NITROGEN-CONTAINING ORGANOSILICON COMPOUNDS

IX. Piperidinosilanes*

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Khimiya Geterotsiklicheskikh Soedinenii, Vol. 5, No. 4, pp. 647–651, 1969

UDC 547.79.128+547.822.3

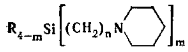
Fifteen previously unknown piperidinosilanes of the type

$R_{4-m}Si[(CH_2)_nNC_5H_{10}]_m$ $(m=1-3;\ n=0-3)$.

have been synthesized by the reaction of piperidine with diethylaminotrimethylsilane, bis(diethylamino)dimethylsilane, chlorobis(dimethylamino)methylsilane, trichloro(methyl)silane, trialkyl(chloromethyl)silanes, dialkoxy(alkyl)(chloromethyl)silanes, trialkylvinylsilanes, trialkyl(3-chloropropyl)silanes, and 3-chloropropyl(diethoxy)methylsilane. The piperidinosilanes (n > 0) have been converted into the corresponding hydrochlorides and methiodides.

In a study of organosilicon amines we observed that diethoxy(methyl)(3-piperidinopropyl)silane possesses a fairly high toxicity, its mean lethal dose for white mice being 6 mg/kg (on intraperitoneal administration).

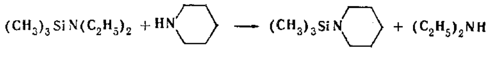
To study the dependence of the toxicity of the piperidinosilanes on their structure in more detail, we have performed the synthesis of a number of compounds of this type having the general formula



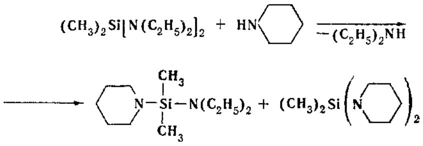
R - alkyl, alkoxyl, m = 1–3; n = 0–3

Previously, four methods of preparing piperidinosilanes (n = 0) were known: 1) by the reaction of piperidine with organylchlorosilanes [2–6], 2) by the transamination of aminosilanes with piperidine [2], 3) by the reaction of piperidine with hexaalkyldisilazanes [2, 7], and 4) by the silylation of piperidine with triphenylsilyllithium [8]. Trialkylpiperidinosilanes have been obtained with the highest yield (89%) by the second method, but for this it was necessary to heat the reaction mixture to the boil for 10 hr [2].

We have found that when diethylaminotrimethylsilane is heated with piperidine with the simultaneous elimination of diethylamine by distillation, trimethyl(piperidino)silane is formed rapidly in high yield (~90%)

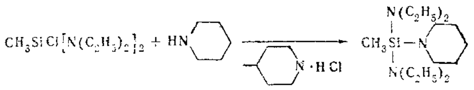


Bis(dimethylamino)dimethylsilane reacts with piperidine with considerably greater difficulty. The replacement of the diethylamino groups by piperidino groups takes place stepwise, and even with an excess of piperidine a mixture of diethylamino(dimethyl)piperidinosilane and dimethyldipiperidinosilane is formed:

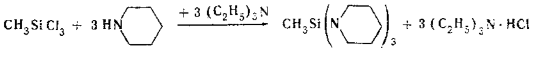


When the reaction of tris(diethylamino)(methyl)silane with piperidine was carried out under similar conditions, no methyltripiperidinosilane was formed.

In the reaction of chlorobis(diethylamino)methylsilane with an excess of piperidine the only organosilicon product was bis(diethylamino)(methyl)piperidinosilane:

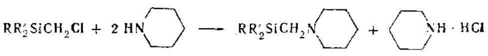


It was possible to obtain methyltripiperidinosilane in low yield (~23%) by the prolonged (60 hr) boiling of a benzene solution of trichloro(methyl)silane, piperidine, and triethylamine



(Piperidinomethyl)silanes (n = 1) have been obtained previously by three methods: 1) by the reaction of piperidine with trialkyl(chloromethyl)silanes [9, 10], 2) by the cleavage of the C—O bond in N-(alkoxymethyl)piperidines with triphenylsilyllithium [11], and 3) by the condensation of pentane-1, 5-diols with aminomethylsilanes [12, 13].

Using the first method, we have synthesized a number of new trialkyl(piperidinomethyl)silanes and dialkoxy(alkyl)(piperidinomethyl)silanes:



2-Piperidinoethylsilanes (n = 2) have been synthesized by the reaction of 2-aminoalkylsilanes with 1, 5-dibromopentane [14] and by the addition of piperidine to triorganylvinylsilanes in the presence of metallic lithium [15, 16].

We carried out the addition of piperidine to trialkylvinylsilanes in the presence of metallic lithium. It was found that after the reaction products—trialkyl(2-piperidinoethyl)silanes—had been distilled off solid residues remained. On decomposition with water they were converted into trialkyl(2-piperidinoethyl)silanes. The amount of these residues depends on the time of the reaction and decreases as the reaction is prolonged. This shows that the final reaction products (or, in any case, part of them) are formed as a result of the addi-

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*For part VIII, see [1].

Table 1

Piperidinosilanes

Compound	Formula	Bp, °C (pressure, mm)	n_D^{20}	d_4^{20}	MR_D		Empirical formula	Found, %			Calculated, %			Yield, %
					found	calculated		C	H	Si	C	H	Si	
I	$(CH_3)_2Si(NC_5H_{10})N(C_2H_5)_2$*	73 (2)	1.4595	0.8839	66.38	66.60	$C_{11}H_{26}N_2Si$	61.73	12.25	12.60	61.61	12.22	13.10	
II	$(CH_3)Si(NC_5H_{10})[N(C_2H_5)_2]_2$	103—104 (2)	1.4650	0.8715	83.26	83.51	$C_{14}H_{33}N_3Si$	62.37	11.97	10.47	61.93	12.25	10.34	22
III	$(CH_3)_2Si(NC_5H_{10})_2$	91—92 (3)	1.4760	0.9279	68.83	69.10	$C_{12}H_{26}N_2Si$	63.59	11.72	12.08	63.65	11.57	12.40	32
IV	$CH_3Si(NC_5H_{10})_3$	161 (5)	1.4980	0.9799	88.41	88.51	$C_{16}H_{33}N_3Si$	65.09	11.37	9.23	65.02	11.25	9.50	23.2
V	$CH_3(C_2H_5)_2SiCH_2NC_5H_{10}$	112 (22)	1.4630	0.8533	64.37	64.13	$C_{11}H_{25}NSi$	65.76	12.74	13.90	66.25	12.64	14.08	60.4
VI	$CH_3(C_2H_5O)_2SiCH_2NC_5H_{10}$	103—106 (14)	1.4400	0.9268	65.81	65.89	$C_{11}H_{25}NO_2Si$	57.18	10.89	12.16	57.09	10.89	12.14	57.8
VII	$CH_3(C_3H_7)_2SiCH_2NC_5H_{10}$	126—127 (17)	1.4600	0.8517	73.15	73.63	$C_{13}H_{29}NSi$	68.32	13.05	12.15	68.64	12.85	12.35	20
VIII	$CH_3(C_4H_9O)_2SiCH_2NC_5H_{10}$	110—113 (2)	1.4445	0.9087	84.13	84.41	$C_{15}H_{33}NO_2Si$	62.61	11.64	9.68	62.66	11.57	9.77	48.6
IX	$(C_2H_5)_3SiCH_2NC_5H_{10}$	121—122 (22)	1.4680	0.8619	68.84	68.64	$C_{12}H_{27}NSi$	67.14	12.98	12.94	67.53	12.75	13.16	55.6
X	$(C_2H_5O)_3SiCH_2NC_5H_{10}$	118—120 (15)	1.4357	0.9525	71.71	71.28	$C_{12}H_{27}NO_3Si$	51.70	10.42	10.95	51.21	10.41	10.74	68.5
XI	$(C_3H_7)_3SiCH_2NC_5H_{10}$	111 (2)	1.4652	0.8562	82.53	82.89	$C_{15}H_{33}NSi$	71.01	13.13	11.18	70.51	13.02	10.99	27
XII	$CH_3(C_2H_5)_2SiCH_2CH_2NC_5H_{10}$	79—80 (2)	1.4652	0.8572	68.86	68.76	$C_{12}H_{27}NSi$	67.44	12.72	13.02	67.53	12.75	13.16	43
XIII	$(C_2H_5)_3SiCH_2CH_2NC_5H_{10}$**	107—108 (3)	1.4700	0.8652	73.35	73.27	$C_{13}H_{29}NSi$	68.66	12.83	—	68.64	12.85	12.35	35.1
XIV	$CH_3(C_2H_5)_2Si(CH_2)_3NC_5H_{10}$	136—138 (15)	1.4561	0.8593	73.17	73.39	$C_{13}H_{29}NSi$	68.48	12.71	12.15	68.64	12.85	12.35	54.2
XV	$CH_3(C_2H_5O)_2Si(CH_2)_3NC_5H_{10}$	96—97.5 (1.5)	1.4465	0.9196	75.26	75.15	$C_{13}H_{29}NO_2Si$	60.59	11.37	10.36	60.18	11.27	10.82	25.4
XVI	$(C_2H_5)_3Si(CH_2)_3NC_5H_{10}$	100 (1)	1.4701	0.8647	77.93	77.90	$C_{14}H_{31}NSi$	69.33	12.86	11.28	69.63	12.94	11.63	63.5

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*$C_5H_{10}N$–piperidino.

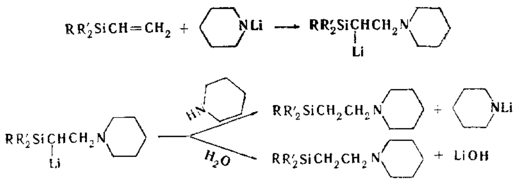
**Literature data [15]: bp 89° C (1 mm); n_D^{20} 1.4700; d_4^{20} 0.8652.

Table 2

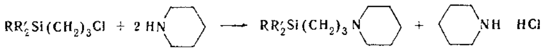
Piperidinosilane Hydrochlorides and Methiodides

Compound	Mp. °C	Empirical formula	Found, %			Calculated, %		
			C	H	Si	C	H	Si
V · HCl	170.5—172	$C_{11}H_{26}ClNSi$	56.22	11.64	11.43	56.01	11.11	11.91
VII · HCl	125—127	$C_{13}H_{30}ClNSi$	58.82	11.78	10.21	59.16	11.46	10.64
IX · HCl	174.5—176.5	$C_{12}H_{28}ClNSi$	57.97	11.45	10.94	57.67	11.29	11.24
IX · CH_3I	200—202	$C_{13}H_{30}INSi$	43.52	8.88	7.45	43.94	8.51	7.90
XII · HCl	259—261.5	$C_{12}H_{28}ClNSi$	57.85	11.37	11.03	57.67	11.29	11.24
XIII · HCl	261.5—263	$C_{13}H_{30}ClNSi$	58.92	11.00	10.21	59.16	11.46	10.64
XIV · HCl	227—228.5	$C_{13}H_{30}ClNSi$	59.46	11.88	10.89	59.16	11.46	10.64
XIV · CH_3I	180—181	$C_{14}H_{32}INSi$	45.62	8.77	7.49	45.52	8.73	7.60
XVI · HCl	230.5—232.5	$C_{14}H_{32}ClNSi$	60.93	11.64	9.54	60.50	11.60	10.10

tion of piperidinolithium to the trialkylvinylsilanes with subsequent demetallation, which takes place on heating with unsubstituted piperidine:



The first representative of the 3-piperidinopropylsilanes (n = 3)—trimethyl(3-piperidinopropyl)silane—was obtained by condensing 1, 5-dibromopentane with 3-aminopropylsilane [14]. We have obtained trialkyl-(3-piperidinopropyl)silanes and dialkoxy(alkyl)(3-piperidinopropyl)silanes by a simpler method—the reaction of trialkyl(3-chloropropyl)silanes with piperidine in boiling toluene:



All the piperidinosilanes synthesized are colorless liquids soluble in the usual organic solvents. Their physicochemical properties, yields, and analytical data are given in Table 1.

The (piperidinoalkyl)silanes with n = 1–3 are insoluble in water, and the piperidinosilanes with n = 0 are readily hydrolyzed by it with the cleavage of the Si—N bond. The reaction of the (piperidinoalkyl)silanes (n = 1–3) with hydrogen chloride forms their hydrochlorides, and their reaction with methyl iodide forms their methiodides (Table 2).

EXPERIMENTAL

Dimethyldipiperidinosilane (III). A mixture of 6.07 g (0.03 mole) of bis(diethylamino)dimethylsilane and 5.10 g (0.06 mole) of piperidine was placed in a round-bottomed flask with a Vigreux condenser and was heated to the boil with the simultaneous removal by distillation of the dimethylamine formed. After 8 hr, 4.9 hr (79%) of $(C_2H_5)_2NH$ had been evolved. The fractional distillation of the residue in vacuum gave 2.19 g of diethylamino(dimethyl)(piperidino)silane (I) and 2.19 g (32%) of III.

Similarly, 14.5 g (0.1 mole) of diethylamino(trimethyl)silane and 8.5 g (0.1 mole) of piperidine gave 14.7 g (88.4%) of trimethyl(piperidino)silane [2, 7] in 45 min.

Bis(diethylamino)(methyl)piperidinosilane (II). A mixture of 12.9 g (0.058 mole) of chlorobis(diethylamino)methylsilane and 21.3 g (0.25 mole) of piperidine was heated to the boil for 8 hr. The precipitate was filtered off and the unchanged piperidine was distilled off from the filtrate. Vacuum distillation of the residue yielded 6 g (22%) of II.

Methyltripiperidinosilane (IV). A three-necked flask fitted with a reflux condenser with a calcium chloride tube, a mechanical stirrer with a gas-tight seal, and a dropping funnel was charged with a solution of 38.3 g (0.45 mole) of piperidine and 45.5 g (0.45 mole) of triethylamine in 200 ml of benzene. With ice-water cooling and vigorous stirring a solution of 22.4 g (0.15 mole) of trichloro(methyl)silane in 30 ml of benzene was added, and then the reaction mixture was heated to the boil for 48 hr. The precipitate was filtered off and washed with benzene. To the filtrate was added 25.5 g (0.3 mole) of piperidine and the mixture was heated again for 12 hr. The precipitate that deposited was filtered off with suction, and the solvent and the unchanged starting materials were distilled off. Three vacuum fractionations of the residue yielded 10.3 g (23.2%) of IV.

(Piperidinoalkyl)silanes (n = 1.3). Pyridine dried over sodium was Pyridine dried over sodium was used for the synthesis of the trialkyl-, trialkoxy-, and dialkoxy(alkyl)piperidinomethylsilanes and the 3-piperidinopropylsilanes. The toluene was dried and distilled over sodium.

A mixture of 0.1 mole of the appropriate (chloroalkyl)silane and 0.2 mole of piperidine in toluene solution was heated for 7–14 hr (until 80–100% of piperidine hydrochloride had been formed). The precipitate was filtered off and washed with toluene. The solvent and the unchanged starting materials were distilled off in the vacuum of a water pump. The reaction product was isolated and purified by two vacuum distillations. The physical constants of compounds V–XI obtained in this way and their analytical data and yields (after the first distillation) are given in Table 1.

Diethyl(methyl)(2-piperidinoethyl)silane (XII). Diethyl(methyl)-vinylsilane and piperidine freshly distilled and dried over calcium hydride were used for the synthesis.

A three-necked flask fitted with a stirrer and a reflux condenser was charged with 8.72 g (0.68 mole) of diethyl(methyl)vinylsilane and 8.98 g (0.106 mole) of piperidine. The mixture was well stirred, and 0.3 g of lithium was added to it. After some time a reaction which took place with the liberation of heat began. After the reaction mixture had cooled, it was heated at 70–80° C for 2 hr. The unchanged lithium was filtered off and the unchanged starting materials were distilled off. The residue was distilled in vacuum giving 4.11 g of XII. After the distillation, a light brown solid substance remained in the flask which was soluble in tetrahydrofuran and sparingly soluble in heptane. It was dissolved in water and extracted with ether, and the ethereal layer was dried with magnesium sulfate. The ether was driven off and the residue was distilled in vacuum, giving another 2.18 g of XII.

Preparation of the methiodides. Methyl iodide (2.5 ml) was added to 5.17 g of XIV dissolved in 2 ml of absolute ethanol. A reaction took place with the evolution of heat. Then the reaction mixture heated in the water bath for about 1 hr. Ether was added to the heated solution, whereupon a precipitate immediately deposited. It was filtered off, washed with ether, dried, and recrystallized from absolute ethanol. The yield of diethyl(methyl)-3-piperidinopropylsilane methiodide was 4.8 g.

Preparation of the hydrochlorides. Anhydrous ether saturated with hydrogen chloride was added in small portions to compounds **V**, **VII**, **IX**, and **XII–XIV**. Heat was evolved and there was an immediate precipitation of the hydrochlorides. They were washed with ether, dried, and recrystallized from ethanol.

The melting points and analytical data of the methiodides and hydrochlorides are given in Table 2.

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6 April 1967

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