesis of B-tris(triphenylsilyl)-*N*-trimethylborazine,[1] the first compound containing a boron-silicon bond to be reported, prompted us to search for other systems in which a boron–other metal bond might be capable of existence. We report here another type of compound in which a boron atom is bonded to silicon or germanium.

The stability of the tetraphenylborate anion is well known,[2] and the reaction between an aryllithium compound and a triarylborane appears to be a general one. This suggested that triphenylsilyllithium[3] and its germanium analog[4] might react with triphenylborane to give lithium triphenylsilyltriphenylborate and the corresponding germanium compound. This expectation was supported by the report of Wittig and his co-workers that tritylsodium and triphenylborane form $Na[(C_6H_5)_3CB(C_6H_5)_3]$, a complex, which, due to steric hindrance, was barely stable in the solid state and nearly completely dissociated in solution,[5] but that replacement of the boron atom by the larger aluminum atom permits formation of the stable salt, $Na[(C_6H_5)_3CAl(C_6H_5)_3]$, *from tritylsodium and triphenylaluminum.*[6] In our case we are keeping the Group III atom constant and decreasing steric hindrance by replacing carbon by its larger congeners.

The reaction of triphenylsilyllithium and triphenylgermyllithium with triphenylborane resulted in the expected complexes.

$$(C_6H_5)_3MLi + (C_6H_5)_3B \longrightarrow Li[(C_6H_5)_3\,MB(C_6H_5)_3]\ (M = Si\ or\ Ge)$$

The germanium derivative is the first example of a compound containing a germanium-boron bond. Both complexes are very readily hydrolyzed. However, they are soluble and sufficiently stable in methanol to permit various precipitation reactions to be carried out. Like all tetraarylborates, they form insoluble compounds with large inorganic and organic cations, e.g., $[(CH_3)_4N][(C_6H_5)_3SiB(C_6H_5)_3]$. The tetramethylammonium salts of both compounds when suspended in chloroform readily decolorized bromine. In the case of $[(CH_3)_4N][(C_6H_5)_3GeB(C_6H_5)_3]$, tetramethylammonium bromide (subliming *ca.* 380–390° in an open tube) and triphenylgermanium bromide, m.p. 136°, were isolated from the bromination reaction.

EXPERIMENTAL[7]

Lithium triphenylsilyltriphenylborate and its derivatives. A solution of triphenylsilyllithium was prepared by cleavage of 15 g. (0.029 mole) of hexaphenyldisilane with 3.0 g. (0.43 g.

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(7) Analyses were performed by Dr. S. M. Nagy of the MIT Microchemical Laboratory and by the Schwarzkopf Microanalytical Laboratory, Woodside, N. Y. Melting points were taken using a Mel-Temp apparatus. Reactions of the silyl- and germyllithium reagents were carried out in an atmosphere of prepurified nitrogen. Tetrahydrofuran and ethylene glycol dimethyl ether were purified by preliminary drying and subsequent distillation from lithium aluminum hydride.