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(Chloromethyl)alkoxysilanes, Silethanes, and Silethenes in the Synthesis of Linear and Heterocyclic Compounds

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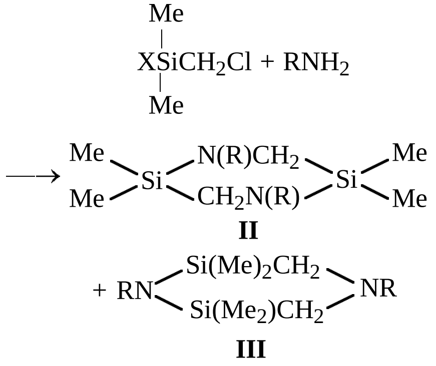
Abstract—The use of *N*,*N*-dimethylhydrazine or its trimethylsilyl derivatives in silylation, silamethylation, silethenation, and transsilylation allows synthesis of previously unknown linear and heterocyclic compounds.

Primary amines react with (chloromethyl)dimethylsilanes **I** to form 2,5-disilapiperazines **II** or their mixture with 2,6-disilapiperazines **III** [1–3].



II

III

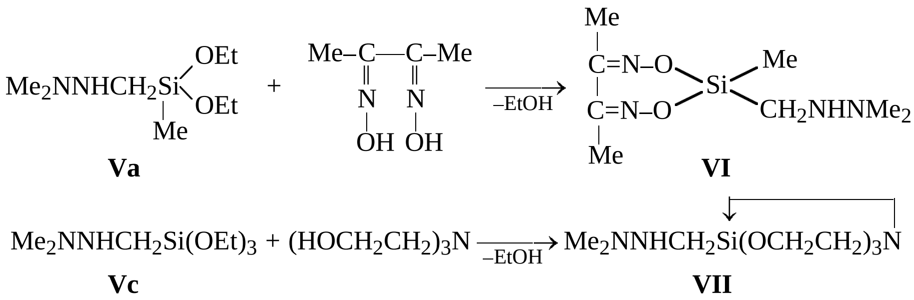
R = Pr, All, Bu, *i*-Bu, Ph; X = Cl, OMe.

We found that the use in this reaction of *N*,*N*-dimethylhydrazine instead of amines not only changes the reaction direction, but also allows practically valuable compounds to be synthesized [4].

$$\underset{\textbf{IV}}{Me_n(RO)_{3-n}SiCH_2Cl} + Me_2NNH_2 \longrightarrow \underset{\textbf{Va–Vc}}{Me_n(RO)_{3-n}SiCH_2NHNMe_2}.$$

Compared with primary amines, *N*,*N*-dimethylhydrazine more difficultly reacts with dimethyl(alkoxy)silanes **IV**, which reduces the yield of target products by a factor 1.5–2 at the same reaction time (Table 1).

The resulting hydrazinomethylsilanes **V** are readily transetherified, yielding previously unknown compounds: heterocycle **VI** and silatrane **VII**.



Va **VI** **Vc** **VII**

Table 1. Reaction conditions, physicochemical constants, and elemental analyses of carbofunctional organosilicon *N*,*N*-dimethylhydrazine derivatives **Va–Vc**

Comp. no.	Yield, %	bp, °C (*p*, mm Hg)	n_D^{20}	Reaction time, h	Found, %			Formula	Calculated, %		
					C	H	Si		C	H	Si
Va	31.4	118–120 (3)	1.4153	42.0	46.61	10.84	13.72	$C_8H_{22}N_2O_2Si$	46.57	10.75	13.60
Vb	23.5	58–60 (12)	1.4290	35.5	44.54	11.22	17.20	$C_6H_{18}N_2OSi$	44.40	11.18	17.30
Vc	37.3	190	1.4018	30.0	45.68	9.96	12.00	$C_9H_{24}N_2O_3Si$	45.76	10.17	11.96

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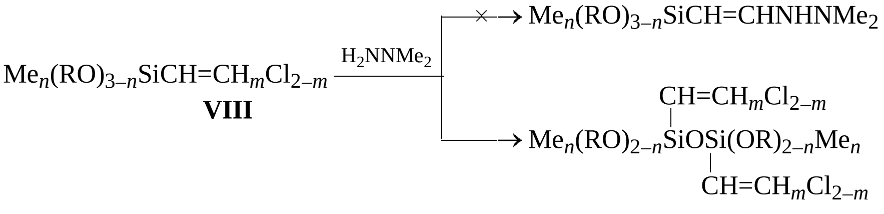
Table 2. Physicochemical constants and elemental analyses of organovinyldisiloxanes **IXa**–**IXd**

Comp. no.	Yield, %	bp, °C (p, mm Hg)	n_D^{20}	Found, %				Formula	Calculated, %			
				C	H	Cl	Si		C	H	Cl	Si
IXa	75.0	70 (2)	1.4515	37.53	6.17	27.62	–	$C_8H_{16}Cl_2OSi_2$	37.64	6.32	27.77	–
IXb	37.3	103–105 (1.5)	1.4181	38.35	6.47	–	15.60	$C_{12}H_{24}Cl_2O_5Si_2$	38.39	6.45	–	14.97
IXc	65.0	110–112 (2)	1.4210	31.62	4.91	32.01	–	$C_{12}H_{22}Cl_4O_5Si_2$	32.44	4.99	31.92	–
IXd	32.1	80 (2)	1.4079	38.47	7.26	–	22.33	$C_8H_{18}O_5Si_2$	38.51	7.29	–	22.52

The conversion of (chloromethyl)alkoxysilanes **IV** to silethenes **VIII**, chlorine-containing inclusive, allowed us to conclude that the structure and composition of the final reaction products are primarily controlled by the type of the starting organosilicon compound. Because of the mutial effect of the chlorine atom and vinyl and silyl groups in *C*-chlorovinylsilanes, we failed to accomplish ethenation of *N*,*N*-dimethylhydrazine.

At the same time, fractionation of the reaction mixture after heating allowed isolation of individual organovinyldisiloxanes **IXa**–**IXd** (Table 2).



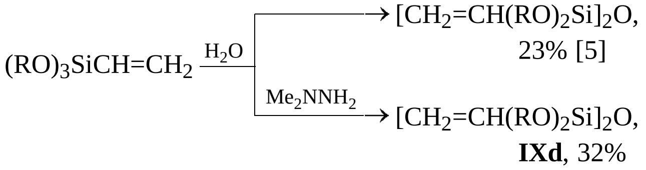
IXa–**IXd**

R = Me, Et; n = 0, 2; m = 0, 1, 2.

The formation of disiloxanes **IX** was presumably favored by the hydration water in *N*,*N*-dimethylhydrazine (ca. 10 wt%), since it directed the process to hydrolysis products.

$$\underset{\textbf{VIII}}{Me_n(RO)_{3-n}SiCH{=}CH_mCl_{2-m}} \xrightarrow{H_2O} \underset{\textbf{X}}{Me_n(RO)_{2-n}(HO)SiCH{=}CH_mCl_{2-m}} + ROH$$

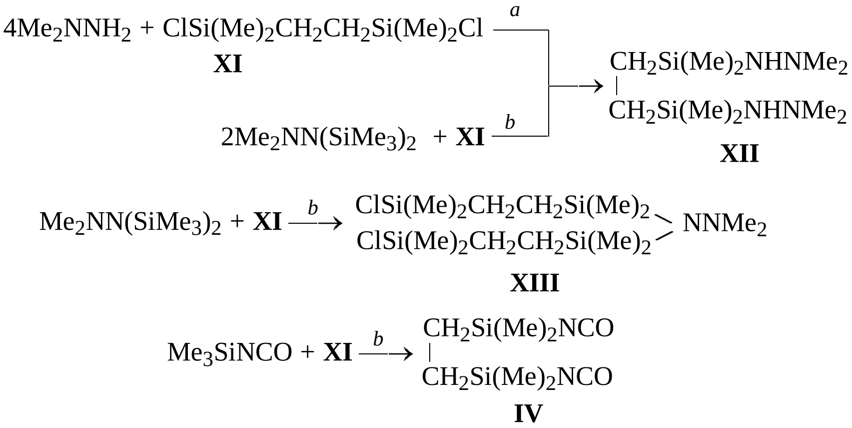
The increased yield of disiloxanes **IX** compared with hydrolysis of alkoxyvinylsilanes with water [5] is presumably explained by the fact that *N*,*N*-dimethylhydrazine, like amines, catalyzed condensation of silanols **X**.



Silethane **XI** reacts much easier. For this reason, by silylation (a) and transsilylation (b), we could synthesize practically perspective monomers: dihydrazine **XII**, disilazane **XIII**, and organosilicon diisocyanate **XIV**.

EXPERIMENTAL

All starting materials and solvents were thoroughly dried and distilled. Synthetic operations, product isolation, and sampling for analysis were performed under dry argon. The reaction mixtures and pure compounds were analyzed by GLC on a Shimadzu G-8 chromatograph (stainless steel column, 1500 ×



$$4Me_2NNH_2 + ClSi(Me)_2CH_2CH_2Si(Me)_2Cl\ (\mathbf{XI}) \xrightarrow{a} \mathbf{XII}$$

$$2Me_2NN(SiMe_3)_2 + \mathbf{XI} \xrightarrow{b} CH_2Si(Me)_2NHNMe_2\text{–}CH_2Si(Me)_2NHNMe_2\ (\mathbf{XII})$$

$$Me_2NN(SiMe_3)_2 + \mathbf{XI} \xrightarrow{b} [ClSi(Me)_2CH_2CH_2Si(Me)_2]_2NNMe_2\ (\mathbf{XIII})$$

$$Me_3SiNCO + \mathbf{XI} \xrightarrow{b} CH_2Si(Me)_2NCO\text{–}CH_2Si(Me)_2NCO\ (\mathbf{IV})$$

3 mm, packing SE-30 on Chromaton N-AW, carrier gas helium).

The IR spectra were obtained on a Specord IR-75 instrument in thin films (liquids) and mineral oil (solids). The 1H NMR spectra were recorded on a Bruker WP-8 instrument (80 MHz), solvent and internal reference $CDCl_3$.

2-{[Diethoxy(methyl)silyl]methyl}-1,1-dimethylhydrazine (Va). A mixture of 65.60 g of (chloromethyl)(diethoxy)methylsilane and 43.15 g of 1,1-dimethylhydrazine was heated for 42 h at 60°C. Fractionation gave 23.26 g (31.4%) of compound Va, bp 118–120°C (3 mm Hg), n_D^{20} 1.4153. ^{1}H NMR spectrum, δ, ppm: 0.01 s (3H, $SiCH_3$), 2.28 s (6H, NCH_3), 2.76 s (2H, $SiCH_2$). Found, %: C 46.61; H 10.84; Si 13.72. $C_8H_{22}N_2O_2Si$. Calculated, %: C 46.57; H 10.75; Si 13.60.

Compounds **Vb** and **Vc** were obtained in a similar way (Table 1).

2-[(2,2-Dimethylhydrazino)methyl]-2,5,6-trimethyl-1,3,4,7,2-dioxadiazasilepine (VI). A mixture of 4.53 g of compound **Va**, 2.55 g of butane-2,3-dione dioxime, and a catalytic amount of lithium was heated with a distillation head until ethanol no longer distilled. The reaction mixture was subjected a vacuum (15 mm Hg) to obtain 4.02 g (79.5%) of compound **VI** as a viscous oil. IR spectrum, ν, cm^{-1}: 3350 (NH), 1600 (C=N). Found, %: C 41.47; H 7.91; Si 11.11. $C_8H_{18}N_4O_2Si$. Calculated, %: C 41.69; H 7.87; Si 12.19.

(2,2-Dimethylhydrazino)methylsilatrane (VII). 1,1-Dimethyl-2-(triethoxylsilyl)hydrazine (**Vc**), 16.19 g, was added dropwise at 80°C to a mixture of 10.23 g of triethanolamine and 2 g of freshly prepared sodium methylate. The reaction mixture was refluxed for 3 ½. After 12 h, the crystals that formed were filtered off, washed with ether (2 × 100 ml), and dried in a vacuum. Ether, 200 ml, was distilled off from the mother liquor, the residue was cooled, and the precipitate was filtered off to obtain an additional crop of the reaction product. Total yield 15.93 g (94%), mp 90–92°C. ^{1}H NMR spectrum, δ, ppm: 1.43 s (6H, NCH_3), 2.29 t (6H, NCH_2), 3.59 t (6H, OCH_2,), 4.2 s (2H, $SiCH_2$). Found, %: C 43.22; H 8.56; N 16.49; Si 10.89. $C_9H_{21}N_3O_3Si$. Calculated, %: C 43.70; H 8.56; N 16.99; Si 11.35.

1,3-Bis(2-chloroethenyl)-1,1,3,3-tetramethyldisiloxane (IXa). A mixture of 23.26 g (2-chloroethenyl)(ethoxy)dimethylsilane (*cis/trans* ratio 3 : 1) and 16.97 g of 1,1-dimethylhydrazine was heated with a distillation head until ethanol no longer distilled, after which it was fractionated to isolate 9.04 g (75%) of compound **IXa** (*cis/trans* ratio was not estimated), bp 70°C (2 mm) n_D^{20} 1.4515. IR spectrum, ν, cm^{-1}: 1040 (SiOSi); 1560 and 3040 (C=C). ^{1}H NMR spectrum, δ, ppm: 0.35 s (12H, $SiCH_3$), 6.2 d and 6.5 d (2H, CH=CH). Found, %: C 37.53; H 6.17; Cl 27.62. $C_8H_{16}Cl_2OSi_2$. Calculated, %: C 37.64; H 6.32; Cl 27.77.

Compounds **IXb**–**IXd** were obtained in a similar way (Table 2).

2,4,4,7,7,9-Hexamethyl-2,3,8,9-tetraza-4,7-disiladecane (XII). *a*. A mixture of 30 g of 1,1-dimethylhydrazine and 26.86 g of chloro{2-[chloro(dimethyl)silyl]ethyl}dimethylsilane (**XI**) was heated for 41 h at 60°C and fractionated to isolate 22.28 g (68%) of compound **XII**, bp 111°C, n_D^{20} 1.4561. IR spectrum, ν, cm^{-1}: 3110 (NH). ^{1}H NMR spectrum, δ, ppm: 0.35 s (12H, $SiCH_3$), 0.86 t (4H, $SiCH_2CH_2$), 2.62 s (6H, NCH_3). Found, %: C 45.01; H 11.31. $C_{10}H_{30}N_4 \cdot Si_2$. Calculated, %: C 45.75; H 11.52.

b. A mixture of 10.93 g of compound **XI** and 13.44 g of 1,1-dimethyl-2-(trimethylsilyl)hydrazine was heated with a distillation head until chlorotrimethylsilane no longer distilled. Fractionation gave

12.14 g (91%) of compound **XII**, bp 110°C, n_D^{20} 1.4560.

1,3-Bis[2-(chlorodimethylsilyl)ethyl]-2-(dimethylazanyl)-1,1,3,3-tetramethyldisilazane (XIII). A mixture of 5.30 g of 1,1-bis(trimethylsilyl)-2,2-dimethylhydrazine, 5.59 g of compound **XI**, and 40 ml of 1,4-dioxane was heated with a distillation head until chlorotrimethylsilane no longer distilled and fractionated to isolate 10.39 g (96%) of compound **XIII**, bp 55–56°C (2.5 mm Hg), n_D^{20} 1.4460. ^1H NMR spectrum, δ, ppm: 0.2 s and 0.33 s (12H, $SiCH_3$), 0.70 t (4H, $SiCH_2CH_2$), 0.76 t (4H, $SiCH_2CH_2$), 2.55 s (6H, NCH_3). Found, %: C 41.41; H 9.95; Cl 16.90; N 7.22. $C_{14}H_{38}Cl_2N_2Si_4$. Calculated, %: C 40.24; H 9.18; Cl 16.97; N 6.70.

{2-[Isocyanato(dimethyl)silyl]ethyl}(dimethyl)silyl isocyanate (XIV). A mixture of 9.00 g of compound **XI**, 9.63 g of trimethylsilyl isocyanate, and a catalytic amount of $SnCl_4$ was heated with a distillation head until chlorotrimethylsilane no longer distilled and fractionated to isolate 8.25 g (86%) of compound **XIV**, bp 125–126°C (15 mm Hg), n_D^{20} 1.4471. IR spectrum, ν, cm^{-1}: 2270 (NCO). ^1H NMR spectrum, δ, ppm: 0.24 s (12H, $SiCH_3$), 0.61 s (4H, CH_2CH_2). Found, %: C 41.95; H 6.93; N 12.27. $C_8H_{16}N_2O_2Si_2$. Calculated, %: C 42.07; H 7.06; N 12.27.

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