Bis[2'-(methoxycarbonylethyl)-5'-tetrahydrofuryl]methane was obtained by the hydrogenation of bis[2'-(β-methoxycarbonylethyl)-5'-furyl]methane over Raney nickel at 100–110° C and an initial pressure of hydrogen of 200 atm with a yield of 70%. Bp 164–165° C (3 mm); n_D^{20} 1.4737; d_4^{20} 1.1119. Found, %: C 62.06, 62.30; H 8.48, 8.23; MR_D 82.95. Calculated for $C_{17}H_{28}O_6$, %: C 62.17; H 8.59%; MR_D 82.90.

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NITROGEN-CONTAINING ORGANOSILICON COMPOUNDS

XIV. N-Morpholyl-, N-Thiamorpholyl-, N-Methylpiperazinyl-, and N-Perhydroazepinylalkylsilanes*

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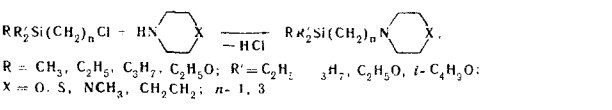
By the reaction of trialkylsilanes and dialkoxy- or di(chloroalkyl)alkylsilanes with morpholine, thiamorpholine, N-methylpiperazine, and hexamethyleneimine, 14 new organosilicon derivatives of these heterocycles have been synthesized. The addition of perhydroazepine to diethylmethylvinylsilane has been performed.

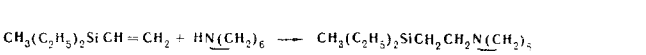
The usual method for obtaining morpholylsilanes [2] and piperazinylsilanes [3–7] containing the Si—N bond is the reaction of organylchlorosilanes with morpholine and piperazine, respectively. Their triphenylsilyl derivatives have been obtained by the reaction of the heterocycles mentioned with triphenylsilyl-lithium [8].

N-Piperazinylsilanes are also formed by the transamination of piperazine with alkylaminosilanes [9], dehydrocondensation with triorganylsilanes in the presence of potassium [10], and the thermal rearrangement of N-aziridinylsilanes [11]. N-Morpholinylmethylsilanes have been synthesized by the reaction of triorganylchloromethylsilanes with morpholine [12]. N-Piperazinylalkylsilanes containing the Si—C_n—N grouping have been obtained by the addition of piperazine to trialkylvinylsilanes in the presence of alkali metals [13] and also by the thermal rearrangement of aziridinylalkylsilanes [13, 14]. Triphenoxy-N-perhydroazepinylsilane is formed by the reaction of chlorotriphenoxysilane with hexamethylenediamine. Di-n-butoxy(methyl)-(N-perhydroazepinylmethyl)silane has been obtained by the reaction of hexamethyleneimine with di-n-butoxy-(chloromethyl)methylsilane [16]. Organosilicon derivatives of thiamorpholine were not previously known.

By heating trialkylsilanes, dialkoxyalkyl- and di(chloromethyl)alkylsilanes, and (3-chloropropyl)silanes with morpholine, thiamorpholine, N-methylpiperazine, and hexamethyleneimine (perhydroazepine) in toluene in the presence of triethylamine for 15–20 hr, we have obtained the corresponding alkyl-N-heterylsilanes with yields of 40–60%:



By the addition of hexamethyleneimine to diethylmethylvinylsilane in the presence of lithium, we have obtained diethylmethyl(2-N-perhydroazepinylethyl) silane:



The method of performing the syntheses was similar to that described previously [17]. The physicochemical constants, the analytical data, and the yields of the compounds synthesized are given in the table. A

*For part XIII, see [1].

N-Morpholyl-, N-Thiamorpholyl-, N-Methylpiperazinyl-, and N-Perhydroazepinylalkylsilanes (NC_4H_8O = = N-morpholyl, NC_4H_8S = N-thiamorpholyl, $NC_4H_8NCH_3$ = N-methylpiperazinyl, NC_6H_{12} = N-perhydroazepinyl).

Compound	Bp, °C (pressure, mm)	n_D^{20}	d_4^{20}	MR_D found	MR_D calculated	Empirical formula	Found, % C	Found, % H	Found, % Si	Calculated, % C	Calculated, % H	Calculated, % Si	Yield %
$CH_3(C_2H_5)_2SiCH_2NC_4H_8O$	79—81.5 (3)	1.4623	0.9067	61.09	61.27	$C_{10}H_{23}NOSi$	59.64	11.87	13.81	59.64	11.51	13.95	65
$CH_3(i\text{-}C_4H_9O)_2SiCH_2NC_4H_8O$	104—108 (2)	1.4402	0.9421	81.10	81.01	$C_{14}H_{31}NO_3Si$	57.37	10.39	9.71	58.08	10.79	9.70	41.9
$(C_2H_5)_3SiCH_2NC_4H_8O$	96.5—98 (4)	1.4680	0.9169	65.31	65.78	$C_{11}H_{25}NOSi$	61.10	12.01	12.20	61.33	11.70	13.04	62
$(C_3H_7)_3SiCH_2NC_4H_8O$	123 (4)	1.4621	0.8817	80.30	80.03	$C_{14}H_{31}NOSi$	65.22	12.28	—	65.30	12.13	10.91	40
$(C_2H_5O)_3SiCH_2NC_4H_8O$	127.5—129 (15)	1.4339	1.0024	68.42	68.42	$C_{11}H_{25}NO_4Si$	50.54	9.54	10.84	50.16	9.57	10.66	69.2
$CH_3(C_2H_5)_2Si(CH_2)_3NC_4H_8O$	114—117 (6)	1.4640	0.8999	70.35	70.53	$C_{12}H_{27}NOSi$	62.99	12.07	11.95	62.82	11.86	12.24	55.4
$CH_3(C_2H_5O)_2Si(CH_2)_3NC_4H_8O$	96 (0.5)	1.4460	0.9662	72.16	72.29	$C_{12}H_{27}NO_3Si$	54.43	10.34	11.06	55.13	10.41	10.74	41.5
$CH_3(C_2H_5O)_2Si(CH_2)_3NC_4H_8S$	125—128 (1.5)	1.4741	0.9970	78.24	78.37	$C_{12}H_{27}NO_2SSi$	*	9.84	10.43	51.94	9.81	10.12	40
$CH_3(C_2H_5)_2SiCH_2NC_4H_8NCH_3$	110—114 (15)	1.4660	0.8722	68.05	67.94	$C_{11}H_{26}N_2Si$	61.35	12.20	12.65	61.61	12.22	13.10	37
$CH_3(C_2H_5)_2Si(CH_2)_3NC_4H_8NCH_3$	115.5—118 (3)	1.4663	0.8712	77.13	77.20	$C_{13}H_{30}N_2Si$	64.54	12.37	11.40	64.39	12.47	11.58	38
$CH_3(C_2H_5O)_2Si(CH_2)_3NC_4H_8NCH_3$	124—126 (3)	1.4513	0.9327	78.96	79.28	$C_{13}H_{30}N_2O_2Si$	56.98	10.96	10.09	56.89	11.02	10.23	32
$CH_3(C_2H_5)_2SiCH_2NC_6H_{12}$	93—94 (4)	1.4675	0.8662	68.43	68.76	$C_{12}H_{27}NSi$	68.11	12.93	12.52	67.53	12.75	13.16	42
$CH_3(C_2H_5)_2Si(CH_2)_2NC_6H_{12}$	113 (4)	1.4713	0.8680	73.29	73.39	$C_{13}H_{29}NSi$	69.00	13.13	12.47	68.64	12.85	12.35	30
$CH_3(C_2H_5)_2Si(CH_2)_3NC_6H_{12}$	113—117 (3)	1.4698	0.8663	77.77	78.02	$C_{14}H_{31}NSi$	69.79	12.98	11.17	69.63	12.94	11.63	33

* Found, %: S 11.27. Calculated, %: S 11.5.

separate communication is devoted to the pharmacological characteristics of the diethoxymethyl derivatives [18].

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