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LETTERS TO THE EDITOR

Carboxylation of Aminosilanes

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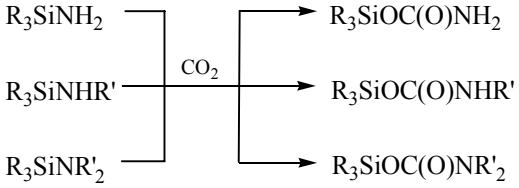
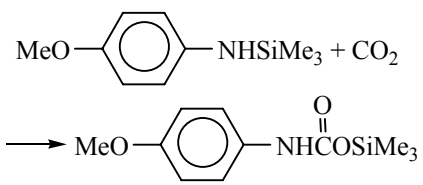
It has been established that *O*-silylurethanes can be obtained via carboxylation of compounds containing Si–N bonds [1]. This reaction is generally exothermic and is practically independent of a number of substituents at the nitrogen atom.



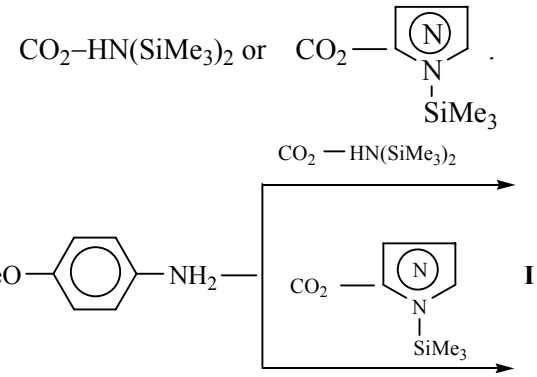
The presence of bulky substituents at nitrogen and silicon atoms in the initial compounds is seemingly the only factor preventing the absorption of carbon dioxide even under harsh conditions [2]; such aminosilanes include $PhNHSiMe_3$, $Ph(Et)NSiMe_3$, and Ph_2NSiMe_3.

We demonstrated that introduction of electron-donating substituents into such compounds allows preparation of *O*-silylurethanes using the described reaction, probably because of the enhanced nucleophilicity of the sunstrate.



I

Compound **I** was obtained independently using (4-methoxyphenyl)amine and *N*-siloxycarbonylating systems:



Trimethylsilyl(4-methoxyphenyl)carbamate (I). *a*. Carbon dioxide was passed through 3.20 g of (4-methoxyphenyl)-1,1,1-trimethylsilylamine at 50°C during 3 h. Yield 3.89 g (99 %), mp 53–54°C. IR-spectrum, ν, cm^{-1}: 3358 (N–H), 2955 (C–H), 1670 (C=O). ^1H NMR spectrum, δ, ppm: 0.33 s (9H, $SiCH_3$), 3.24 s (3H, OCH_3), 5.99 br. s (1H, NH), 6.70 d (2H, CH), 7.24 d (2H, CH). Found, %: C 55.22; H 7.15; N 5.83. $C_{11}H_{17}NO_3Si$. Calculated, %: C 55.20; H 7.16; N 5.85.

b. Carbon dioxide was passed through a mixture of 10.00 g of (4-methoxyphenyl)amine and 13.11 g of hexamethyldisilazane at 55°C during 4 h. Yield 18.47 g (95 %), mp 52–53 °C.

c. Carbon dioxide was passed through a mixture of 5.62 g (4-methoxyphenyl)amine and 7.04 g of 3(5)-methyl-1-(trimethylsilyl)-1*H*-pyrazole at 50°C during 2.5 h. Yield 10.59 g (97 %), mp 52–54°C.

IR-spectra of suspensions in Vaseline oil were registered using a Specord 75 IR spectrometer. ^1H NMR

spectrum was recorded using a Bruker WP-300 spectrometer (300 MHz), benzene-d_6 was used as solvent, and its residual protons were used as internal reference. The starting compound was purified via the fractional distillation. Synthetic operations including isolation and sampling were carried out under dry nitrogen atmosphere. Carbon dioxide was dried over sulfuric acid.

ACKNOWLEDGMENTS

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