Interaction of hydrosilanes with carbon dioxide and secondary amines or silylamines

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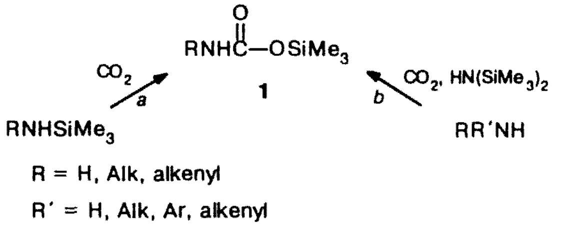
The reaction of hydrosilanes with carbon dioxide and secondary amines or silylamines was studied for the first time. The dependence of the composition and the structure of the products obtained on the nature of the reagents and on the reaction conditions was found. The hydrosilane—carbon dioxide system, unknown previously, can be used as an *N*-siloxycarbonylating reagent in the synthesis of *O*-silylurethanes. A scheme for the formation of *O*-silylurethanes was proposed.

Key words: hydrosilanes, amines, *N*-siloxycarbonylation, carbon dioxide; *O*-silylurethanes, synthesis; hexamethyldisilazane.

It has been shown previously[1-3] that *O*-silylurethanes **1** can be obtained by two methods, namely, by carboxylation of aminosilanes (reaction *a*) and by *N*-siloxycarbonylation of amines (reaction *b*); in the latter case, the hexamethyldisilazane—CO_2 system was used as the *N*-siloxycarbonylating reagent.

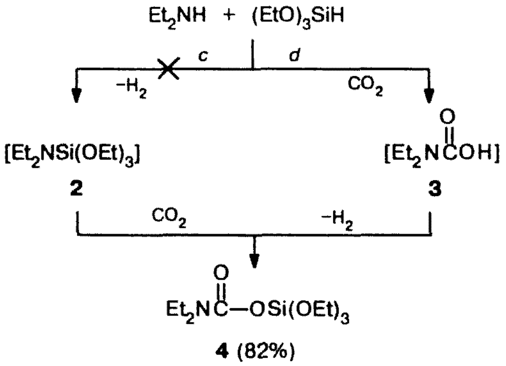


The use of *N*-siloxycarbonylation not only facilitates substantially the preparation of practically valuable[4] compounds, but also makes it possible to synthesize aromatic *O*-silylurethanes, which have previously been inaccessible. In view of the advantages of the *N*-siloxycarbonylation process,[5] it seemed expedient to continue studies in this field in order to extend the limits of applicability of this reaction.

We were the first to find that not only the hexamethyldisilazane—CO_2 system but also the hydrosilane—CO_2 system can serve as an *N*-siloxycarbonylating reagent.

For example, the reaction of diethylamine with carbon dioxide and triethoxysilane (Scheme 1) affords triethoxysilyl diethylcarbamate (**4**) in a virtually quantitative yield.

Scheme 1



Of the two possible routes of the process (*c* and *d*), the latter route (*d*) should apparently be preferred. First, the interaction of amines with triethoxysilane without a catalyst is known[6,7] to occur with difficulty and to end in the formation of aminoethoxysilanes in relatively low yields. Second, diethylaminotriethoxysilane (**2**) cannot be isolated from the reaction mixture,[6] due to its low yield and the presence of impurities, although *O*-silylcarbamate **4** is formed in a high yield over a period of 3 h.

It should be noted that the rate of the dehydrocondensation of hydrosilane with the diethylcarbamic acid **3** formed (route *d*) is so high that when tetramethyldisilazane is used, the reaction cannot be arrested at the stage of the formation of dimethylsilyl diethylcarbamate (**5**) and affords bis-*O*-silylurethane (**6**) as the final reaction product (Scheme 2).

Thus, the rapid synthesis of compounds **4** and **6** in nearly quantitative yields can be apparently explained by the formation of diethylcarbamic acid **3** in the first stage of the reaction; the relatively high acidity of the latter

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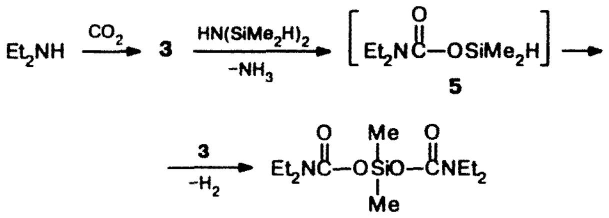
Scheme 2



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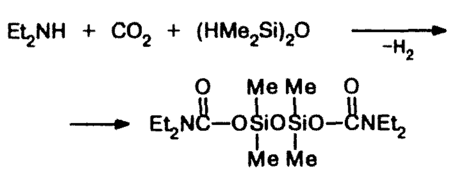
facilitates the subsequent dehydrocondensation (see Schemes 1 and 2).

The reaction involving 1,1,3,3-tetramethyldisiloxane also occurs smoothly to yield disiloxane 7.



$$Et_2NH + CO_2 + (HMe_2Si)_2O \xrightarrow[-H_2]{} Et_2NC(O)OSiMe_2OSiMe_2OC(O)NEt_2$$

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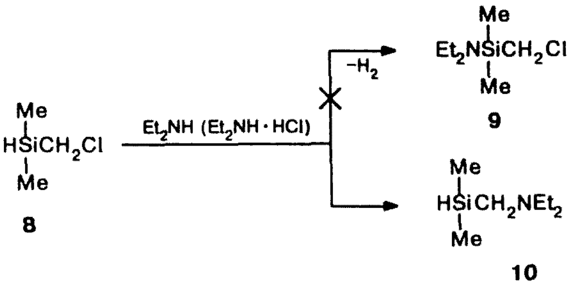
The replacement of triethoxysilane by a carbofunctional hydrosilane, *viz.*, chloromethyldimethylsilane (**8**), allowed us to establish some regularities of this process.

The reaction of compound **8** with diethylamine or its hydrochloride would have been expected to yield chloromethyl(diethylamino)dimethylsilane (**9**). However, in both cases, we isolated only the amination product **10** rather than dehydrocondensation product **9** (Scheme 3).

Scheme 3

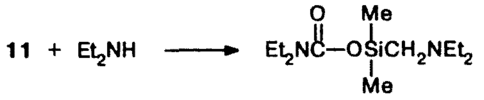


However, when carbon dioxide was used, *i.e.*, when it was ensured that the generation of diethylcarbamic acid was possible, or when diethylammonium diethylcarbamate, which is a precursor of this acid, was used, the reaction occured as *N*-siloxycarbonylation to yield *O*-silylurethane **11** (Scheme 4).

The preparation of aminomethylsilane **10** and the successful synthesis of *O*-silylurethane **11** by means of the hydrosilane **8**—CO_2 *N*-siloxycarbonylating system serve as additional evidence supporting our suggestion that the reaction occurs preferably *via* the formation of diethylcarbamic acid (see Scheme 1).

It should be noted that product **11** was also prepared by an alternative reaction route, *viz.*, transsilylation of trimethylsilyl diethylcarbamate with chloro(chloromethyl)dimethylsilane (see Scheme 4, reaction *e*).

Compound **11** is readily aminated. For example, by its reaction with excess diethylamine, the previously unknown *O*-silylurethane **12** was prepared in a high yield.



$$\mathbf{11} + Et_2NH \longrightarrow Et_2NC(O)OSiMe_2CH_2NEt_2$$

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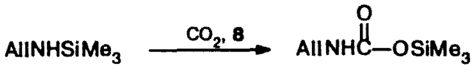
When diethylamine was replaced by silylated amines, the reaction route dramatically changed. In the case of a monosilylamine, *viz.*, allylamino(trimethyl)silane, only trimethylsilyl allylcarbamate (**13**) was obtained, whereas with a disilylamine, hexamethyldisilazane, the reaction did not occur at all.



$$AllNHSiMe_3 \xrightarrow{CO_2,\ \mathbf{8}} AllNHC(O)OSiMe_3$$

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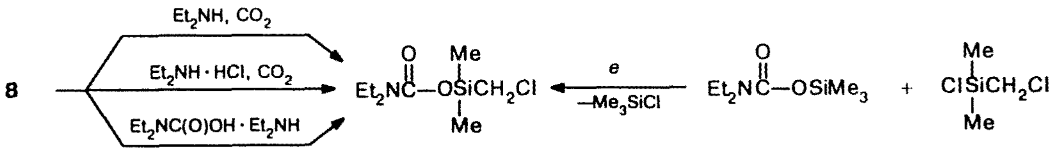
Thus, of the several possible routes of the reaction involving allylamino(trimethyl)silane, carboxylation (following reaction *a*) predominates. In this case, no intermediate formation of the substituted carbamic acid [All(Me_3Si)NC(O)OH] is observed and no dehydrocondensation or amination involving hydrosilane **8** occurs. This is apparently due either to steric factors or to the fact that the N atom in allylamino(trimethyl)silane is less nucleophilic than that in aliphatic amines.

It has been shown previously[3,5] that in the case of the bis-silylated amine, hexamethyldisilazane (in which the nucleophilicity of the N atom is even lower), carboxylation also becomes impossible.

Scheme 4



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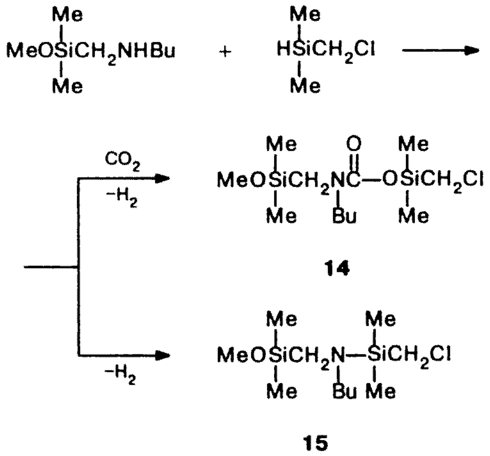
Finally, the replacement of aminosilane by aminomethylsilane unambiguously directs the process toward dehydrocondensation (Scheme 5), and this pathway is independent of whether or not carbon dioxide is used in the reaction (compound **14** or **15**, respectively, is formed).

Scheme 5



Experimental

All the initial compounds and solvents were thoroughly dried and distilled prior to use. All operations (preparation and isolation of compounds and withdrawing samples for analyses) were carried out in an atmosphere of dry nitrogen. The compositions of reaction mixtures and of pure products were checked by GLC using an LKhM-80 instrument (1.5 m × 3 mm stainless-steel columns, SE-30 on Chromaton N-AW as the stationary phase, and He as the carrier gas).

^{1}H NMR spectra were recorded on a Bruker WP-80 instrument (80 MHz) using C_6D_6 as the solvent and as the internal standard.

IR spectra were recorded on a Specord 75 IR spectrometer in thin film (for liquids), in pellets with KBr, or in Vaseline oil (for crystalline substances).

Triethoxysilyl diethylcarbamate (4). Carbon dioxide was passed for 3 h through a mixture of triethoxysilane (51.2 g, 0.31 mol) and diethylamine (29.2 g, 0.40 mol) heated to 50—55 °C in an atmosphere of dry nitrogen; after that, 71.5 g (82.1%) of compound **4** was isolated by fractionation, b.p. 102 °C (2 Torr), n_D^{20} 1.4125. Found (%): C, 47.32; H, 9.07; Si, 10.11. $C_{11}H_{25}NO_5Si$. Calculated (%): C, 47.27; H, 9.03; Si, 10.05. IR, ν/cm^{-1}: 1690 (C=O).

Bis(diethylaminocarbonyloxy)dimethylsilane (6). Carbon dioxide was passed for 3 h through a mixture of 1,1,3,3-tetramethyldisilazane (89.6 g, 0.67 mol) and diethylamine (9.83 g, 1.35 mol) heated to 50 °C in an atmosphere of dry nitrogen; after that, 125 g (72%) of bis(carbamate) **6** was isolated by fractionation, b.p. 78—80 °C (2 Torr), n_D^{20} 1.4385. Found (%): C, 49.69; H, 9.10; Si, 9.88. $C_{12}H_{26}N_2O_4Si$. Calculated (%): C, 49.62; H, 9.04; Si, 9.67. IR, ν/cm^{-1}: 1690 (C=O).

1,3-Bis(diethylaminocarbonyloxy)-1,1,3,3-tetramethyldisiloxane (7). The reaction of 1,1,3,3-tetramethyldisiloxane (20.6 g, 0.15 mol) with diethylamine (25 g, 0.34 mol) carried out in a similar way gave 55.7 g (94.6%) of bis(carbamate) **7**, b.p. 138—140 °C (2 Torr), n_D^{20} 1.4338. Found (%): C, 46.33; H, 8.99; Si, 15.34. $C_{14}H_{32}N_2O_5Si_2$. Calculated (%): C, 46.12; H, 8.85; Si, 15.41. ^{1}H NMR, δ: 0.13 (s, 12 H, $SiMe_2$); 0.98 (t, 6 H, C—CH_3); 3.12 (q, 4 H, C—CH_2).

(Diethylaminomethyl)dimethylsilane (10). A mixture of chloromethyldimethylsilane (10.1 g, 0.09 mol), diethylamine (6.8 g, 0.09 mol), and 15 mL of hexane was heated for 10 h. The precipitate was filtered off. Fractionation of the filtrate gave 12.25 g (90.7%) of compound **10**, b.p. 39 °C (23 Torr), n_D^{20} 1.4230. Found (%): C, 57.77; H, 13.21; Si, 19.41. $C_7H_{19}NSi$. Calculated (%): C, 57.84; H, 13.20; Si, 19.32. ^{1}H NMR, δ: 0.13 (s, 6 H, $SiMe_2$); 2.0 (s, 2 H, $SiCH_2$); 1.12 (t, 6 H, C—CH_3); 2.89 (q, 4 H, C—CH_2); 4.09 (s, 1 H, SiH). IR, ν/cm^{-1}: 2100 (Si—H).

(Chloromethyl)dimethylsilyl diethylcarbamate (11). *A.* Carbon dioxide was passed for 5 h through a mixture of chloromethyldimethylsilane (10.1 g, 0.09 mol) and diethylamine (6.7 g, 0.09 mol) heated to 50 °C. Fractionation of the reaction mixture gave 18.7 g (90.8%) of *O*-silylurethane **11**, b.p. 97 °C (3 Torr), n_D^{20} 1.4408. Found (%): C, 42.99; H, 8.10; Si, 12.57. $C_8H_{18}ClNO_2Si$. Calculated (%): C, 42.93; H, 8.12; Si, 12.55. ^{1}H NMR, δ: 0.37 (s, 6 H, $SiMe_2$); 3.0 (s, 2 H, $SiCH_2$); 1.14 (t, 6 H, C—CH_3); 3.10 (q, 4 H, C—CH_2).

B. A similar reaction in a mixture of chloromethyldimethylsilane (18.9 g, 0.17 mol) and diethylamine hydrochloride (11.3 g, 0.10 mol) through which CO_2 was passed for 10 h at 60 °C gave 20.1 g (86.9%) of compound **11**, b.p. 97 °C (3 Torr), n_D^{20} 1.4252.

C. Heating chloromethyldimethylsilane (5.29 g, 0.05 mol) and diethylammonium diethylcarbamate (4.63 g, 0.02 mol) for 5 h gave 4.6 g (84.6%) of compound **11**, b.p. 73 °C (2 Torr), n_D^{20} 1.4452.

D. A mixture of trimethylsilyl diethylcarbamate (19.3 g, 0.1 mol) and chloro(chloromethyl)dimethylsilane (14.3 g, 0.1 mol) was refluxed with the head of a fractionation column until the evolution of chlorotrimethylsilane was completed. Fractionation of the mixture afforded 22.2 g (95.9%) of compound **11**, b.p. 73 °C (2 Torr), n_D^{20} 1.4453.

(Diethylaminomethyl)dimethylsilyl diethylcarbamate (12). A mixture of chloromethyldimethylsilyl diethylcarbamate (22.4 g, 0.1 mol) and diethylamine (14.9 g, 0.2 mol) was kept at 55 °C for 5 h. Fractionation of the reaction mixture gave 25.4 g (97.7%) of *O*-silylurethane **12**, b.p. 148 °C (2.5 Torr), n_D^{20} 1.4485. Found (%): C, 55.37; H, 7.47; Si, 10.91. $C_{12}H_{28}N_2O_2Si$. Calculated (%): C, 55.32; H, 7.37; Si, 10.78.

Trimethylsilyl allylcarbamate (13). Carbon dioxide was passed for 7 h through a mixture of chloromethyldimethylsilane (9.98 g, 0.09 mol) and allylamino(trimethyl)silane (11.88 g, 0.09 mol) heated to 60 °C. Fractionation of the reaction mixture gave 15.3 g (98.1%) of *O*-silylurethane **13**, b.p. 63 °C (2.5 Torr), n_D^{20} 1.4383 (see Ref. 3: b.p. 60—61 °C (2.5 Torr), n_D^{20} 1.4380).

(Chloromethyl)dimethylsilyl *N*-butyl-(*N*-methoxydimethylsilylmethyl)carbamate (14). Carbon dioxide was passed for 5 h through a mixture of chloromethyldimethylsilane (8.7 g, 0.07 mol) and (*n*-butylaminomethyl)dimethylmethoxysilane (12.9 g, 0.07 mol), heated to 55 °C; then 20.25 g (83.9%) of *O*-silylurethane **14** was isolated, m.p. 152—155 °C (from ether). Found (%): C, 44.15; H, 9.02; Si, 16.74; Cl, 10.99. $C_{12}H_{28}ClNO_3Si_2$. Calculated (%): C, 44.25; H, 8.66; Si, 17.23;

Cl, 10.88. IR, ν/cm^{-1}: 1670 (C=O). ^{1}H NMR, δ: 0.43 (s, 12 H, SiMe$_2$); 2.23 and 2.43 (both s, 2 H, SiCH$_2$); 3.1 (s, 3 H, SiOMe).

[(Chloromethyldimethylsilyl)butylaminomethyl]methoxydimethylsilane (15). A mixture of chloromethyldimethylsilane (2.33 g, 0.02 mol) and (*n*-butylaminomethyl)dimethylmethoxysilane was allowed to stand overnight and then kept for 3 h at 65 °C. It gave 5.1 g (84.6%) of silane **15**, m.p. 168—170 °C (from ether). Found (%): C, 46.72; H, 10.08; Si, 19.08; Cl, 12.44. $C_{11}H_{28}ClNOSi_2$. Calculated (%): C, 46.86; H, 10.01; Si, 19.92; Cl, 12.57. ^{1}H NMR, δ: 0.4 (s, 12 H, SiMe$_2$); 2.30 and 2.43 (both s, 2 H, SiCH$_2$); 3.1 (s, 3 H, SiOMe).

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