The reaction of chloromethylsilanes with amines, hexamethyldisilazanes, and silylcarbamates

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The reactions of chloromethylsilanes with amines, hexamethyldisilazane, and silylcarbamates were studied. The dependence of the composition and structure of the resulting products on the nature of the reagents used and reaction conditions was determined. A scheme for the synthesis of 4,9-diaza-2,7-dioxa-1,6-disilacyclodecane-3,8-dione derivatives was suggested.

Key words: synthesis, chloromethylsilanes, silylcarbamates, hexamethyldisilazane, transsilylation and silicomethylation.

The reactions of (chloromethyl)silanes with various silicon- and nitrogen-containing compounds do not finish with the usual exchange of substituents at the N and Si atoms. The process proceeds in a much more complex way. In the case of amides of formic acid[1–4] and silylcarbamates,[5–7] Cl—C—Si—N → Cl—Si—C—N rearrangement takes place; the presence of a Si←O intramolecular coordination bond predetermines the high reactivity of the resulting compounds.

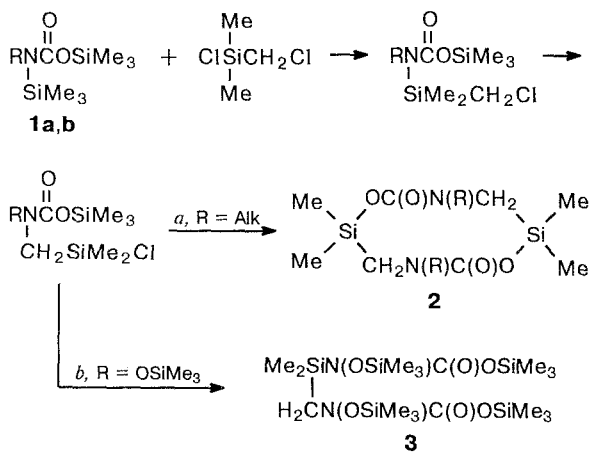
It was interesting to study the effect of the nature of the reagents and the reaction conditions used on the formation of various silylcarbamates.

We have shown previously[4,6] that chloromethyldimethylchlorosilane reacts with trimethylsilyl *N*-alkyl-*N*-trimethylsilylcarbamates (**1a**) and trimethylsilyl *N,O,O'*-tris(trimethylsilyl)-*N*-hydroxycarbamate (**1b**) *via* a three-step mechanism. The first step (Scheme 1) involves transsilylation of the starting silylcarbamate at the Si—N bond by chloromethyldimethylchlorosilane. At the second step, the compound that formed isomerizes into a *N*-silicomethylation product, which subsequently undergoes transsilylation with another molecule of the same compound (R = Alk) or with the original molecule (R = $OSiMe_3$).

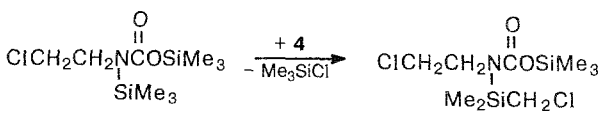
It was found that the type of the compound formed and, hence, the realization of a particular step of the process is determined by the substituent at the nitrogen atom in silylcarbamate **1**.

For example, the reaction of trimethylsilyl *N*-trimethylsilyl-*N*-(β-chloroethyl)carbamate (**1c**) with chloromethyldimethylchlorosilane (**4**) ceases at the first step, namely, *N*-transsilylation (Scheme 2).

Scheme 1



Scheme 2



A similar reaction of trimethylsilyl methylcarbamate **1** with chlorosilane **4** does not give an *O*-transsilylation product but yields a more complex heterocyclic compound **2a** (Scheme 3).

The specific feature is that heterocycle **2a** is formed from the preceding member in the series of chemical transformations of silylcarbamates **1** ($RNHC(O)OSiMe_3$), which does not contain a Si—N bond; this should also

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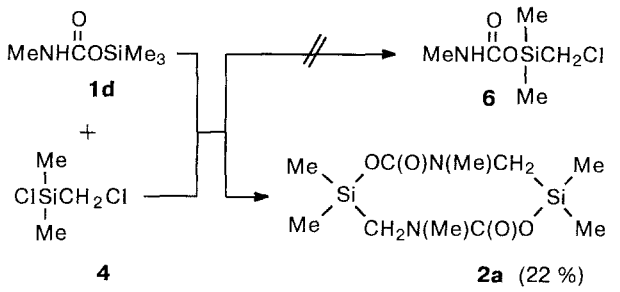
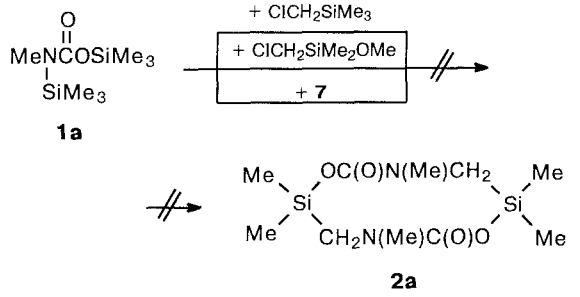
Scheme 3



eliminate the possibility of transsilylation at the nitrogen atom. Taking into account the previously proven fact[1,8] that the process involves three steps (see Scheme 1), this would not give heterocycle **2a** but had to yield compound **6**, in agreement with the well studied chemical properties of silylcarbamates.[9]

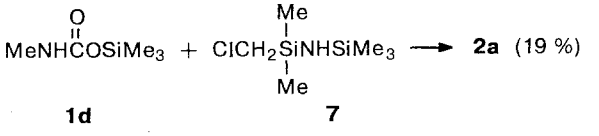
Special experiments demonstrated that chlorosilane **4**, chloromethyldimethylmethoxysilane (**4a**), and 1-(chloromethyl)-1,1,3,3,3-pentamethyldisilazane (**7**) do not react with silylcarbamate **1a** (R = Me) even with heating (Scheme 4).

Scheme 4



On the other hand, silylcarbamate **1d** reacts with chloromethyldisilazane **7** to give heterocycle **2a**, although in a low yield (Scheme 5).

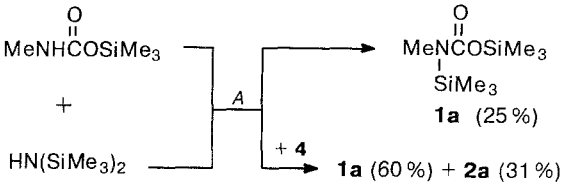
Scheme 5



Thus, first, chloromethyldisilazane **7** is capable of *N*-(chloromethyldimethyl)silylation; second, it is its subsequent transformations (taking into account the passivity of the **1a** analog in reactions according to Scheme 4) that produce heterocycle **2a**.

The possibility of *N*-silylation of silylcarbamates **1** with organodisilazanes is confirmed by the formation of $MeN(SiMe_3)C(O)OSiMe_3$ (**1a**, 25 %) on heating trimethylsilyl methylcarbamate with hexamethyldisilazane (Scheme 6).

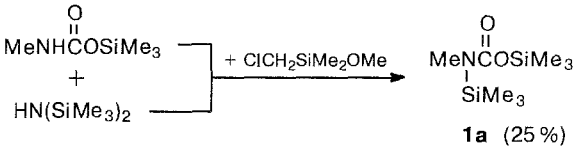
Scheme 6



Finally, it was shown that the presence of chlorosilane **4** as a coreagent in the reaction of silylcarbamate **1** with hexamethyldisilazane (Scheme 6) considerably increases both the yield of compound **1a** (to 60 %) and that of heterocycle **2a** (to 31 %).

When chlorosilane **4** is replaced by chloromethyldimethylmethoxysilane (Scheme 7), the direction of the reaction changes completely. As a result, one cannot obtain heterocycle **2a** and increase the yield of silylcarbamate **1a**.

Scheme 7

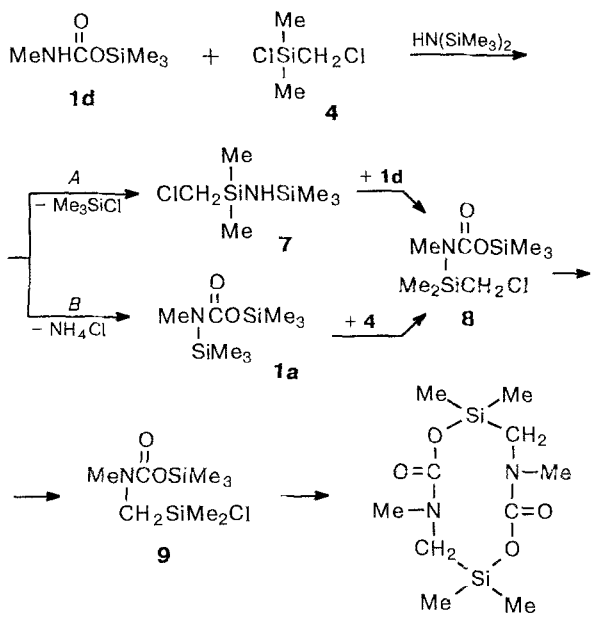


The results can probably be explained both by the introduction of a less electronegative substituent into the starting chloromethylsilane and by an insufficiently high reaction temperature.

Thus, the syntheses of heterocycle **2a** from chloromethyldisilazane **7** (see Scheme 5) or from the HMDS—chloromethyldimethylchlorosilane (see Scheme 6), as well as the absence of any products in the reaction of compounds **7** with **1a** (see Scheme 4), indicates that the synthesis of 1,1,4,6,6,9-hexamethyl-4,9-diaza-2,7-dioxa-1,6-disilacyclodecane-3,8-dione can occur by two pathways (Scheme 8). The first one (pathway *A*) starts with the formation of intermediate **7**. Then, depending on the starting compounds and reaction conditions used, *N*-silylation of the starting silylcarbamate **1d** occurs. The *N*-silylation product, **8**, isomerizes into an *N*-silicomethylation product **9**. Finally, the latter undergoes desilylation (or transsilylation) according to Scheme 1 to give heterocycle **2a**.

In the second case (pathway *B*), silylcarbamate **1d** first undergoes *N*-silylation to give compound **1a** (see Scheme 6). The latter is then transformed into heterocycle **2a** according to Scheme 1 shown above.

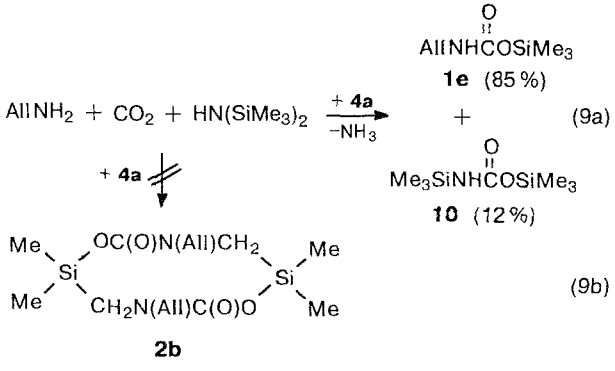
Scheme 8



Heterocycles **2** can also be obtained by *N*-siloxycarbonylation of alkylaminomethyldimethylalkoxysilanes.[10] Therefore, we attempted to synthesize them in one stage using chloromethyldimethylmethoxysilane **4a**.

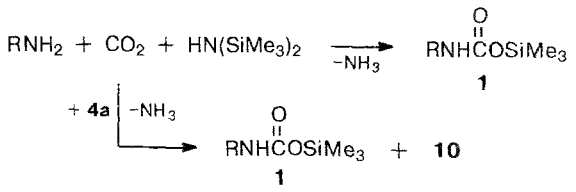
However, instead of heterocycle **2b**, we obtained trimethylsilyl allylcarbamate **1e** and *N,O*-bis(trimethylsilyl)carbamate **10** (Scheme 9).

Scheme 9



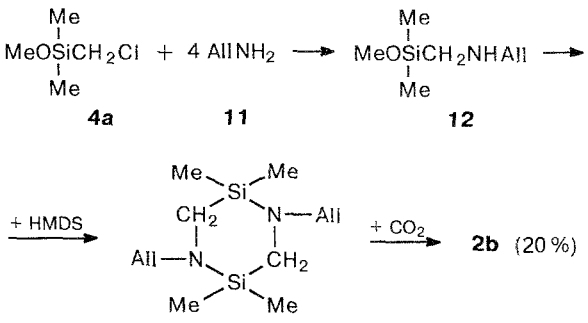
The formation of compounds **1e** and **10** and the full absence of any effect of chloromethyldimethylmethoxysilane **4a** on the yield of silylcarbamate **1a** according to Scheme 7 allows us to assume that the role of compound **4a** involves the catalysis of *N*-siloxycarbonylation of the ammonia liberated in reaction 9a (Scheme 10). It is difficult to explain this; however, it is generally known that when *N*-siloxycarbonylation of amines is carried out in the absence of compound **4a**, the reaction products do not contain *N,O*-bis(trimethylsilylcarbamate).[10]

Scheme 10



It should be pointed out that an increase in the content of allylamine (**11**) in the starting mixture (above the stoichiometric value, *i.e.*, **11** : HMDS : **4a** = 2 : 1 : 2) makes it possible to obtain heterocycle **2b**, although in a low yield (20 %) (Scheme 11). However, in our opinion, this takes place because excess allylamine reacts with chloromethyldimethylmethoxysilane to give allylaminomethyldimethylmethoxysilane (**12**), whose transformation into heterocycle **2b** following treatment with hexamethyldisilazane has been reported previously.[11]

Scheme 11



Experimental

All starting reagents and solvents were thoroughly dried and purified by distillation prior to use. The syntheses of all compounds, their isolation, and withdrawal of samples for analyses were carried out under dry nitrogen. The compositions of reaction mixtures and pure products were determined by GLC on a LKhM-80 chromatograph (1.5 m×3 mm columns made of stainless steel, the SE-30 phase on Chromaton N-AW, helium as the carrier gas).

^{1}H NMR spectra were recorded on a Varian T-60 spectrometer (60 and 100 MHz) using methylene dichloride as the solvent and internal standard.

IR spectra were obtained in thin films (for liquids) and in KBr pellets or in vaseline oil (for crystalline compounds) on UR-20 and IKS-29 spectrophotometers.

Trimethylsilyl *N*-trimethylsilyl-*N*-methylcarbamate (1a). A. A mixture of trimethylsilyl methylcarbamate (53 g, 0.36 mol) and hexamethyldisilazane (58.1 g, 0.36 mol) was heated for 5 h at 100—110 °C. The residue was fractionated to give 20 g (25 %) of compound **1a**, b.p. 63 °C (2 Torr), n_D^{20} 1.4270. ^{1}H NMR, δ: 0.2 and 0.27 (s, 9 H, $SiMe_3$), 2.66 (s, 3 H, NMe). A similar procedure starting from silylcarbamate **1d** (53 g,

0.36 mol), hexamethyldisilazane (58.1 g, 0.36 mol), and chloromethyldimethylmethoxysilane (25 g, 0.18 mol) gave 20.5 g (25 %) of compound **1a**, b.p. 63 °C (2 Torr), n_D^{20} 1.4270.

B. Carbon dioxide was passed for 10 h at 45—47 °C through a mixture of allylamine (11.4 g, 0.22 mol), hexamethyldisilazane (16.1 g, 0.1 mol), and chloromethyldimethylmethoxysilane (27.7 g (0.2 mol). This procedure gave 2.5 g (12 %) of *N,O*-bis(trimethylsilyl)carbamate, m.p. 80—83 °C (hexane), and 29.8 g (85 %) of trimethylsilyl allylcarbamate (**1e**), b.p. 78 °C (2.5 Torr), n_D^{20} 1.4378. (see Ref. 10: b.p. 60—61 °C (2.5 Torr), n_D^{20} 1.4380).

1,1,4,6,6,9-Hexamethyl-4,9-diaza-2,7-dioxa-1,6-disilacyclodecan-3,8-dione (2a). A. A mixture of trimethylsilyl methylcarbamate (29.4 g, 0.19 mol) and chloromethyldimethylmethoxysilane (28.6 g, 0.19 mol) was heated until evolution of trimethylchlorosilane ceased. This gave 12.7 g (22 %) of compound **2a**, m.p. 135—140 °C. ^{1}H NMR, δ: 0.35 (s, 12 H, $SiMe_3$); 2.33 (s, 4 H, NCH_2), and 2.63 (s, 6 H, NMe). Found (%): C, 40.99; H, 7.64; Si, 19.25. $C_{10}H_{22}N_2O_4Si_2$. Calculated (%): C, 41.35; H, 7.63; Si, 19.34.

B. A similar procedure starting from trimethylsilyl methylcarbamate (13.2 g, 0.09 mol) and 1-(chloromethyl)-1,1,3,3,3-pentamethyldisilazane gave 5 g (19 %) of heterocycle **2a**, m.p. 136—140 °C.

C. A similar procedure starting from trimethylsilyl methylcarbamate (29.4 g, 0.20 mol), hexamethyldisilazane (32.3 g, 0.20 mol), and chloromethyldimethylchlorosilane (14.3 g, 0.10 mol) gave 8.8 g (60 %) of compound **1a**, b.p. 63 °C (2 Torr), n_D^{20} 1.4272, and 5.9 g (31 %) of heterocycle **2a**, m.p. 136—140 °C.

Trimethylsilyl *N*-chloromethyldimethylsilyl-*N*-chloroethylcarbamate (5). A mixture of trimethylsilyl *N*-trimethylsilyl-*N*-chloroethylcarbamate (30 g, 0.11 mol) and chloromethyldimethylchlorosilane (15.7 g, 0.11 mol) was heated until evolution of trimethylchlorosilane ceased. Fractionation of the residue gave 19.7 g (58 %) of compound **5**, m.p. 175—178 °C. ^{1}H NMR, δ: 0.16 (s, 9 H, $SiMe_3$); 0.21 (s, 6 H, $SiMe_2$); 2.8 (s, 2 H, CH_2Si); 3.65 and 3.95 (t, 4 H, CH_2CH_2). Found (%): C, 35.81; H, 7.11; Si, 18.61; Cl, 23.57. $C_9H_{21}NO_2Cl_2Si_2$. Calculated (%): C, 35.75; H, 7.01; Si, 18.58, Cl, 23.45.

1-(Chloromethyl)-1,1,3,3,3-pentamethyldisilazane (7). A similar procedure starting from hexamethyldisilazane (266 g, 1.65 mol) and chloromethyldimethylchlorosilane (236 g, 1.65 mol) gave 95 g (70 %) of compound **7**, b.p. 38—40 °C (1 Torr), n_D^{20} 1.4396. Found (%): C, 36.91; H, 9.33; Si, 28.69. $C_6H_{18}NClSi_2$. Calculated (%): C, 36.83; H, 9.29; Si, 28.64.

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