Synthesis and chemical transformations of silicon-containing derivatives of *N*,*N*-dimethylhydrazine

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Reactions of carbofunctional organosilicon compounds with *N*,*N*-dimethyl-*N*'-trimethylsilylhydrazine and *N*,*N*-dimethyl-*N*',*N*'-bis(trimethylsilyl)hydrazine were studied. The composition and structure of the reaction products were found to be dependent on the reagent nature and the reaction conditions. 1,4-Dimethylamino-2,2,5,5-tetramethyl-1,4-diaza-2,5-disilacyclohexane, a first representative of a new type of 2,5-disilapiperazines, was synthesized. A scheme of its formation was proposed.

Key words: *N*,*N*-dimethylhydrazine; silylation, transsilylation, and silylmethylation; chloro(chloromethyl)dimethylsilane, hexamethyldisilazane.

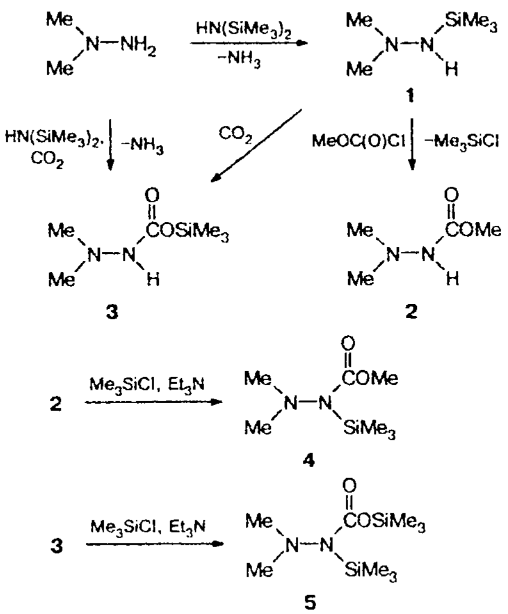
At present, Russia and some other countries have accumulated rather considerable stocks of *N*,*N*-dimethylhydrazine (DMH), which is a component of rocket propellant. That is why an urgent problem is elaboration of methods for annihilation and utilization of highly toxic DMH within the framework of the program of reduction of armament. One of the ways of utilizing DMH is to transform it into less toxic organosilicon products.

Earlier,[1,2] it has been shown that trimethylsilyl derivatives of DMH, in particular *N*,*N*-dimethyl-*N*'-trimethylsilylhydrazine (**1**), can be used as a raw material in the synthesis of urethans **2**—**5** (Scheme 1).

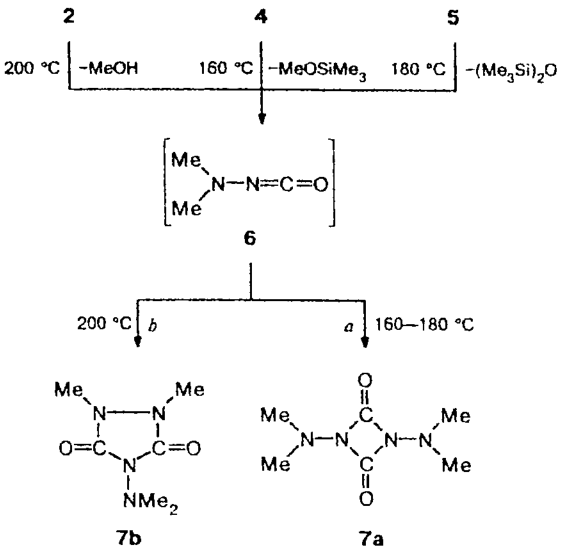
Urethans **2**, **4**, and **5** thus obtained readily decompose into intermediate *N*,*N*-dimethylaminoisocyanate (**6**), which can, depending on the reaction conditions, follow two pathways of dimerization (Scheme 2, reactions *a* and *b*).

Note that isocyanate **6** is unstable, which is why it could not be isolated in the individual state even at considerable temperature lowering as well as when *N*,*N*-dimethyl-*N*',*N*'-bis(trimethylsilyl)hydrazine (**8**) was used as the starting compound (Scheme 3).

Scheme 1



Scheme 2



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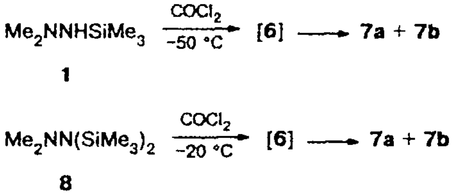
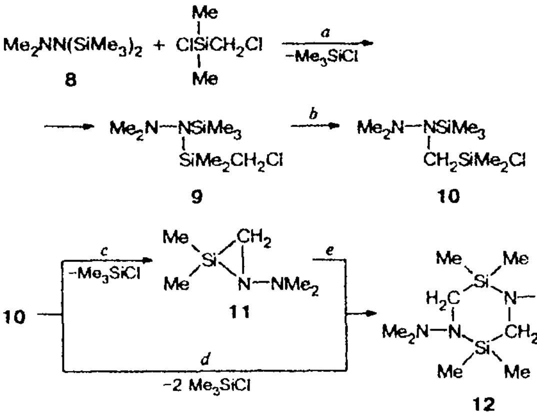
Scheme 3



In continuation of these studies, we established that trimethylsilyl derivatives of DMH can serve as raw materials in the synthesis of both alicyclic and heterocyclic compounds.

Thus, the reaction of hydrazine **8** with chloro(chloromethyl)dimethylsilane (Scheme 4) does not stop at the first stage, *i.e.*, transsilylation (Scheme 4, reaction *a*). Subsequent transformations of the transsilylated product **9**, *viz.*, 1,2(SiN→SiC) rearrangements into hydrazine **10** (reaction *b*) and intra- (reactions *c* and *e*) or intermolecular (reaction *d*) desilylation of the latter, result in 1,4-dimethylamino-2,2,5,5-tetramethyl-1,4-diaza-2,5-disilacyclohexane (**12**).

Scheme 4



An analysis of ^{1}H NMR chemical shifts of the methyl and methylene protons (Table 1) suggests that silacyclane **12** has the dimeric structure. In the case of strained three-membered silaaziridine **11**, resonance signals for the protons at the ring carbon atom should be markedly shifted upfield. It can be seen from Table 1 that the shifts of the methyl and methylene protons remain virtually unchanged in passing from chloromethyl(methoxy)dimethylsilane to heterocycle **12**. Moreover, the molar mass of compound **12** obtained by cryoscopic measurements in benzene was found to be equal 246.8 g mol^{-1} (calculated: M = 260.5).

However, the question of whether the formation of the intermediate three-membered heterocycle **11** is necessary or bimolecular cyclocondensation of compound **10** occurs immediately is still open.

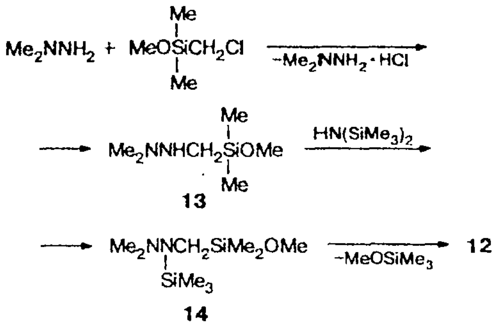
Table 1. ^{1}H NMR chemical shifts of the methyl and methylene protons of carbofunctional organosilicon products

Compound	δ		Reference
	SiCH$_3$	SiCH$_2$	
MeOSiMe$_2$CH$_2$Cl	0.25	2.73	3
ClSiMe$_2$CH$_2$Cl	0.50	2.80	3
ClSiMe$_2$CH$_2$N(All)C(O)H	0.56	2.51	3
Me$_2$SiCH$_2$N(Me)Si(Me$_2$)CH$_2$NMe	0.09	2.25	4
Me$_2$SiCH$_2$N(Bu)Si(Me$_2$)CH$_2$NBu	0.20	2.30	4
Me$_2$SiCH$_2$N(Me)C(O)OSi(Me$_2$)CH$_2$NMe OC=O	0.13	2.33	5
Me$_2$SiCH$_2$N(NMe$_2$)Si(Me$_2$)CH$_2$NNMe$_2$ (**12**)	0.35	2.73	*

* The data obtained in the present work.

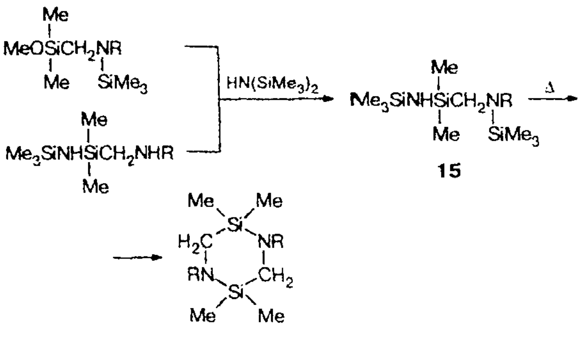
The 2,5-disilapiperazine derivative **12** was also obtained in another way, namely, by 10—15-h keeping of *N*,*N*-dimethyl-*N*′-methoxy(dimethyl)silylmethyl-*N*′-trimethylsilylhydrazine (**14**) synthesized by us for the first time and isolated from the reaction mixture by distillation (Scheme 5).

Scheme 5



It should be noted that the synthesis of heterocycle **12** from hydrazine derivatives **10** and **14** invalidates the statement[6] that 2,5-disilapiperazine derivatives can be obtained only from type **15** disilazanes (Scheme 6).

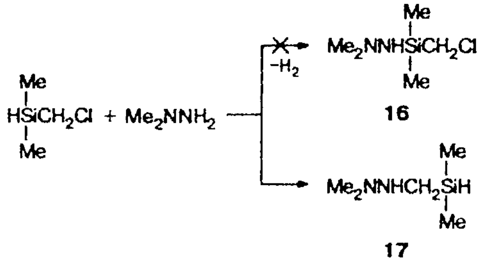
Scheme 6



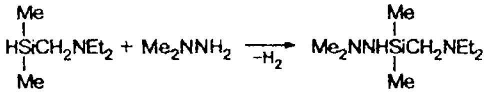
R = Me, All, Pr^n, Bu^n

When chloro(chloromethyl)dimethylsilane is replaced in the reaction with DMH by chloromethyl(dimethyl)silane, *N*,*N*-dimethyl-*N*′-chloromethyl(dimethyl)silane (**16**) could be expected as a reaction product. However, we isolated only silane **17**, a product in which the chlorine atom is replaced by *N*,*N*-dimethylhydrazine compared to the initial compound, rather than dehydrocondensation product **16** (Scheme 7).

Scheme 7



Dehydrocondensation was carried out by using diethylaminomethyl(dimethyl)silane instead of chloromethyl(dimethyl)silane.



$$HSi(Me)_2CH_2NEt_2 + Me_2NNH_2 \xrightarrow{-H_2} Me_2NNHSi(Me)_2CH_2NEt_2$$

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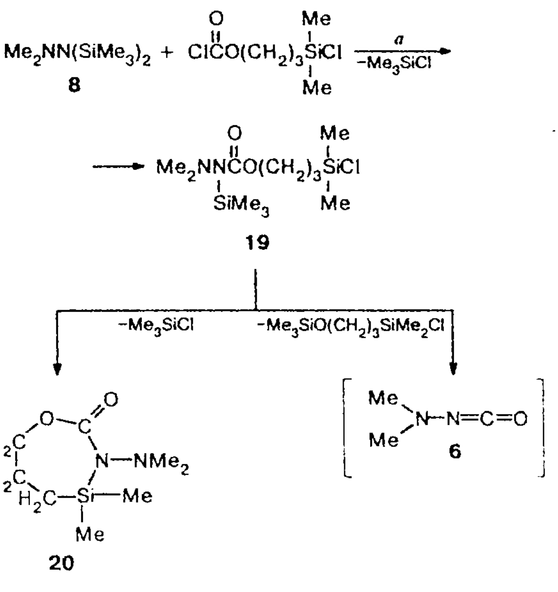
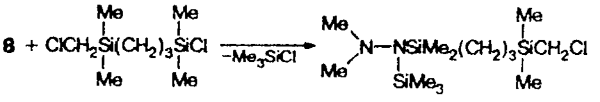
In attempting to isolate product **19** resulting from the reaction of hydrazine **8** with chloro[γ-(chlorocarbonyloxy)propyl]dimethylsilane, we obtained another unknown silacyclane **20** (Scheme 8).

Scheme 8



Monomeric isocyanate **6** was thereby detected for a prolonged period of time in the reaction mixture by IR spectroscopy (an intense absorption peak of the NCO group at 2300 cm^{-1}) both in the stage of removing chlorotrimethylsilane (reaction *a*) and upon distillation of chlorosilane **19**.

In the case of another chlorosubstituted silane, namely, chloro{γ-[chloromethyl(dimethyl)silyl]propyl}dimethylsilane, the character of process changes. It turned out that the reaction stops in the stage of formation of transsilylation product **21**, which does not contradict the known facts.[7,8]



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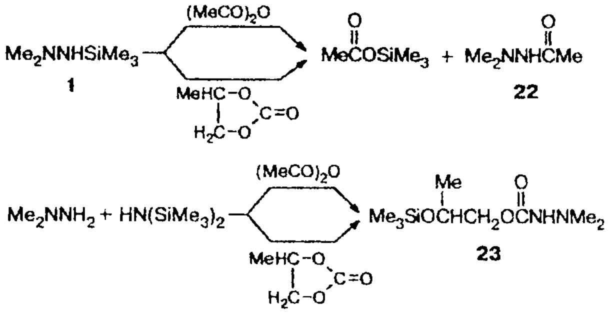
We also studied the reactions of silylhydrazine **1** with acetic anhydride and propylene carbonate. Both compound **1** and a mixture of DMH with hexamethyldisilazane easily affords the corresponding hydrazine derivatives **22** and **23** (Scheme 9).

Scheme 9



The reactions with acetic anhydride are exothermic and accompanied by cleavage of the anhydride C—O bond, while those with propylene carbonate are initiated at 60 °C to stop only after 8—10 h.

Thus, introduction of trimethylsilyl groups into DMH not only makes the latter less toxic but also allows one to obtain easily unknown hydrazine derivatives.

Experimental

All of the initial compounds and solvents were thoroughly dried and purified by distillation before use. Synthetic manipulations, including isolation and sampling for analysis, were performed in an atmosphere of dry nitrogen. The composition of reaction mixtures and individual products was determined by GLC on an LKhM-80 chromatograph (1500 × 3-mm stainless steel columns, stationary phase SE-30 on Chromaton N-AW, helium as carrier gas). ^{1}H NMR spectra were recorded on a Bruker WP-80 instrument (80 MHz) with C_6D_6 as the solvent and internal standard. IR spectra were obtained on a Specord 75 IR instrument (in thin films for liquids and in KBr pellets or Vaseline oil for crystalline compounds).

1,4-Dimethylamino-2,2,5,5-tetramethyl-1,4-diaza-2,5-disilacyclohexane (12). ***A.*** A mixture of silylhydrazine **8** (8.18 g, 0.04 mol) with chloro(chloromethyl)dimethylsilane (5.72 g, 0.04 mol) was heated with a full-condensation distillation head until chlorotrimethylsilane ceased to evolve. The residue was fractionated to give compound **12** (4.48 g, 86%), b.p. 70—72 °C (11 Torr), n_D^{20} 1.4365. Found (%): C, 46.62; H, 10.71; Si, 21.48. $C_{10}H_{28}N_4Si_2$. Calculated (%): C, 46.10; H, 10.83; Si, 21.56. ^{1}H NMR, δ: 0.35 (s, 12 H, SiMe$_2$); 2.24 (s, 12 H, NMe$_2$); 2.73 (s, 4 H, Si–CH$_2$).

B. Silylmethylhydrazine **14** was kept at 20 °C for 15 h to give compound **12** in 82% yield.

(*N*,*N*-Dimethylhydrazinomethyl)methoxydimethylsilane (13). A mixture of chloromethyl(methoxy)dimethylsilane (44.37 g, 0.32 mol), *N*,*N*-dimethylhydrazine (38.46 g, 0.64 mol), and 150 mL of hexane was stirred at 50—55 °C for 15 h. The precipitate that formed was filtered off, and the filtrate was fractionated to give compound **13** (42.07 g, 81%), b.p. 60 °C (12 Torr), n_D^{20} 1.4300. Found (%): C, 44.85; H, 11.03; Si, 17.12. $C_6H_{18}N_2OSi$. Calculated (%): C, 44.40; H, 11.18; Si, 17.30. ^{1}H NMR, δ: 0.028 (s, 6 H, SiMe$_2$); 2.18 (s, 6 H, NMe$_2$); 2.71 (s, 2 H, SiCH$_2$); 3.25 (s, 3 H, SiOMe); 6.45 (s, 1 H, NH).

***N*,*N*-Dimethyl-*N*′-methoxy(dimethyl)silylmethyl-*N*′-trimethylsilylhydrazine (14).** A mixture of methoxysilane **13** (29.22 g, 0.18 mol), hexamethyldisilazane (14.53 g, 0.09 mol), and two to three drops of H_2SO_4 was stirred at 90 °C for 12 h. Fractionation gave compound **14** (35.45 g, 84%), b.p. 65—67 °C (12 Torr), n_D^{20} 1.4310. Found (%): C, 46.26; H, 11.03; Si, 23.42. $C_9H_{26}N_2OSi_2$. Calculated (%): C, 46.10; H, 11.18; Si, 23.95. ^{1}H NMR, δ: 0.03 (s, 6 H, SiMe$_2$); 0.21 (s, 9 H, SiMe$_3$); 2.38 (s, 6 H, NMe$_2$); 2.68 (s, 2 H, SiCH$_2$); 3.07 (s, 3 H, SiOMe).

(*N*,*N*-Dimethylhydrazinomethyl)dimethylsilane (17). A mixture of chloromethyl(dimethyl)silane (10.86 g, 0.1 mol), *N*,*N*-dimethylhydrazine (12.02 g, 0.2 mol), and 50 mL of hexane was stirred at 40 °C for 5 h. The precipitate that formed was filtered off, and the filtrate was fractionated to give compound **17** (10.53 g, 79.6%), b.p. 119 °C, n_D^{20} 1.4130. Found (%): C, 45.60; H, 12.40; Si, 21.01. $C_5H_{16}N_2Si$. Calculated (%): C, 45.40; H, 12.19; Si, 21.23. IR, ν/cm^{-1}: 2100 (Si—H).

(Diethylaminomethyl)(*N*,*N*-dimethylhydrazino)dimethylsilane (18). A mixture of (diethylaminomethyl)dimethylsilane (5.81 g, 0.04 mol) with *N*,*N*-dimethylhydrazine (2.40 g, 0.04 mol) was stirred at 60—65 °C for 6 h. Fractionation gave compound **18** (6.63 g, 81.5%), b.p. 73—75 °C (10 Torr), n_D^{20} 1.4290. Found (%): C, 53.32; H, 12.74; Si, 13.40. $C_9H_{25}N_3Si$. Calculated (%): C, 53.13; H, 12.41; Si, 13.81. ^{1}H NMR, δ: 0.16 (s, 6 H, SiMe$_2$); 0.99 (t, 6 H, C—CH$_3$); 1.92 (s, 2 H, SiCH$_2$); 2.45 (s, 6 H, NMe$_2$); 2.47 (q, 4 H, C—CH$_2$); 4.85 (s, 1 H, NH).

3-Dimethylamino-4,4-dimethyl-1-oxa-3-aza-4-silacycloheptan-2-one (20). A mixture of silylhydrazine **8** (6.13 g, 0.03 mol) with chloro[γ-(chlorocarbonyloxy)propyl]dimethylsilane (6.45 g, 0.03 mol) was heated with a full-condensation distillation head until chlorotrimethylsilane ceased to evolve. Fractionation gave compound **20** (4.75 g, 78.3%), b.p. 121—123 °C (3 Torr), n_D^{20} 1.4479. Found (%): C, 47.82; H, 8.51; Si, 13.25. $C_8H_{18}N_2O_2Si$. Calculated (%): C, 47.49; H, 8.97; Si, 13.88. ^{1}H NMR, δ: 0.29 (s, 6 H, SiMe$_2$); 0.58 (t, 2 H, C–CH$_2$); 0.72 (t, 2 H, C—CH$_2$); 1.65 (m, 2 H, C—CH$_2$); 2.70 (s, 6 H, NMe$_2$). IR, ν/cm^{-1}: 1740 (C=O).

8-Chloro-2-trimethylsilyl-1,1,3,3,7,7-hexamethyl-1,2-diaza-3,7-disilaoctane (21). A mixture of silylhydrazine **8** (8.18 g, 0.04 mol) with 1,6-dichloro-1,1,5,5-tetramethyl-1,5-disilahexane (9.73 g, 0.04 mol) was heated with a full-condensation distillation head until chlorotrimethylsilane ceased to evolve. The residue was fractionated to give compound **21** (11.21 g, 82.6%), b.p. 94—96 °C (3 Torr), n_D^{20} 1.4553. Found (%): C, 45.95; H, 10.68; Si, 24.60; Cl, 10.38 (nonhydrolyzed chlorine). $C_{13}H_{35}ClN_2Si_3$. Calculated (%): C, 46.04; H, 10.40; Si, 24.84; Cl, 10.45. ^{1}H NMR, δ: 0.03 (s, 6 H, SiMe$_2$); 0.10 (s, 9 H, SiMe$_3$); 0.29 (s, 6 H, SiMe$_2$); 0.64 (t, 2 H, C—CH$_2$); 0.78 (t, 2 H, C—CH$_2$); 1.42 (m, 2 H, C—CH$_2$); 2.54 (s, 2 H, Si—CH$_2$); 2.60 (s, 6 H, NMe$_2$).

N*,*N*-Dimethyl-*N*′-acetylhydrazine (22).** ***A. Acetic anhydride (4.08 g, 0.04 mol) was added dropwise to silylhydrazine **1** (5.29 g, 0.04 mol), and the reaction mixture was stirred at 50 °C for 3 h. Fractionation gave compound **22** (3.90 g, 95.4%), b.p. 100 °C (11 Torr), n_D^{20} 1.4515. Found (%): C, 46.95; H, 9.94; N, 27.24. $C_4H_{10}N_2O$. Calculated (%): C, 47.04; H, 9.87; N, 27.43. ^{1}H NMR, δ: 1.89 (s, 3 H, C—CH$_3$); 2.55 (s, 6 H, NMe$_2$); 9.29 (s, 1 H, NH).

B. In a similar way, acetic anhydride (5.10 g, 0.05 mol) was added dropwise to a mixture of *N*,*N*-dimethylhydrazine (3.01 g, 0.05 mol) with hexamethyldisilazane (4.04 g, 0.025 mol), and the reaction mixture was stirred at 50 °C for 2 h. Fractionation gave compound **22** (4.81 g, 94.2%), b.p. 96 °C (10 Torr), n_D^{20} 1.4520.

1,1,1,3,8,8-Hexamethyl-2,5-dioxa-7,8-diaza-1-silaoctan-6-one (23). ***A.*** A mixture of *N*,*N*-dimethylhydrazine (7.21 g, 0.12 mol), hexamethyldisilazane (9.68 g, 0.06 mol), and propylene carbonate (12.25 g, 0.12 mol) was stirred at 60 °C for 8 h. Fractionation gave compound **23** (23.46 g, 83.4%), b.p. 125—127 °C (10 Torr), n_D^{20} 1.4366. Found (%): C, 46.36; H, 9.25; Si, 11.78. $C_9H_{22}N_2O_3Si$. Calculated (%): C, 46.12; H, 9.46; Si, 11.98. ^{1}H NMR, δ: 0.06 (s, 9 H, SiMe$_3$); 1.05 (d, 3 H, C—CH$_3$); 1.20 (d, 3 H, C—CH$_3$); 2.50 (s, 6 H, NMe$_2$); 3.55 (m, 1 H, C—CH); 4.75 (s, 1 H, NH).

B. In a similar way, a mixture of silylhydrazine **1** (15.87 g, 0.12 mol) with propylene carbonate (12.25 g, 0.12 mol) was stirred at 60 °C for 10 h. Fractionation gave compound **23** (24.24 g, 86.2%), b.p. 125—127 °C (10 Torr), n_D^{20} 1.4360.

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