Organosilicon Derivatives of 1,1-Dimethylhydrazine

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Abstract

A review of the literature data is presented, as well as the results of the own authors' investigations in the area of development of synthesis procedures, studies of the reactivity, and search for the ways of the practical application of mono- and bis-triorganylsilyl derivatives of 1,1-dimethylhydrazine with the general formula $R_{4-n}Si(NH-NMe_2)_n$ where $n = 1-4$, and $(R_3Si)_2N-NMe_2$.

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INTRODUCTION

In the second half of the past century, attention of researchers [1, 2] had been attracted to the chemistry of organosilicon derivatives of hydrazine and its monosubstituted derivatives, especially the compounds similar to 1,1-dimethylhydrazine (DMH) [3, 4]. This attention was caused by the fact that, according to the international agreements on the reduction of strategic armaments, the huge accumulated amounts of DMH, a highly toxic and explosive component of the liquid propellant, should be destroyed or processed into non-toxic and safe chemical substances and materials [5–8]. These products include its organosilicon derivatives that are easily formed in the interaction of DMH with organylchlorosilanes, organylhydrochlorosiloxanes, organylsilazanes and other functionally substituted organosilicon compounds produced on an industrial scale. The organosilicon derivatives of DMH contain highly reactive bonds: Si–N, Si–H, N–H, which opens wide possibilities for their use as new initial reagents for fine organic synthesis and intermediate products to manufacture medical and agricultural preparations.

Due to the advantageous combination of silicon, carbon and nitrogen atoms in the molecules of these compounds, their decomposition in the low-temperature plasma of the high-frequency electric discharge results in the deposition of high-quality thin dielectric layers which are necessary for the development of modern microelectronic devices.

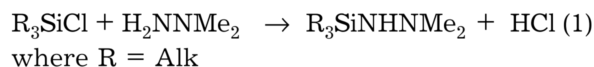
This impelled us to systematize literature data and the results of our own investigations in the area of synthesis, reactivity and outlooks of the practical use of organosilicon derivatives of DMH with the general formula $R_{4-n}Si(NHNMe_2)_n$, where $n = 1–4$, and $(R_3Si)_2NNMe_2$.

MONOSILYL DERIVATIVES OF DMH

Synthesis procedures

The methods of synthesis of this type of compounds can be divided into four groups: 1) reactions of DMH with organylchlorosilanes (hydrazinolysis); 2) the interaction of DMH with organylaminosilanes (hydrazination); 3) dehydrocondensation of DMH with organylhydridosilanes; 4) organometallic synthesis.

Hydrazinolysis reactions. The first representatives of triorganylsilylhydrazines were obtained with the yield of 50–70 % in the 50-es of the past century by means of the reaction of DMH with organylhalosilanes [9]. Triethyl amine or DMH excess were used as an acceptor for the formed HCl:



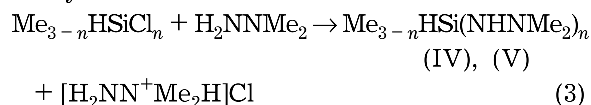
$$R_3SiCl + H_2NNMe_2 \rightarrow R_3SiNHNMe_2 + HCl \quad (1)$$

where R = Alk

$$H_2NNMe_2 + HCl \rightarrow [H_2NN^+Me_2H]Cl^- \quad (2)$$

The use of benzene as a solvent did not cause an increase in the yield of trialkyl(2,2-dimethylhydrazino)silanes. However, when the reaction was carried out in the ether, $Me_2SiNHNMe_2$ is formed with the yield of 88 % [10]. To increase the yield of triorganylsilylhydrazines, we carried out the reaction of trimethyl-, dimethylphenyl- and triethoxychlorosilane with the ether solution of DMH in excess at 0 °C, followed by boiling of the reaction mixture for 1 h. As a result, $Me_3SiNHNMe_2$ (I), $Me_2PhSiNHNMe_2$ (II) and $(EtO)_3SiNHNMe_2$ (III) were obtained with the yield of 85–90 %. A nonpolar solvent – pentane – turned out to be even more convenient for this purpose. Though the yield of the final product increases only by several percent, the low solubility of the formed DMH hydrochloride simplifies isolation and purification of the target products.

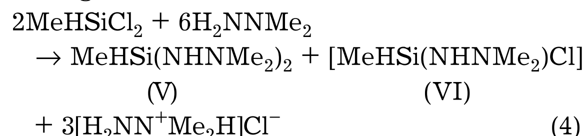
Side processes bring complications into the interaction of DMH with organylhydrochlorosilanes, so the yield of the target products was 10–40 % [11, 12]. However, carrying out the reaction of DMH with methylhydrochlorosilanes in the ether we obtained the organosilicon derivatives of DMH (IV), (V) containing Si–H bonds with the yield 58–65 %, respectively:



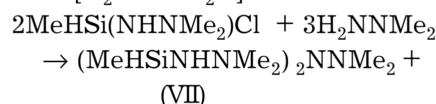
$$Me_{3-n}HSiCl_n + H_2NNMe_2 \rightarrow \underset{(IV),\ (V)}{Me_{3-n}HSi(NHNMe_2)_n} + [H_2NN^+Me_2H]Cl \quad (3)$$

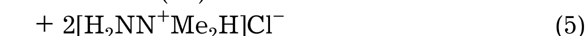
where n = 1 (IV), 2 (V).

After the interaction of methylchlorosilane with DMH at the molar ratio of 1 : 4, along with the expected compound (V), product (VII) was isolated; it contains a $Si–N(NMe_2)–Si$ group. Compound (VII) is likely to be formed as a result of the nucleophilic substitution of chlorine atoms in the unstable intermediate (VI) during the interaction with DMH:



$$2MeHSiCl_2 + 6H_2NNMe_2 \rightarrow \underset{(V)}{MeHSi(NHNMe_2)_2} + \underset{(VI)}{[MeHSi(NHNMe_2)Cl]} + 3[H_2NN^+Me_2H]Cl^- \quad (4)$$





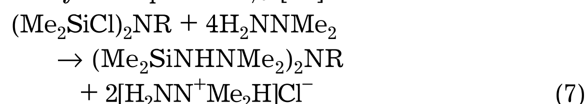
$$2MeHSi(NHNMe_2)Cl + 3H_2NNMe_2 \rightarrow \underset{(VII)}{(MeHSiNHNMe_2)_2NNMe_2} + 2[H_2NN^+Me_2H]Cl^- \quad (5)$$

The yield of compounds (V) and (VII) was 24 and 54 %, respectively.

By means of hydrazinolysis of he corresponding functionally substituted organylchlorosilanes, the organosilicon derivatives of DMH containing $Si–N–Me_3$, Si–N–Si and Si–Si groups were synthesized. For instance, by treating dimethyl(dimethylamino)chlorosilane with DMH in naphtha, dimethyl(dimethylamino)-(2,3-dimethylhydrazone)silane was obtained [13]:

$$Me_2NSiMe_2Cl + 2H_2NNMe_2 \rightarrow Me_2NSiMe_2(NHNMe_2) + [H_2NN^+Me_2H]Cl^- \quad (6)$$

Using the reaction of 1,1,3,3-tetramethyl-1,3-dichlorodisilazanes with DMH, corresponding hydrazinosilazanes were synthesized with the yield up to 70 % [14]:



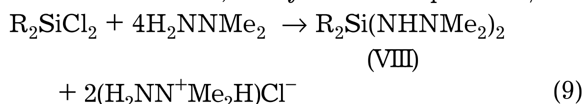
$$(Me_2SiCl)_2NR + 4H_2NNMe_2 \rightarrow (Me_2SiNHNMe_2)_2NR + 2[H_2NN^+Me_2H]Cl^- \quad (7)$$

On addition of 1,1,2,2-tetramethyl-1,2-1,2-dichlorodisilane to the solution of DMH, an exothermal formation of 1,1,2,2-tetramethyl-1,2-bis(2^1,2^1-dimethylhydrazino)disilane occurs [13]:

$$(Me_2SiCl)_2 + 4H_2NNMe_2 \rightarrow (Me_2SiNHNMe_2)_2 + 2[H_2NN^+Me_2H]Cl^- \quad (8)$$

Hydrazinolysis of diorganyldichloro-, organyltrichloro- and tetrachlorosilanes is insufficiently investigated.

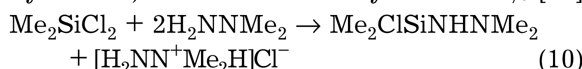
The first representative of diorganylbis(2,2-dimethylhydrazino)silanes was obtained with a small yield in the reaction of DMH with diphenyldichlorosilane [13–16]. Dialkyl-bis(2,2-dimethylhydrazino)silanes were synthesized in a similar manner; the yield was up to 60 %:



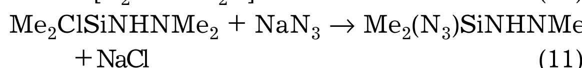
$$R_2SiCl_2 + 4H_2NNMe_2 \rightarrow \underset{(VIII)}{R_2Si(NHNMe_2)_2} + 2(H_2NN^+Me_2H)Cl^- \quad (9)$$

where R = Ph, Et, Me

The reaction of DMH with dimethyldichlorosilane taken in excess leads to the formation of dimethyl(2,2-dimethylhydrazino)chlorosilane. Further interaction with sodium azide transforms it into dimethyl(2,2-dimethylhydrazino)azidosilane with a yield of 70 % [17]:

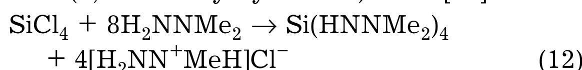


$$Me_2SiCl_2 + 2H_2NNMe_2 \rightarrow Me_2ClSiNHNMe_2 + [H_2NN^+Me_2H]Cl^- \quad (10)$$



$$Me_2ClSiNHNMe_2 + NaN_3 \rightarrow Me_2(N_3)SiNHNMe + NaCl \quad (11)$$

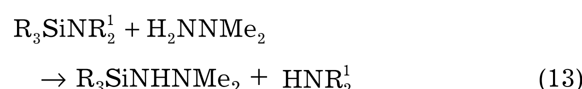
The interaction of DMH with tetrachlorosilane result in the formation of unstable tetrakis(2,2-dimethylhydrazino)silane [18]:



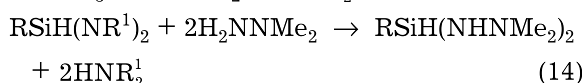
$$SiCl_4 + 8H_2NNMe_2 \rightarrow Si(HNNMe_2)_4 + 4[H_2NN^+MeH]Cl^- \quad (12)$$

On the whole, hydrazinolysis of organosilicon compounds containing a Si–Cl bond is the most general method of obtaining Si-substituted DMH derivatives. Its undoubted advantages are simplicity of reaction conduction and the availability of the initial reagents. However, synthetic capacities of this method are limited in a number of cases by rather low yields of final products; their formation and purification are accompanied by the formation of a large amount of precipitated DMH hydrochlorides or HCl acceptor (triethyl amine).

Hydrazination reaction. The above-mentioned disadvantages are absent from the method of obtaining monosilyl DMH derivatives by means of the reaction of organylaminosilanes with DMH called hydrazination [19, 20]:



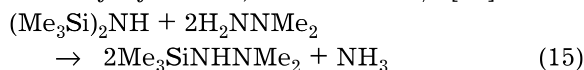
$$R_3SiNR^1_2 + H_2NNMe_2 \rightarrow R_3SiNHNMe_2 + HNR^1_2 \quad (13)$$



$$RSiH(NR^1)_2 + 2H_2NNMe_2 \rightarrow RSiH(NHNMe_2)_2 + 2HNR^1_2 \quad (14)$$

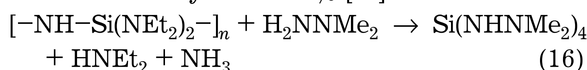
where R = Me, Et; R^1 = Et.

These processes are catalysed by ammonium chloride and sulphate or by DMH hydrochloride. The yield of the target products of hydrazination reaches 50 %. Hexametyldisilazane can also be used as the silylating agent. In this case, the yield of trimethyl(2,2-dimethylhydrazino)silane is 67.5 % [19]:



$$(Me_3Si)_2NH + 2H_2NNMe_2 \rightarrow 2Me_3SiNHNMe_2 + NH_3 \quad (15)$$

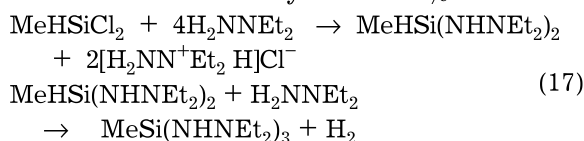
The interaction of a mixture of hexa(diethylamino)cyclotrisilazane with DMH leads to the formation of tetrakis(2,2-dimethylhydrazino)-silane with the yield of 28 % [18]:



$$[-NH-Si(NEt_2)_2-]_n + H_2NNMe_2 \rightarrow Si(NHNMe_2)_4 + HNEt_2 + NH_3 \quad (16)$$

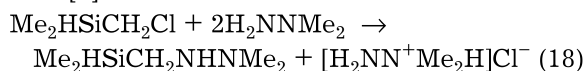
where n = 3, 4.

Dehydrocondensation reaction. A principal possibility to obtain the organosilicon derivatives of DMH by means of dehydrocondensation of organylsilanes with hydrogen-containing hydrazines was demonstrated for the first time for the interaction of methyldichlorosilane with 1,1-diethylhydrazine [12]. Along with the product of hydrazination, methylbis(2,2-diethylhydrazino)silane (yield: 18 %), the product of dehydrocondensation of the latter with DMH – methyl-tris(2,2-diethylhydrazino)silane – was isolated with the yield of 22 %:



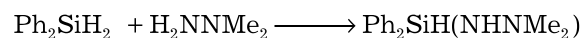
$$\left.\begin{array}{l} MeHSiCl_2 + 4H_2NNEt_2 \rightarrow MeHSi(NHNEt_2)_2 + 2[H_2NN^+Et_2H]Cl^- \\ MeHSi(NHNEt_2)_2 + H_2NNEt_2 \rightarrow MeSi(NHNEt_2)_3 + H_2 \end{array}\right\} \quad (17)$$

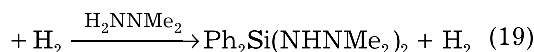
At the same time, the reaction of dimethyl(chloromethyl)silane with DMH leads only to the formation of hydrazination products [3]:



$$Me_2HSiCH_2Cl + 2H_2NNMe_2 \rightarrow Me_2HSiCH_2NHNMe_2 + [H_2NN^+Me_2H]Cl^- \quad (18)$$

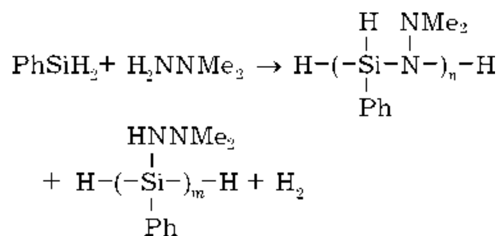
One hydrogen atom or both of them participate in dehydrocondensation product [21]:





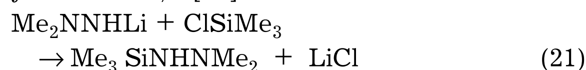
$$Ph_2SiH_2 + H_2NNMe_2 \longrightarrow Ph_2SiH(NHNMe_2) + H_2 \xrightarrow{H_2NNMe_2} Ph_2Si(NHNMe_2)_2 + H_2 \quad (19)$$

The interaction of phenylsilane with DMH leads to the formation of poly[(phenyl)-N-(dimethylamino)azane] and poly[phenyl(dimethylhydrazino)silane, respectively [21, 22]:



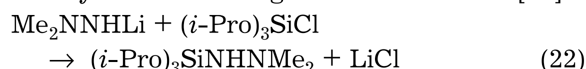
In spite of rather high yield and simplicity of carrying out the reaction, dehydrocondensation method did not win wide application in synthesis.

Organometallic synthesis. A method to introduce triorganylsilyl groups to the nitrogen atom has been developed. It is based on the use of the lithium derivative of DMH. Thus, in the interaction of 1,1-dimethyl-2-lithiumhydrazine with trimethylchlorosilane, trimethyl(2,2-dimethylhydrazino)silane was obtained with a yield of 61 % [10]:



$$Me_2NNHLi + ClSiMe_3 \rightarrow Me_3SiNHNMe_2 + LiCl \quad (21)$$

Triisopropoxy(2,2-dimethylhydrazino)silane was synthesized using a similar reaction [13]:



$$Me_2NNHLi + (i\text{-}Pro)_3SiCl \rightarrow (i\text{-}Pro)_3SiNHNMe_2 + LiCl \quad (22)$$

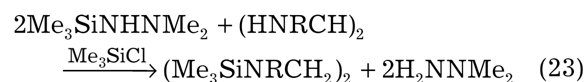
A shortcoming of this method is the necessity to obtain the corresponding lithium derivatives.

Chemical transformations

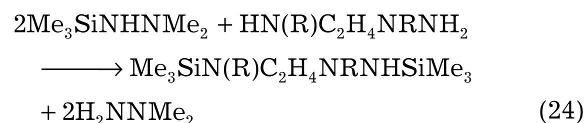
Reactions proceeding with the rupture of Si–N bond. Trialkyl(2,3-dimethylhydrazino)-silanes are mobile liquids with typical odour, rather stable to heating and to the moisture of the air but readily splitting at the Si–N bond under the action of acids and bases. With an increase in the amount of 2,2-dimethylhydrazine substituents at the silicon atom, the rate of their removal increases. Diorganyl-bis(2,3-dimethylhydrazino)silanes readily react with water, alcohols or dry hydrogen chloride; the interaction results in the release of DMH or its hydrochloride, and in the formation of the corresponding organosilicon compounds: diorganylsilanodiols, diorganyldialkoxysilanes or diorganyldichlorosilanes.

Splitting of hydrazinohydrosilanes by water or alcohol proceeds at the Si–N and Si–H bonds with the release of DMH and hydrogen; it is accompanied by heat evolution, which can lead to explosions.

Reactions proceeding with Si–N bond rupture include silylation of diamines [23] or non-symmetric aminohydrazines [24] with trimethyl(2,2-dimethylhydrazino)silane in the presence of catalytic amounts of trimethylchlorosilane:



$$2Me_3SiNHNMe_2 + (HNRCH)_2 \xrightarrow{Me_3SiCl} (Me_3SiNRCH_2)_2 + 2H_2NNMe_2 \quad (23)$$

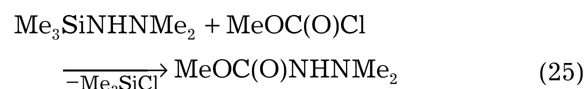


$$2Me_3SiNHNMe_2 + HN(R)C_2H_4NRNH_2 \longrightarrow Me_3SiN(R)C_2H_4NRNHSiMe_3 + 2H_2NNMe_2 \quad (24)$$

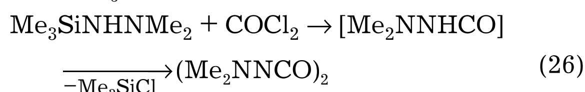
where R = CH_3, C_4H_9.

In the case when dimethylbis(2,3-dimethylhydrazino)silane as a silylating agent, the corresponding cyclic organosilicon compounds are formed [25, 26].

The reaction of trimethyl(2,2-dimethylhydrazino)silane with methyl chloroformiate or phosgene proceeds at the Si–N bond, too [27, 28]:

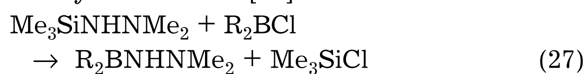


$$Me_3SiNHNMe_2 + MeOC(O)Cl \xrightarrow[-Me_3SiCl]{} MeOC(O)NHNMe_2 \quad (25)$$



$$Me_3SiNHNMe_2 + COCl_2 \rightarrow [Me_2NNHCO] \xrightarrow[-Me_3SiCl]{} (Me_2NNCO)_2 \quad (26)$$

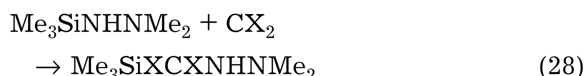
The reaction of trimethyl(2,2-dimethylhydrazino)silane with a diorganylchloroboranes proceeds similarly leading to the corresponding diorganyl(2,2-dimethylhydrazino)boranes and trimethylchlorosilane [29]:



$$Me_3SiNHNMe_2 + R_2BCl \rightarrow R_2BNHNMe_2 + Me_3SiCl \quad (27)$$

where R = C_4H_9, C_6H_5.

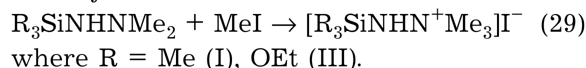
Heterocumulenes like CX_2 (X = O, S) get inserted at the Si–N bond of trimethyl(2,2-dimethylhydrazino)silane [30, 31]:



$$Me_3SiNHNMe_2 + CX_2 \rightarrow Me_3SiXCXNHNMe_2 \quad (28)$$

Reactions proceeding with the conservation of the Si–N bond. 2-Alkyl-2,2-dimethylhydrazinium halides $[H_2MeNN^+RMe_2]Hal^-$ exhibit clearly expressed biological effect, in particular high antimicrobial and fungicidal activity [6–8]. For the purpose of obtaining similar quaternary salts of organosilicon derivatives of DMH, we investigated the reactions of com-

pounds (I) and (III) with methyl iodide in acetonitrile [32, 33]. Corresponding quaternary hydrazinium salts were isolated with a quantitative yield:

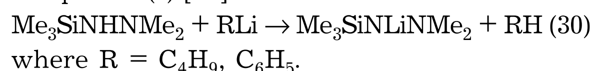


$$R_3SiNHNMe_2 + MeI \rightarrow [R_3SiNHN^+Me_3]I^- \quad (29)$$

where R = Me (I), OEt (III).

In the interaction of 1,1,2,2-tetramethyl-1,2-bis(2^1,2^1-dimethylhydrazino)disilane with methyl iodide taken in the molar ratio of 1 : 2, the salt $I^-[Me_2(Me_3N^+NH)Si{-}Si(NHN^+Me_3)Me_2]I^-$ is formed with the yield of 93 %.

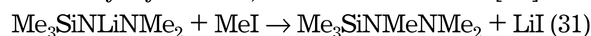
Butyl or phenyl lithium easily metalate compound (I) [10]:



$$Me_3SiNHNMe_2 + RLi \rightarrow Me_3SiNLiNMe_2 + RH \quad (30)$$

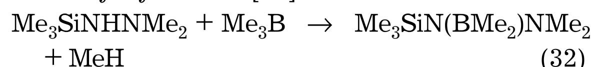
where R = C_4H_9, C_6H_5.

The resulting organolithium compound allows one to introduce various substituents at the nitrogen atom. For instance, after its treatment with methyl iodide, trimethyl(1,2,2-trimethylhydrazino)silane was isolated [34]:



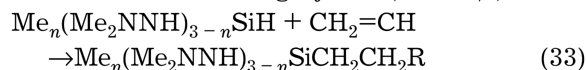
$$Me_3SiNLiNMe_2 + MeI \rightarrow Me_3SiNMeNMe_2 + LiI \quad (31)$$

Trimethylborate interacts with (I) and forms 1-trimethylsilyl-1-dimethylboryl-2,2-dimethylhydrazine [35]:



$$Me_3SiNHNMe_2 + Me_3B \rightarrow Me_3SiN(BMe_2)NMe_2 + MeH \quad (32)$$

Monosilyl DMH derivatives containing the Si–H bond undergo hydrosilylation with unsaturated compounds with the conservation of the Si–N bond [36]. Thus, dimethyl(2,2-dimethylhydrazino)silane and methyl-bis(dimethylhydrazino)silane in the presence of catalytic amounds of rhodium (dicarbonyl)-acetylacetonate undergo addition to the terminal atom of the double bond of 1-hexene and styrene forming adducts with rather high yields (45–84 %):



$$Me_n(Me_2NNH)_{3-n}SiH + CH_2{=}CH \rightarrow Me_n(Me_2NNH)_{3-n}SiCH_2CH_2R \quad (33)$$

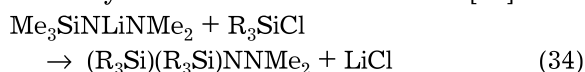
where R = C_4H_9, C_6H_5; n = 1, 2.

The interaction with acetylene compounds containing a terminal triple bond proceeds in a more complicated manner. Heating an equimolar mixture of the same hydride silanes with phenyl acetylene in the presence of a rhodium catalyst one obtains a complex mixture of products with boiling points varied within a broad range. The fractions representing, as suggested by the NMR ^{1}H data, mainly the products of addition to the triple bond were isolated (with the yields of 10–20 %); however, attempts to purify them finally with the help of vacuum distillation failed. Phenyl acetylene, a CH acid, is likely to act as a catalyst causing disproportionation of organosilicon DMH derivatives containing a Si–H bond.

DISILYL DMH DERIVATIVES

Synthesis procedures

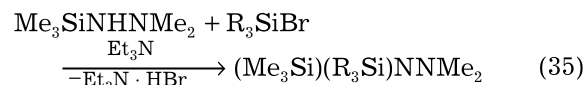
Separate representatives of this class of compounds were obtained by means of a reaction of the lithium derivative of (I) with trimethylchloro- or tetrachlorosilane [10]:



$$Me_3SiNLiNMe_2 + R_3SiCl \rightarrow (R_3Si)(R_3Si)NNMe_2 + LiCl \quad (34)$$

where R = Me, Cl.

A more convenient method to synthesize disilyl DMH derivatives with the yield up to 90 % is the reaction of (I) with trimethylbromo- or trichlorobromosiloane in ether in the presence of triethylamine [33]:



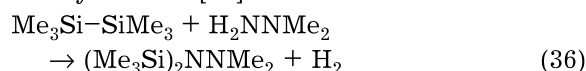
$$Me_3SiNHNMe_2 + R_3SiBr \xrightarrow[-Et_3N \cdot HBr]{Et_3N} (Me_3Si)(R_3Si)NNMe_2 \quad (35)$$

where R = Me, Cl.

The interaction of DMH and its monosilyl derivatives $R_3SiNHNMe_2$ with organylhalosilanes qualitatively differs from the reactions with MeI and other primary alkyl halides. While alkylation proceeds at the NMe_2 group, silylation proceeds at NH_2 or R_3SiNH groups (in the case of Me_3SiBr and Cl_3SiBr). One of the factors affecting the reaction direction can be the steric factor because it is known that branched organyl halides (isopropyl iodide, picryl chloride, 2,4-dinitrochlorobenzene) do not quaternize DMH but form 1,1-dimethyl-2-organylhydrazines [37]. At the same time, the formation of sterically hindered $(Me_3Si)_2NNMe_2$ according to scheme (35) points to the fact that the direction of the reaction is determined not only by steric factors but also electron ones. To understand the reasons of differences in the behaviour of DMH in alkylation and silylation reactions, reagents and products were calculated by means of MP2/6-31G(d) [33]. Calculation of MeCl and Me_3SiCl molecules showed that silylation is determined to a large extent by the charge control, while alkylation by the orbital one. For example, unlike for a small pos-

itive charge of the methyl group in MeCl, there is a large positive charge on the silicon atom in Me_3SiCl molecule. This means that alkylation of DMH should proceed at the N^2 atom, of the NMe_2 group, the atomic orbitals of which make the largest contribution into the highest occupied molecular orbital, while silylation should proceed at the N^1 atom, of the NH_2 group, which has the largest negative charge.

An original method to obtain a disilyl derivative of hydrazine with almost the quantitative yield is the reaction of DMH with hexamethyldisilane [38]:

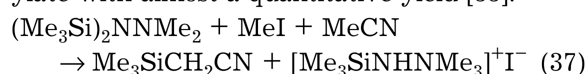


$$Me_3Si{-}SiMe_3 + H_2NNMe_2 \rightarrow (Me_3Si)_2NNMe_2 + H_2 \quad (36)$$

However, this reaction has a limited application due to the necessity to synthesize the initial disilanes.

Chemical transformations

In contrast to the monosilyl derivatives of DMH, $Me_3Si(Cl_3Si)NNMe_2$ does not react with MeI either in low-polar solvents or in acetonitrile. The compound $(Me_3Si)_2NNMe_2$ does not interact with MeI in the ether, THF, CH_2Cl_2 even under heating. However, in acetonitrile, trimethylsilylation of acetonitrile proceeds with the formation of trimethylsilylacetonitrile and trimethyl(2,2-dimethylhydrazino)silane iodomethylate with almost a quantitative yield [33]:

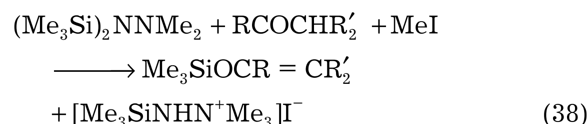


$$(Me_3Si)_2NNMe_2 + MeI + MeCN \rightarrow Me_3SiCH_2CN + [Me_3SiNHNMe_3]^+I^- \quad (37)$$

A possible intermediate of this reaction is 1,1,1-trimethyl-2,2-bis(trimethylsilyl)hydrazinium iodide $[(Me_3Si)_2NHNMe_3]^+I^-$ which is able silylate such CH acids as acetonitrile.

To confirm this assumption, we investigated the reaction of $(Me_3Si)_2NNMe_2$ with phenyl acetylene and trimethylpropargyloxysilane in the presence of MeI. However, the reaction does not proceed in nonpolar solvents; in acetonitrile, only $[Me_3SiNHNMe_3]^+I^-$ and Me_3SiCH_2CN were isolated. Products of silylation of the C–H bond of acetylenes are not formed even in trace amounts, so the mechanism of this reaction requires further investigation.

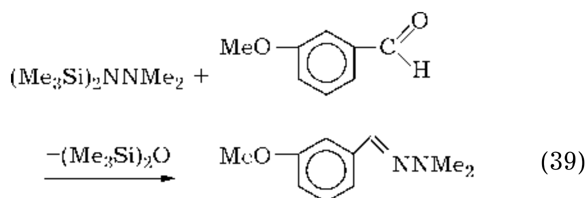
A new preparative method to synthesize difficultly available silyl ethers of enols with a high yield was developed on the basis of the reaction of 1,1-dimethyl-2,2-bis(trimethylsilyl)hydrazine and easily enol-forming ketones in the presence of MeI [39]:



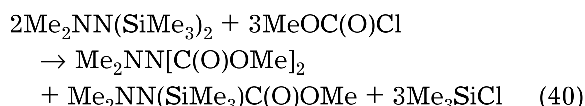
$$(Me_3Si)_2NNMe_2 + RCOCHR'_2 + MeI \longrightarrow Me_3SiOCR = CR'_2 + [Me_3SiNHN^+Me_3]I^- \quad (38)$$

where R = Ph, t-Bu; $R' = H, Me$.

1,1-Dimethyl-2,2-bis(trimethylsilyl)hydrazine is easily transformed into the hydrazone by the interaction with aldehydes [38]:

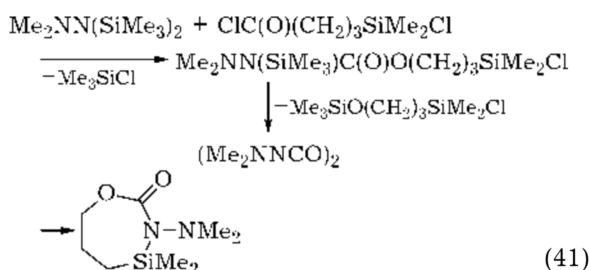


The reaction of bis(silyl)hydrazines with methylchloroformiate proceeds mainly with detachment of both silyl groups. The product of detachment of one silyl group is formed only as a by-product [3, 28]:

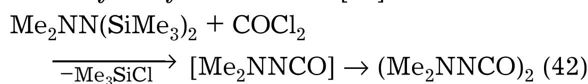


$$2Me_2NN(SiMe_3)_2 + 3MeOC(O)Cl \rightarrow Me_2NN[C(O)OMe]_2 + Me_2NN(SiMe_3)C(O)OMe + 3Me_3SiCl \quad (40)$$

In the investigation of the reaction of bis(silyl)hydrazines with organosilicon chloroformiate, the formation of isocyanate was observed; however, the prime isolated products were linear and cyclic urethanes [3]:



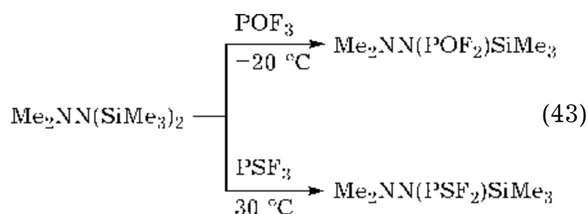
Phosgene easily splits the Si–N bonds in the disilyl DMH derivatives with the formation of dimethylisocyanate dimer [28]:

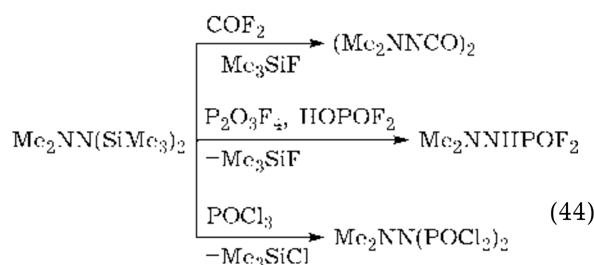


$$Me_2NN(SiMe_3)_2 + COCl_2 \xrightarrow{-Me_3SiCl} [Me_2NNCO] \rightarrow (Me_2NNCO)_2 \quad (42)$$

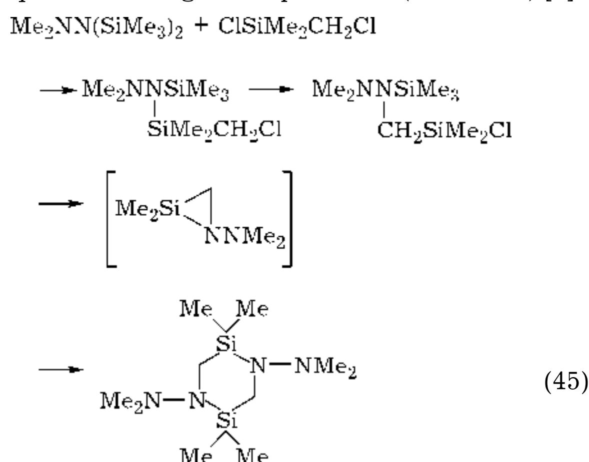
The interaction of 1,1-dimethyl-2,2-bis(trimethylsilyl)hydrazine with POF_3 and PSF_2 porceeds with the detachment of one trimethylsilyl group, while the reactions with

COF_2, $P_2O_3F_4$ and $POCl_3$ are participated by both Si–N bonds [41, 40]:





1,1-Dimethyl-2,2-bis(trimethylsilyl)hydrazine is able to transsilylate dimethylchloromethylsilane. The product of substitution of one trimethylsilyl group for chloromethyldimethylsilyl which is formed at the first stage is transformed into 2,2,5,5-tetramethyl-1,4-dimethylamino-1,4-diaza-2.5-disilacyclohexane as a result of subsequent rearrangement processes (SiN a SiC) [3]:



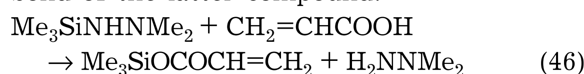
PRACTICAL APPLICATION OF THE ORGANOSILICON DERIVATIVES OF DMH

Organosilicon compounds containing the Si–N bonds have found wide application in various areas of science and technology. These compounds include first of all organylsilylamines and silazanes which are used as efficient silylating agents, initial reagents for fine organic synthesis, surface modifying agents, raw material for obtaining ceramic materials, reagents for the formation of thin film structures etc. The data on the practical use of organosilicon derivatives of hydrazines are scarce [4], perhaps because they are insufficiently investigated.

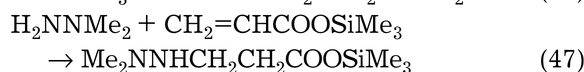
Organylsilylhydrazines are strong reducing agents; their reducing properties increase if a molecule contains the Si–H bonds.

The high reactivity of the Si–N bond in silylhydrazines allows one to use these compounds as silytating agents in the synthesis of polyamines, azasylacyclohexanes [4, 17], and as a raw material in the synthesis of urethanes and silicon- and nitrogen-containing linear and cyclic compounds [3].

The interaction of trimethyl(2,2-dimethylhydrazino)silane with acrylic acid leads to the formation of trimethylsilyl ester of 3-(2,2-dimethylhydrazinyl)propionic acid with the yield of 85 % [42]. The reaction proceeds through the stage of Si–N bond splitting in the initial organosilicon compound with the release of DMH and trimethylsilylacrylate. 1,1-Dimethylhydrazine then adds to the unsaturated bond of the latter compound:

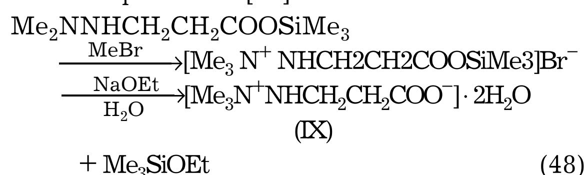


$$Me_3SiNHNMe_2 + CH_2{=}CHCOOH \rightarrow Me_3SiOCOCH{=}CH_2 + H_2NNMe_2 \quad (46)$$



$$H_2NNMe_2 + CH_2{=}CHCOOSiMe_3 \rightarrow Me_2NNHCH_2CH_2COOSiMe_3 \quad (47)$$

The resulting compound is an intermediate product for the synthesis of Mildronat preparation (IX) possessing a clearly exhibited cardiotropic effect [43]:



$$Me_2NNHCH_2CH_2COOSiMe_3 \xrightarrow{MeBr} [Me_3N^+NHCH2CH2COOSiMe3]Br^- \xrightarrow[H_2O]{NaOEt} [Me_3N^+NHCH_2CH_2COO^-]\cdot 2H_2O\ (IX) + Me_3SiOEt \quad (48)$$

A new direction of the practical application of organosilicon DMH derivatives is their use as precursors for the plasmachemical deposition of thin dielectric layers for various functional purposes in modern microelectronic technology [44, 45]. A large set of high-purity organosilicon derivatives of DMH was synthesized and tested during the joint investigations carried out by the Institute of Chemistry, SB RAS (Irkutsk) and Institute of Inorganic Chemistry, SB RAS (Novosibirsk). The most efficient compounds were $Me_3SiNHNMe_2$ (I),

$Me_2HSiNHNMe_2$ (IV) and $Me_2Si(NHNMe_2)_2$ (VIII). During decomposition in the plasma of high-frequency (HF) electric discharge, depending on the composition of the vapour and gas mixture and on reactor type, the films of different chemical composition are formed [44]. For instance, high-quality silicon dioxide layers are deposited from a vapour-gas mixture of (I) or (II) with oxygen at 150–300 °C. The films of phosphorus-silicate glass with the required phosphorus to silicon atomic ratio were obtained from a mixture of (I) or (II), oxygen and trimethylsilyldimethylphosphate $Me_2SiOP(OMe)_2$.

A favourable combination of silicon, carbon and nitrogen atoms n the molecules of organosilicon DMH derivatives makes these compounds promising precursors for obtaining silicon carbonitride.

Silicon carbonitride $Si_xC_yN_z$ is a unique composite multifunctional material that combines the best properties of carbon nitride and silicon nitride; it is a promising compound for wide application in modern technology. In microelectronic technology, silicon carbonitride thin films can be used as gate dielectrics, reinforcing, passivating, radioresistant, protective and other coatings. At present, silicon carbonitride layers are obtained with the help of different physical sputtering methods (ionic, magnetron, electron) or by means of chemical vapour deposition (CVD) at a temperature about 1300 K. However, the use of physical methods does not allow one to obtain high-quality layers. In addition, the CVD procedure implies high-energy consumption and the use of explosive gas mixtures (monosilane and methane with hydrogen, nitrogen or ammonia), which brings about essential technological problems in achieving stable results and in providing the safety of processes. In this connection, the processes based on the use of organosilicon derivatives of DMH take on special significance.

A new process of obtaining high-quality silicon carbonitride films was developed on the basis of compounds (IV) or (VIII) using vapour deposition by means of the remote HF plasma discharge in the atmosphere of helium or hydrogen [46–50].

Another promising direction of the use of organosilicon derivatives of DMH in microelectronic and other modern technologies is connected with the presence of easily hydrolizing Si–N bonds in these compounds. Silicon- and nitrogen-containing compounds (hexamethyldisilazane, organylsilylamines) are widely used as adhesives and for hydrophobization of various materials. Comparative tests showed that compounds (I) and (IV) are more efficient than the known adhesives, which are explained by the increased reactivity of the Si–N bond in (I) and in (IV).

CONCLUSIONS

The introduction of organosilicon substituents is a promising direction of the utilization of toxic and explosive 1,1-dimethylhydrazine. The formed safe organosilicon derivatives of DMH easily enter various chemical transformations, which proceed, depending on the composition, structure of substrate and reaction conditions, with the participation of Si–N, Si–H and N–H bonds, and the ternary nitrogen atom, which is able to undergo quaternization.

Because of this, the organosilicon derivatives of DMH can be and are widely used in fine organic and organoelement synthesis (to obtain polyamines, azasilacyclohexanes, urethanes, silyl esters of enoles, *etc.*), and also as semi-products for the synthesis of medical preparations (for example, cardioprotecting Mildronat).

Due to the favourable combination of atoms Si, N and C in the molecules of these compounds, treatment with the plasma of the high-frequency electric discharge allows one to deposit thin dielectric layers for various purposes (including such a promising material as silicon carbonitride) which are necessary for the development of modern microelectronic devices.

High reactivity of the Si–N bond in the molecules of organosilicon derivatives of DMH allows recommending these compounds as new promoters of photoresist adhesion in microelectronic technologies, and these promoters are more efficient than hexamethyldisilazane used for this purpose at present.

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