Reaction of Organosilicon Derivatives of 1,1-Dimethylhydrazine with Methyl Iodide

Academician M. G. Voronkov, B. A. Gostevskii, B. A. Shainyan, V. I. Rakhlin, R. G. Mirskov, and O. S. Makarova

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The reactions of haloalkanes with 1,1-dimethylhydrazine (DMH) give 1,1-dimethyl-1-alkylhydrazonium salts, which possess practically valuable properties [1-3]. Similar reactions of organosilicon derivatives of DMH have not been studied. To study these reactions, we synthesized organosilicon DMH derivatives: Me₃SiNHNMe₂ (1), (EtO)₃SiNHNMe₂ (2), Me₂NNHSi(Me)₂Si(Me)₂NHNMe₂ (3), (Me₃Si)₂NNMe₂ (4), and (Me₃Si)(Cl₃Si)NNMe₂ (5).

Compounds 1–3 were prepared by reactions of the corresponding triorganylchlorosilanes with DMH in ether [4]. Previously, compounds 4 and 5 were prepared by the reaction of lithiated 1,1-trimethyl-2-triorganyl-silylhydrazines with chlorosilane according to the following pattern [5]:

$$R_3SiNLiNMe_2 + R_3^1SiCl \longrightarrow (R_3Si)(R_3^1Si)NNMe_2.$$

We developed a method for the synthesis of 4 and 5 in yields of up to 80% by the reaction of 1 with triorganylbromosilanes in the presence of triethylamine:

$$R_{3}SiNHNMe_{2} + R_{3}^{1}SiBr \xrightarrow{Et_{3}N}_{-Et_{3}NH^{+}Br} (R_{3}Si)(R_{3}^{1}Si)NNMe_{2},$$
$$R = Me; R^{1} = Me, Cl.$$

The reactions of organosilicon DMH derivatives with MeI were carried out in evacuated glass tubes in ether or acetonitrile. Compounds 1-3 readily react with MeI to give products in almost quantitative yields:

$$R_{3}SiNHNMe_{2} + MeI \longrightarrow [R_{3}SiNHNMe_{3}]_{2}^{+}I^{-},$$

$$R = Me, EtO.$$

$$[Me_{2}NNHSiMe_{2}]_{2}$$

$$+ MeI \longrightarrow [Me_{3}N^{+}NHSiMe_{2}]_{2}2I^{-}.$$

The reactions of compounds 4 and 5 with MeI follow an unexpected route. Compound 5 does not react with MeI in low-polarity solvents or acetonitrile. Compound 4 also does not react with MeI in ether, THF,

Favorsky Institute of Organic Chemistry,

ul. Favorskogo 1, Irkutsk, 664033 Russia

CHCl₃, or CH₂Cl₂ even under long heating to 100°C. The reaction easily proceeds in acetonitrile but still does not give the expected $(Me_3Si)_2NN^+Me_3I^-$ salt. Instead, the cleavage of the Si–N bond by the acetonitrile molecule proceeds almost quantitatively:

 $(Me_3Si)_2NNMe_2 + MeI + MeCN$

$$\rightarrow$$
 [Me₃SiNHNMe₃]⁺I⁻ + Me₃SiCH₂N.

We suggested that this reaction gives intermediately 1,1,1-trimethyl-2,2-bis(trimethylsilyl)hydrazinium iodide $[(Me_3Si)_2NHNMe_3]^+I^-$, which is a good silylating agent able to silylate CH-acids. To verify this assumption, we studied the reactions of compound **4** with MeI, phenylacetylene, and trimethylpropargyloxysilane. However, these reactions do not proceed in nonpolar solvents, while, in acetonitrile, only $[Me_3SiNHNMe_3]^+I^-$ and Me_3SiCH_2CN were isolated. Not even traces of silylation products of the acetylene CH bond were detected by GLC with reference compounds. Therefore, the reaction mechanism requires further investigation.

The reaction of DMH with Me₃SiCl differs qualitatively from its reaction with MeI and other primary alkyl halides. Whereas methylation involves the Me₂N group, silulation involves the NH₂ group. The reaction route may be influenced by the steric factor. Indeed, branched organyl halides (isopropyl iodide, picryl chloride, 2,4-dinitrochlorobenzene) do not quaternize DMH but yield 1,1-dimethyl-2-organylhydrazines [6]. However, the formation of sterically strained $(Me_3Si)_2NNMe_2$ in the reaction of 1 with Me_3SiBr indicates that the reaction pathway is determined by not only steric but also electronic factors. To elucidate the reasons for the different behaviors of DMH toward alkylation and silvlation, we carried out calculations for the reactants and the reaction products using the MP2/6-31G(d) method, which gives the most chemically reasonable charges on atoms [7]. The Mulliken charges, the electrostatic charges, and the degrees of localization of the HOMO on the nitrogen atoms in DMH and compounds 1 and 4 are summarized in Table 1.

Calculations for MeCl and Me₃SiCl attest that silylation is largely dictated by charge control, while alkylation is under orbital control. This is indicated by the

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Molecule	Atom	Mulliken charge	Electrostatic charge	Contribution of nitrogen AOs to the HOMO
H ₂ N ¹ -N ² Me ₂	N ¹	-0.647 (0.012)*	-0.799 (-0.071)	5.0%
	N^2	-0.393	-0.135	53.7%
Me ₃ SiN ¹ H–N ² Me ₂	N^1	-0.738 (-0.403)	-0.757 (-0.394)	34.7%
	N^2	-0.384	-0.188	18.6%
$(Me_{3}Si)_{2}N^{1}-N^{2}Me_{2}^{**}$	N^1	-0.830	-0.711	11.4%
	N^2	-0.401	-0.184	47.2%
MeCl	С	-0.536 (0.103)	-0.096 (0.205)	
Me ₃ SiCl	Si	1.079	0.922	

Table

* The values in parentheses are the charges on heavy atoms summed with the charges on their bonded hydrogen atoms.

** HF/6-31G(d) calculations.

relatively small positive charge of the methyl group in the MeCl molecule and the great positive charge on the silicon atom in Me₃SiCl. This means that DMH should be alkylated at the N² atom, whose atomic orbitals make the greatest contribution to the HOMO, while silvlation of DMH should be directed at the N¹ atom, having the greatest negative charge. According to the calculation for the isomeric H₂NN⁺Me₃ and MeN⁺H₂NMe₂ cations, the methylation at the N² atom is 7.9 kcal/mol more favorable than that at the N¹ atom. Upon consecutive introduction of Me₃Si groups to the N¹ atom, the negative charge on this atom and the Mulliken charge difference increase, $\Delta q(N_M^1 - N_M^2) =$ 0.254, 0.354, 0.429, while the electrostatic charge and the charge difference decrease, $\Delta q (N_{el}^1 - N_{el}^2) = 0.664$, 0.569, 0.527. Nevertheless, in all cases, N¹ bears a much greater negative charge than N². The reaction of compound 4 with a second Me₃SiCl molecule is subject to charge control and also involves the N¹ atom. The contributions of the N1 and N2 AOs to the HOMOs of the calculated molecules (Table 1) are markedly different. For DMH and compound 4, the HOMO is mainly localized on the N^2 atom, while, for compound 1, the contribution of the N¹ AO is almost twice that of the N² AO. These differences might be due to the change in the atom pyramidality upon the introduction of Me₃Si groups into DMH. The Me₃SiN fragment is stabilized via conjugation of the nitrogen lone pair with the Me₃Si group, resulting in flattening of the pyramid, i.e., in an increase in the sum of angles around the N¹ atom from 322.4° for DMH to 351.8° for compound 1 and 359.2° for the nearly planar NNSi₂ fragment in 4. The sum of the bond angles around N² varies as 330.1°, 330.7°, and 342.3° in the same series; i.e., the hybridization of nitrogen does not change on introduction of the first Me₃Si group but markedly changes after the introduction of the second Me₃Si group. Thus, the lack of reactivity of 4 toward MeI is due to the decreased basicity of the N^2 atom, as indicated by its less pronounced pyramidality compared with both DMH and compound 1.

The best localization of the HOMO on the N² atom in the DMH molecule is due to the electron-donating effect of the two methyl groups, while that in molecule 4 is due to the low basicity of the N1 atom in the planar NNSi₂ fragment. The molecule of **1** retains the pyramidality of N^1 , but the pyramidality of N^2 decreases, resulting in some equalization of the contributions of these atoms to the HOMO. Therefore, to interpret the direction of methylation of compound 1, we carried out the HF/6-31G(d) calculation of the isomeric Me₃SiNHN⁺Me₃ and Me₃SiN⁺HMeNMe₂ cations (the MP2/6-31G(d) calculation would be impracticable due to the large size of the system). In this case, methylation at N² proves to be more favorable, although the difference between the methylation energies (3.85 kcal/mol) is smaller than that for DMH (for DMH, this value is 6.05 kcal/mol at the HF/6-31G(d) level).

EXPERIMENTAL

¹H and ²⁹Si NMR spectra were recorded on a Bruker DPX-400 instrument operating at 400 and 80 MHz, respectively, for 10–20% solutions in CDCl₃, CD₃CN, or DMF- d_7 using Me₄Si as the internal standard.

GLC analysis was performed on a Tsvet-500 chromatograph with a heat conductivity detector using 3 m \times 4 mm glass columns, the Inerton-super 0.125–0.150 mm sorbent impregnated with 10% PMS-1000, and helium as the carrier gas.

1. Synthesis of Organosilicon Derivatives of 1,1-Dimethylhydrazine

1.1. Trimethyl(2,2-dimethylhydrazino)silane 1. A solution of DMH (192 g, 3.2 mol) in 250 mL of anhydrous ether was charged into a three-necked flask equipped with a stirrer, a dropping funnel, a reflux condenser, and a calcium chloride tube. The solution was

cooled to 7°C and Me₃SiCl (167 g, 1.6 mol) was added dropwise. The reaction mixture was stirred for 1 h at room temperature and for 1 h at reflux. The precipitate was collected on a Schott filter and washed with anhydrous ether. The combined filtrates were concentrated and the residue was distilled to give 113 g (86%) of compound **1**, bp 96–101°C, n_D^{20} 1.4016 (lit.: bp 100°C,

 n_D^{20} 1.4018 [4]).

1.2. Triethoxy(2,2-dimethylhydrazino)silane 2 was prepared in a similar way using DMH (6.43 g, 0.27 mol) and (EtO)₃SiCl (26.6 g, 0.13 mol) in 50 mL of anhydrous ether. This gave 15 g (50%) of compound 2, bp 65–70°C (5 mm Hg), n_D^{20} 1.4025. ¹H NMR (CDCl₃), δ , ppm: 1.23 (t, 9H, CH₃C), 2.44 (s, 6H, CH₃N), 3.86 (q, 6H, CH₂).

For $C_8H_{22}Si_1N_2O_3$ anal. calcd. (wt %): C, 43.04; H, 9.86; N, 10.31; Si, 13.00.

Found (wt %): C, 43.17; H, 9.88; N, 10.23; Si, 13.03.

1.3. 1,1,2,2-Tetramethyl-1,2-(2',2'-dimethylhydrazino)disilane 3. A mixture of 1,1,2,2-tetramethyl-1,2-dichlorodisilane (8.2 g) and DMH (13 g) in 60 mL of anhydrous ether was heated in an evacuated glass tube for 5 h at 90°C. The precipitate was filtered off and washed (2 × 50 mL) with anhydrous ether. The combined filtrates were concentrated and the residue was distilled in vacuum to give 7.3 g (69.4%) of compound 3, bp 75°C (10 mm Hg), n_D^{28} 1.4484. ¹H NMR (CDCl₃), δ , ppm: 0.14 (s, 12H, SiCH₃), 2.00 (s, 2H, NH), 2.37 (s, 12H, NCH₃). ²⁹Si NMR (CDCl₃), δ_{si} , ppm: -10.91.

1.4. 1,1-Bis(trimethylsilyl)-2,2-dimethylhydrazine 4. A mixture of compound **1** (14 g, 0.1 mol), Me₃SiBr (15 g, 0.09 mol), Et₃N (10 g, 0.09 mol), and 100 mL of anhydrous ether was heated in an evacuated glass tube for 100 h at 90°C. The precipitate was filtered off and washed with anhydrous ether (2 × 50 mL). The combined filtrates were concentrated and distilled in vacuum to give 16.8 g (84%) of compound **4**, bp 63°C (13 mm Hg), n_D^{20} 1.4360 (lit.: bp 67°C (12 mm Hg), n_D^{20} 1.4390 [5]).

1.5. 1-Trimethylsilyl-1-trichlorosilyl-2,2-dimethylhydrazine 5. A mixture of compound 1 (20 g, 0.151 mol), BrSiCl₃ (32.4 g, 0.151 mol), Et₃N (17 g, 017 mol), and 80 mL of anhydrous ether was heated in an evacuated glass tube for 10 h at 90°C. The precipitate was filtered off and washed with anhydrous ether (2 × 50 mL). The combined filtrates were concentrated and distilled to give 23.1 g (57.5%) of compound 5, bp 92–95°C (10 mm Hg), n_D^{20} 1.4688. ¹H NMR (CDCl₃), δ , ppm: 0.34 (s, 9H, SiCH₃), 2.77 (s, 6H, CH₃N). ²⁹Si NMR (CDCl₃), δ_{Si} , ppm: –66.15 (SiCl₃), 10.80 (SiCH₃).

2. Reactions of Organosilicon Derivatives of 1,2-Dimethylhydrazine with MeI

2.1. A mixture of compound **1** (5 g, 0.037 mol), MeI (5.3 g, 0.037 mol), and 30 mL of anhydrous ether was kept in an evacuated glass tube for 1 h and the precipitate was filtered off, washed with anhydrous ether (2 × 10 mL), and dried in vacuum to give 9.2 g (89%) of $[Me_3N^+NHSiMe_3]I^-$, mp 158°C. ¹H NMR (CD₃CN), δ , ppm: 0.313 (s, 9H, SiCH₃), 3.50 (s, 9H, NCH₃), 5.86 (s, 1H, NH). ²⁹Si NMR (CD₃CN), δ_{Si} , ppm: 8.86.

2.2. A mixture of compound **2** (4 g, 0.017 mol), MeI (2.69 g, 0.019 mol), and 20 mL of CH₃CN was placed into a glass tube; warming-up to 50°C was observed. The mixture was heated for 4 h at 90°C. The volatile compounds were recondensed into a clean glass tube at 0.5 mm Hg. The remaining crystalline material was washed with anhydrous ether (2 × 40 mL) and dried at 0.5 mm Hg to give 4.4 g (97%) of the salt [(EtO)₃SiNHN⁺Me₃]I⁻, mp 121–124°C (in an evacuated capillary). ¹H NMR (CD₃CN), δ , ppm: 1.25 (t, 9H, CH₃C), 3.60 (s, 9H, NCH₃), 3.95 (q, 6H, CH₂O), 6.51 (s, FH, NH). ²⁹Si NMR (CD₃CN), δ_{Si} , ppm: –76.98.

2.3. A mixture of compound **3** (3.1 g, 0.013 mol), MeI (5 g, 0.044 mol), and 20 mL of CH₃CN was placed into an evacuated glass tube. The reaction mixture warmed up to 50°C and a crystalline precipitate formed. After 1 h, the crystals were filtered off and washed with anhydrous CH₃CN (2×10 mL) to give 6.4 g (93%) of the salt I⁻[Me₃N⁺NH(Me)₂SiSi(Me)₂HNN⁺Me₃]I⁻, mp 156°C (in an evacuated capillary; decomp.). ¹H NMR (DMF- d_7), δ , ppm: 0.19 (s, 12H, CH₃C), 3.51 (s, 18H, NCH₃).

2.4. A mixture of compound **4** (5 g, 0.024 mol), MeI (6 g, 0.042 mol), and 15 mL of CH₃CN was heated in an evacuated glass tube for 30 h at 100°C. The volatile compounds were recondensed into a clean glass tube at 0.5 mm Hg. The residue was washed with anhydrous ether (2 × 10 mL) and dried in vacuum to give 5.3 g (80.8%) of the salt [Me₃N+NHSiMe₃]I⁻ as yellowish crystals, mp 158°C (decomp.). The ¹H NMR spectrum is identical to that given in Section 2.1. Vacuum fractionation of the condensed liquid fraction gave 2.2 g (92%) of Me₃SiCH₂CN, bp 71°C (30 mm Hg), n_D^{20} 1.4213 (lit.: bp 82–84°C (54 mm Hg), n_D^{20} 1.4203 [8]).

Heating of a mixture of compound 4 (5 g, 0.024 mol) and MeI (6 g, 0.042 mol) in 15 mL of THF, ether, CH_2Cl_2 , or CHCl₃ in an evacuated glass tube for 54 h at 100°C did not result in the formation of a precipitate. GLC of the reaction mixture showed only the starting compounds, which were recovered unchanged by distillation.

2.5. Reaction of compound **4** with MeI in the presence of terminal acetylenes. A mixture of compound **4** (5 g, 0.024 mol), MeI (6 g, 0.042 mol), and a terminal acetylene derivative (0.05 mol) in 15 mL of a solvent was heated in an evacuated glass tube for 30 h at 95°C.

Phenylacetylene or trimethylpropargyloxysilane was used as the acetylene derivative, and CCl_4 , CH_2Cl_2 , $CHCl_3$, and CH_3CN were used as solvents. In the first three solvents, the reaction does not proceed, the starting compounds being recovered unchanged. In acetonitrile, the reaction gives Me_3CH_2CN and $[Me_3N^+NHSiMe_3]I^-$ in an almost quantitative yield within 20 h. According to GLC analysis with reference compounds, products of triple bond silylation are not formed even in trace amounts.

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