ISSN 1070-3632, Russian Journal of General Chemistry, 2014, Vol. 84, No. 6, pp. 1115–1120.
Original Russian Text © L.O. Belova, M.V. Pletneva, M.G. Shamina, N.A. Golub, A.A. Korlyukov, A.D. Kirilin, 2014, published in Zhurnal Obshchei Khimii, 2014, Vol. 84, No. 6, pp. 932–937.

Unusual Behavior Nitrogen-containing Compounds in the Synthesis of *O*-Silylurethanes and Trimethylsilylureas

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Received August 29, 2013

Abstract—The behavior of organic and organosilicon nitrogen-containing compounds—hydrazine, aminopyridine, 2-furylamine, and diazole derivatives – in the synthesis of *O*-silylurethanes, semicarbazides, and ureas was studied. The structure of the synthesized *N,N*'-bis(furan-2-ylmethyl)ureas was studied by X-ray diffraction analysis.

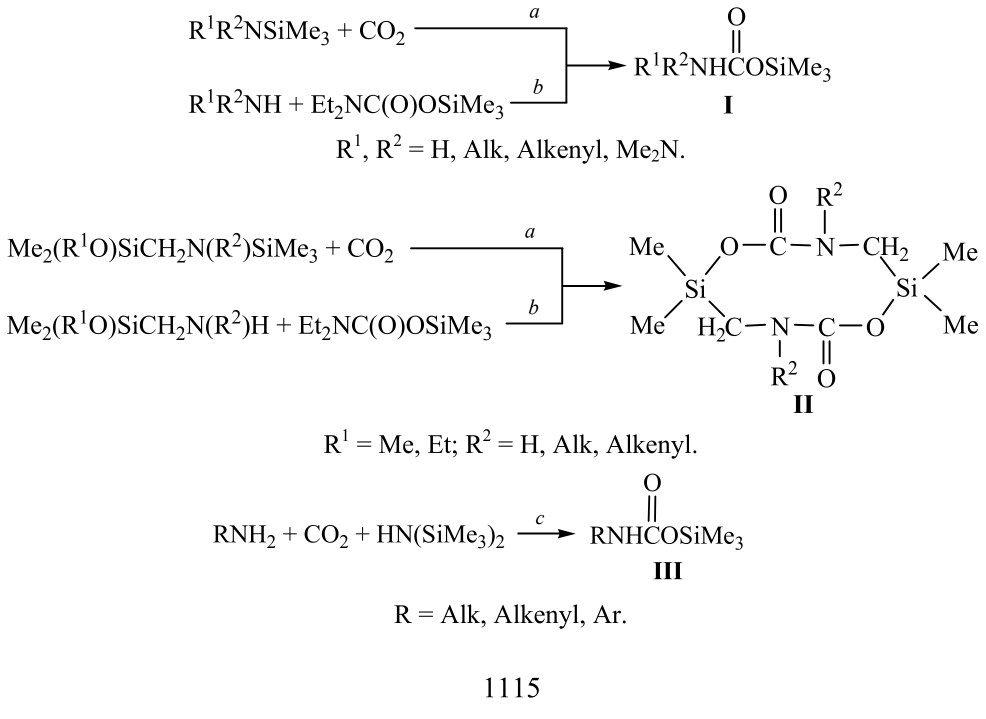
Keywords: *O*-silylurethanes, urea, trimethylsilyl isocyanate, diazole, X-ray diffraction analysis

DOI: 10.1134/S1070363214060103

It was previously shown [1, 2] that amines, hydrazines, and carbaminosilanes can be used to synthesize O-silylurethanes **I–III** by carboxylation (*a*), transamination (*b*), or *N*-siloxycarbonylation (*c*). The products are thermally stable up to 100–130°C [3] but generally prone to hydrolysis [1] (Scheme 1).

Reactions (*a*) and (*b*), and even *N*-siloxycarbonylation (*c*) which is considered a universal reaction not always provide *O*-silylurethanes. The replacement of the organic radical R in the starting amine by a heterocyclic fragment, for example, aminopyridine, makes trimethylsilyl (pyridine-2-yl)carbamate impos-

Scheme 1.



I

R^1, R^2 = H, Alk, Alkenyl, Me_2N.

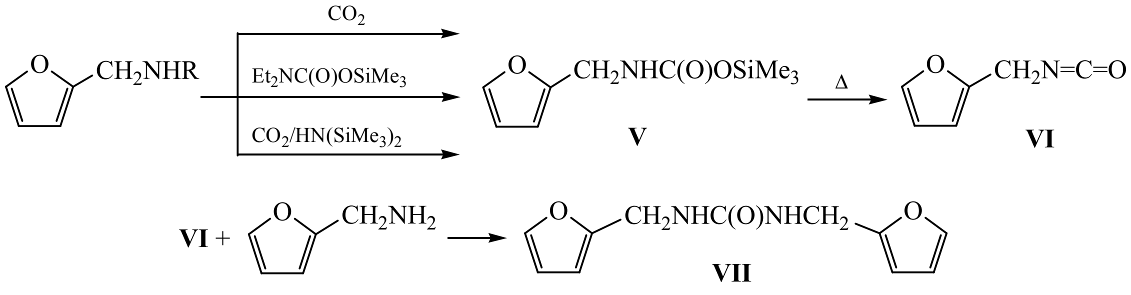
II

R^1 = Me, Et; R^2 = H, Alk, Alkenyl.

III

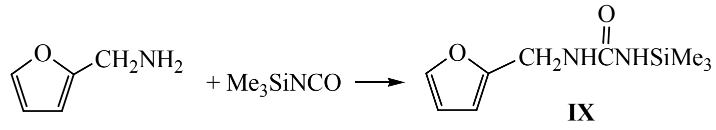
R = Alk, Alkenyl, Ar.

Scheme 2.



R= $SiMe_3$, H.

Scheme 3.



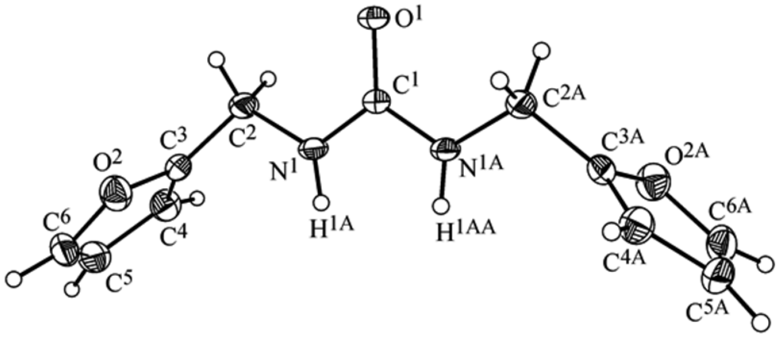
sible to synthesize by any of the mentioned reactions, probably, because of the low nucleophilicity of the amino nitrogen atom.

The synthesis of *O*-silylurethanes becomes possible if the amino group is separated from the heterocycle by at least one methylene group. Starting with (furan-2-ylmethyl)amine we could synthesize previously unknown *O*-(trimethylsilyl) (furan-2-ylmethyl)carbamate (**V**). This product proved to be thermally unstable, and it partially pyrolyzed to isocyanate **VI** under transamination reaction conditions (85–95°C); isocyanate **VI** reacted with the starting (furan-2-ylmethyl)amine to form *N,N′*-bis(furan-2-ylmethyl)urea (**VII**) (Scheme 2).

The composition and structure of compound **VII** were confirmed by IR and ^{1}H NMR spectroscopy, as well as elemental and X-ray diffraction analysis (see figure).

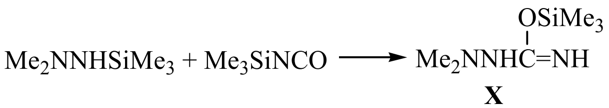
The principal structural parameters and details of crystallographic experiments are listed in Table 1. The symmetry of molecule **VII** is C^2, and it occupies special position in the crystal. The $O{=}C(NH)_2$ fragment is planar, and the C–N bond lengths are typical for urethanes. As the carbonyl groups forms a bifurcated hydrogen bond with the amino groups of neighboring molecules, the C^1–O^1 bond in the crystal cell is markedly elongated compared with the standard value of 1.22 Å [4]. In the crystal, the mentioned hydrogen bonds hold the molecules together to form chains in which the *N,N′*-disubsituted urea planes are parallel to the crystallographic plane (301).

Incorporation of the NH group in a heterocycle prevents synthesis of silicon-substituted ureas. Prolonged heating (60–80°C) of trimethylsilyl isocyanate with diazoles gave no 1-[*N*-(trimethylsilyl)-carbamoyl]diazole even in the presence of tin bis(2-ethylhexanoate). This result is probably explained by the reduced nucleophilicity of nitrogen atoms linked to hydrogen due to the *p*,π conjugation of the lone electron pair.



General view of *N,N′*-bis(furan-2-ylmethyl)urea (**VII**) molecule.

Scheme 4.



$$Me_2NNHSiMe_3 + Me_3SiNCO \longrightarrow Me_2NNH\overset{\overset{OSiMe_3}{|}}{C}{=}NH$$

X

However, like in the synthesis of *O*-silylurethanes, moving the amino group away from the heterocycle allowed us to synthesize organosilicon urea **IX** containing a furan substituent (Scheme 3).

N-trimethylsilyl derivatives of diazoles and hydrazine react with trimethylsilyl isocyanate. The reaction with 1,1-dimethyl-2-(trimethylsilyl)hydrazine occurs fairly easily and gives rise to *O*-trimethylsilyl (2,2-dimethylhydrazine)carboximidoate (**X**) (Scheme 4).

The obtained evidence allows us to suggest two reaction pathways. Initially the heterocumulene is inserted into the Si–N bond of 1,1-dimethyl-2-(trimethylsilyl)hydrazine to form semicarbazide **XI** with two Me_3Si groups. The subsequent elimination of one of the Me_3Si groups by pathway *a* gives rise to 2,2-dimethyl-*N*-(trimethylsilyl)hydrazinecarboxamide (**XII**) which undergoes silatropic isomerization to form the final reaction product **X** (Scheme 5).

Pathway *b* involves isomerization of semicarbazide **XI** into compound **XIII** which is hydrolytically unstable and coverts into carboximidoate **X** under the reac-tion conditions.

We also considered the third reaction pathway *c* involving addition of the NH proton of 1,1-dimethyl-2-(trimethylsilyl)hydrazine by the N=C bond of trimethylsilyl isocyanate.

Table 1. Principal bond lengths and bond angles in *N,N'*-bis-(furan-2-ylmethyl)urea

Bond	*d*, A	Bond angle	ω, deg
$O^1–C^1$	1.2482(19)	$C^3O^2C^6$	106.05(10)
$O^2–C^3$	1.3711(14)	$C^1N^1C^2$	121.03(10)
$O^2–C^6$	1.3731(16)	$O^1C^1N^{1a}$	121.93(7)
$N^1–C^1$	1.3512(12)	$O^1C^1N^1$	121.93(7)
$N^1–C^2$	1.4595(13)	$N^{1a}C^1N^1$	116.14(13)
$C^1–N^{1a}$	1.3512(12)	$N^1C^2C^3$	110.83(9)
$C^2–C^3$	1.4812(15)	$C^4C^3O^2$	109.97(10)
$C^3–C^4$	1.3486(16)	$C^4C^3C^2$	133.30(11)
$C^4–C^5$	1.4289(18)	$O^2C^3C^2$	116.72(10)
$C^5–C^6$	1.336(2)	$C^3C^4C^5$	106.80(11)
		$C^6C^5C^4$	106.24(11)
		$C^5C^6O^2$	110.93(11)

[a] The atom was obtained from the base atom by the symmetry code $-x, y, -z + 1/2$.

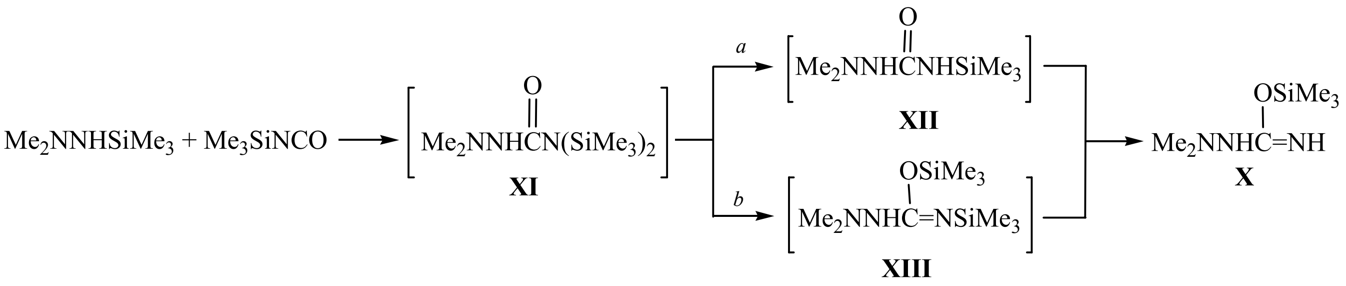
Has pathway *c* been realized, it would have form trimethylsilyl *N,N*-dimethylhydrazonocarbamate (**XIV**) (Scheme 6). However, the IR spectrum of the synthesized compound we found no stretching and deformation vibration bands of the NH_2 group, which gave us grounds to rule out this reaction pathway.

N-(Trimethylsilyl)(furan-2-ylmethyl)amine readily reacts with trimethylsilyl isocyanate (Scheme 7).

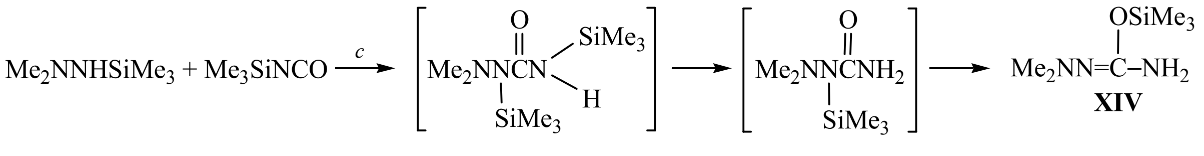
Trimethylsilyl *N*-[(*E*)-(furan-2-ylmethyl)]carbamidate (**XV**) is likely to be formed by the Scheme 8.

The reaction with *N*-trimethylsilyl derivatives of diazoles occurred only in the presence of a catalyst and

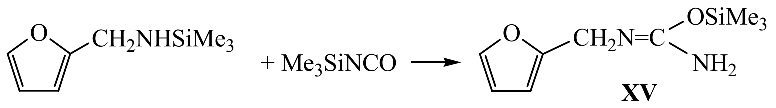
Scheme 5.



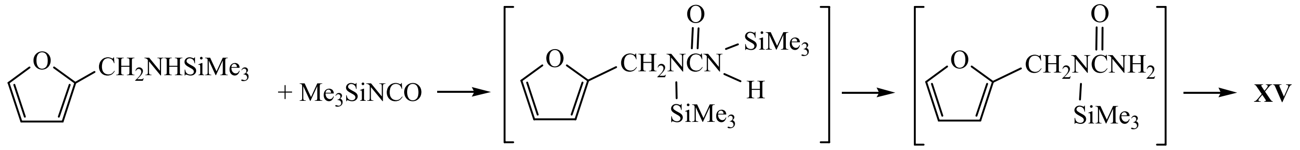
Scheme 6.



Scheme 7.



Scheme 8.



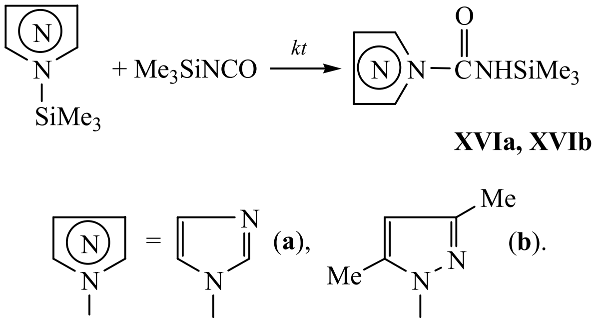
gave previously unknown compounds **XVIa** and **XVIb** (Scheme 9).

The type of the starting reagents and the composition of the resulting compounds together with physicochemical data show that the reaction involves intermediate formation of *N,N*-bis(trimethylsilyl) derivatives **XVIIa** and **XVIIb**. These products are so sensitive to air moisture that we failed to isolate them even under dry argon (Scheme 10).

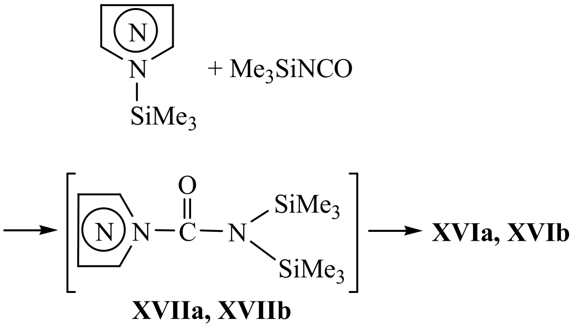
EXPERIMENTAL

The ^{1}H NMR spectra were recorded on a Bruker DRX-400 instrument at 400 MHz, solvent and internal standard $CDCl_3$. The IR spectra were obtained on a Specord 75 IR instrument in thin films (for liquids) and mineral oil (for crystals).

Scheme 9.



Scheme 10.



All starting compounds and solvents were thoroughly dried and distilled. All synthetic operations and isolation manipulation, as well as sampling for analysis were performed in a dry nitrogen atmosphere. The compositions of the reaction mixtures and pure compounds were controlled by GLC on a ShimadzuG-8 chromatograph (stainless steel columns 1500 × 3 mm, stationary phase SE-30 on Chromaton N-AW, carrier gas helium).

X-ray diffraction analysis was performed on a BrukerSMART 1000 CCD diffractometer (MoK_α, λ 0.71073 Å, ω scanning). The structure was solved by a direct method and refined over F^2_{hkl} using full-matrix anisotropic least squares. Hydrogen atoms were located by difference Fourier synthesis and refined isotropically. The principal crystal parameters and refinement parameters are listed in Table 2. All calculations were performed using SHELXTL PLUS [5].

***O*-(Trimethylsilyl) *N*-(furan-2-ylmethyl)carbamate (V).** Carbon dioxide was bubbled through 23.6 g of *N*-(trimethylsilyl)(furan-2-ylmethyl)amine for 1.5 h at 56°C. Fractionation gave 11.60 g (39.2%) of compound **V**, bp 104–108°C (1 mmHg), n_D^{20} 1.4680. IR spectrum, ν, cm^{-1}: 1640 (C=O), 3300 (NH). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 0.30 s (9H, $SiMe_3$), 4.30 s (2H, CH_2), 5.05 s (2H, NH_2), 6.13 d (1H, CCH, *J* 3.2), 6.26 d.d (1H, $CHC\underline{H}$, *J* 3.2, 2.0), 7.32 d (1H, CHO, *J* 2.0). Found, %: C 50.40; H 7.04; N 6.70. $C_9H_{15}NO_3Si$. Calculated, %: C 50.68; H 7.09; N 6.57.

***N,N'*-Bis(furan-2-ylmethyl)urea (VII).** A mixture of 21.1 g (furan-2-ylmethyl)amine, 41.13 g trimethylsilyl *N,N*-diethylcarbamate and 85 ml of absolute benzene was heated with a reflux head until diethylamine and benzene no longer evolved. The crystals were filtered off, washed with heptane, and dried. Yield 21.1 g (88.7%), mp 127–130°C. IR spectrum, ν, cm^{-1}: 1600 (C=O) and 3300 (NH). NMR spectrum^{1}H, δ, ppm (*J*, Hz): 4.3 d (4H, CH_2, *J* 5.6), 5.1 t (2H, NH, *J* 5.6), 6.16 d (2H, CCH, *J* 3.2), 6.28 d.d (2H, CHC<u>H</u>, *J* 3.2, 2.0), 7.30 d (2H, CHO, *J* 2.0). Found, %: C 59.40; H 5.45; N 12.73. $C_{11}H_{12}N_2O_3$. Calculated, %: C 59.99; H 5.49; N 12.72.

***N*-(Furan-2-ylmethyl)-*N'*-(trimethylsilyl)urea (IX).** A mixture of 15.4 g of trimethylsilyl isocyanate and 12.9 g (furan-2-ylmethyl)at mine was heated at 100–110°C for 1 h. The precipitate was filtered off. Yield 11.2 g (40%), mp 95–97°C. IR spectrum, ν, cm^{-1}: 3310 (NH), 1633 (C=O). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 0.25 s (9H, $SiMe_3$), 4.33 s (2H, CH_2), 4.15 br.s (1H, NH), 5.0 br.s (1H, NH), 6.18 d (1H, CCH, *J* 3.2), 6.29 d.d (1H, CHC<u>H</u>, *J* 3.2, 2.0), 7.34 d (1H, CHO, *J* 2.0). Found, %: C 51.10; H 7.64; N 14.41. $C_9H_{16}N_2O_2Si_1$. Calculated, %: C 50.91; H 7.60; N 13.19.

***O*-Trimethylsilyl (2,2-dimethylhydrazine)carboximidoate (X).** A mixture of 10 g 1,1-dimethyl-2-(trimethylsilyl)hydrazine and 8.71 g trimethylsilyl isocyanate was heated at 80–85°C for 7 h. The precipitate was filtered off. Yield 12.06 g (91%), mp 118–119°C. IR spectrum, ν, cm^{-1}: 3280 (NH), 1580 (C=N). ^{1}H NMR spectrum, δ, ppm: 0.06 s (9H, $SiCH_3$), 2.94 s (6H, NCH_3), 4.31 br.s (1H, NH). Found, %: C 41.11; H 9.67; N 23.85. $C_6H_{17}N_3OSi$. Calculated, %: C 41.11; H 9.77; N 23.97.

***O*-Trimethylsilyl *N*-[(*E*)-furan-2-ylmethyl]carbamidate (XV).** A mixture of 29.4 g *N*-(trimethylsilyl)(furan-2-ylmethyl)amine, 20 g of trimethylsilyl isocyanate, and a catalytic amount of tin bis(2-ethylhexanoate) was heated at 80°C for 65 h. The precipitate was filtered off. Yield 17.33 g (47%), mp 80–83°C. IR spectrum, ν, cm^{-1}: 3333 (NH_2), 1634 (NH_2), 1540 (C=N). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 0.05 s (9H, $SiMe_3$), 4.35 s (2H, CH_2), 5.8 br.s (2H, NH_2), 6.23 d (1H, CCH, *J* 3.2), 6.30 d.d (1H, CHC<u>H</u>, *J* 3.2, 2.0), 7.32 d (1H, CHO, *J* 2.0). Found, %: C 50.84; H 7.25; N 13.51. $C_9H_{16}N_2O_2Si$. Calculated, %: C 50.91; H 7.60; N 13.19.

***N*-Trimethylsilyl-1*H*-imidazole-1-carboxamide (XVIa).** A mixture of 15 g of 1-(trimethylsilyl)-1*H*-imidazole, 12.3 g of trimethylsilyl isocyanate, and a catalytic amount of tin bis(2-ethylhexanoate) was heated at 80–85°C for 10 h. Fractionation gave 18.20 g (93%) of compound **XVIa**, bp 67–69°C (1 mmHg), n_D^{20} 1.4632. IR spectrum, ν, cm^{-1}: 3350 (NH), 1700 (C=O). ^{1}H NMR spectrum, δ, ppm: 0.31 s (9H, $SiCH_3$), 1.43 br.s (1H, NH), 6.92 s (2H, NCHCH), 7.43 s (1H, NCHN). Found, %: C 45.73; H 7.37; N 22.81. $C_7H_{13}N_3OSi$. Calculated, %: C 45.87; H 7.15; N 22.93.

Table 2. Principal crystallographic data and refinement parameters for structure **VII**

Parameter	Value
Empirical formula	$C_{11}H_{12}N_2O_3$
M, g/mol	220.23
T, K	120(2)
Wavelength, A	0.71073
Crystal lattice	Monoclinic
Space group	*C*2/*c*
Unit cell parameters	*a* 23.430(3) Å, *b* 4.6054(5) Å, *c* 10.5435(13) Å, β 106.983(2)°
Volume, Å^3	1088.1(2)
Z	4
d_{calc}, mg/m^3	1.344
Absorbance, mm^{-1}	0.100
F(000)	464
Crystal size, mm^3	0.27 × 0.23 × 0.21
Data collection ranges, deg	1.82–30.03
Index ranges	$-32 \leq h \leq 32$, $-6 \leq k \leq 5$, $-14 \leq l \leq 14$
Unique reflections	1582 [*R*(int) – 0.0210]
F^2	1.039
$[I > 2\sigma(I)]$	R_1 0.0420, wR_2 0.1079
R indices	R_1 0.0527, wR_2 0.1143

3,5-Dimethyl-*N*-(trimethylsilyl)-1*H*-pyrazole-1-carboxamide (XVIb). A mixture of 6.5 g 3,5-dimethyl-1-(trimethylsilyl)-1*H*-pyrazole, 5.19 g trimethylsilyl isocyanate, and a catalytic amount of tin bis(2-ethylhexanoate) was heated at 80–85°C for 11 h. Fractionation gave 8.75 g (92%) of compound **XVIb**, bp 81–83°C (1 mmHg), n_D^{20} 1.4621. IR spectrum, ν, cm^{-1}: 3340 (NH), 1690 (C=O). ^{1}H NMR spectrum, δ, ppm: 0.39 s (9H, $SiCH_3$), 1.61 br.s (1H, NH), 2.25 s (6H, CCH_3), 5.72 s (1H, CCH). Found, %: C 51.07; H 8.19; N 19.41. $C_9H_{17}N_3OSi$. Calculated, %: C 51.15; H 8.11; N 19.88.

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