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Synthesis and Some Physicochemical Properties of the Carbazine Acid Silyl Esters

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Abstract—Structure of the dimethylcarbazine acid trimethylsilyl ether and pyrolysis of its derivative, the trimethylsilyl ester of *N,N*-dimethyl-*N'*-trimethylsilylcarbazine acid, were studied by the metods of X-ray diffraction and gas chromatography/mass spectrometry. The presence of the bifurcated hydrogen bonds between the trimethylsilyl dimethylcarbazinate molecules was detected. It was revealed why impossible to obtain dimethylaminoisocyanate even by the low-temperature pyrolysis.

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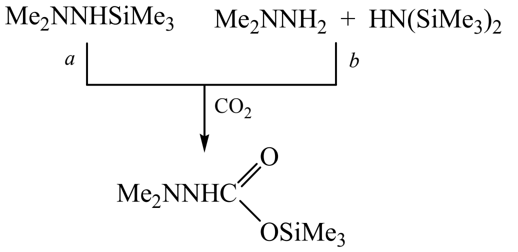
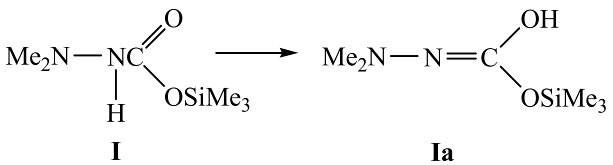
Earlier [1, 2] was shown that by the reactions of carboxylation (*a*) and *N*-siloxycarbonylation (*b*) of *N,N*-dimethylhydrazine can be synthesized the *N,N*-dimethylcarbazine acid trimethylsilyl ester (**I**).



I

As a rule, trimethylsilyl carbazinates and carbamates are hydrolytically unstable compounds [3]. That is why revealing their structure by X-ray diffraction analysis was performed successfully only for some of them: RNHC(O)OSiMe$_3$ (R = Ph [2], Me$_3$Si [4], and H [5]). We synthesized *O*-silyl uretane **I** and found that this compound, on the contrary, remarkable stable when stored in air. It could be assumed that the reason for this is the existence of **I** in the prototropic form **Ia**.



I **Ia**

The presence of two tautomers follows from the data of ^{1}H, ^{13}C and ^{29}Si NMR spectra.

To confirm this hypothesis, we carried out X-ray diffraction study of compound **I** (Figs. 1, 2). The bond lengths obtained are listed in Table 1. The Si^{1}–O^{1} bond (1.694 (1) Å) is longer than the standard Si–O single bond (1.64 Å) [6]. Interatomic distance Si^{1}···O^{1} 2.920(1) Å is less than the sum of the respective Van der Waals radii (3.48 Å) [7], but the angle with the opposite atom C^{2} is 151.35(7)°, which eliminates the presence of intramolecular coordination.

Atom N^{1} is pyramidal, the sum of angles is 332.7°. The bond N^{2}–C^{1} is double and is close by length to the single C–N bond adjacent to the carbonyl group (1.333 Å) [2].

The C^{1}–O^{1} and C^{1}–O^{2} bond lengths [1.351(2) and 1.214(2) Å, rtespectively] are also close to the values of 1.312 Å and 1.235 Å, characteristic of the bonds in the esters of carboxylic acids [6, 7].

All this led to the conclusion that the *N,N*-dimethylcarbazine acid trimethylsilyl ether exists in the hydrazone form **Ia**.

In the crystal, molecules **I** are connected to form chains through the weak hydrogen bonds N^{2}–H^{2}···O^{2} $\{-x, y + 1/2, -z - 1/2\}$ and N^{2}–H^{2}·· N^{1} $\{-x, y + 1/2, -z - 1/2\}$, parallel to the *b* axis of the unit cell (Fig. 2). One can assume that just the presence of these bifurcated hydrogen bonds between molecules leads to an increase in hydrolytic stability of *O*-silyluretane **I**.

We have previously shown that the use of compound **I** for the synthesis of dimethylamino-

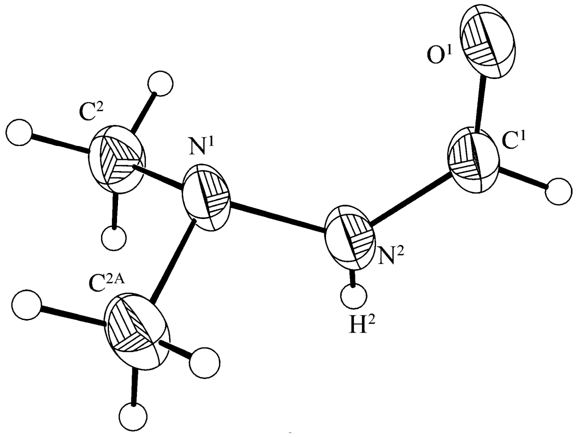
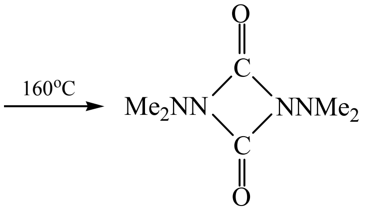


Fig. 1. Structure of molecule of *N,N*-dimethylcarbazine acid trimethylsilyl ester (**I**).

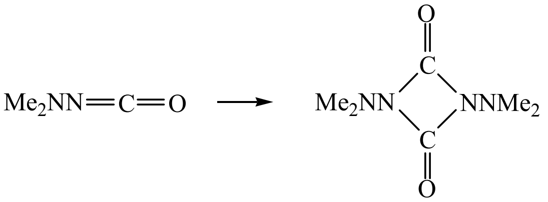
isocyanate (**III**) by pyrolysis at 180°C ended in failure [1].

$$\mathbf{I} \xrightarrow{\mathrm{Me_3SiCl/Et_3N}} \underset{\mathbf{II}}{\mathrm{Me_2NN(SiMe_3)C(O)OSiMe_3}}$$



IV

In our opinion, this is caused by a high temperature of the pyrolysis leading to the dimerization:



III **IV**

Therefore, to study the possibility of synthesizing isocyanate **III** we used the previously developed technique of pyrolysis of *O*-silyl uretanes in the presence of polychlorosilanes [8], which allows performing this reaction at the temperatures close to room temperature:

$$\mathbf{II} + 1.5\mathrm{PhSiCl_3} \xrightarrow[-\mathrm{Me_3SiCl}]{} \mathrm{Me_2NNCOSiMe_3}$$

$$\xrightarrow[-\mathrm{PhSiCl_2OSiMe_3}]{65\text{–}67^\circ\mathrm{C}} \mathbf{III} \longrightarrow \mathbf{IV}$$

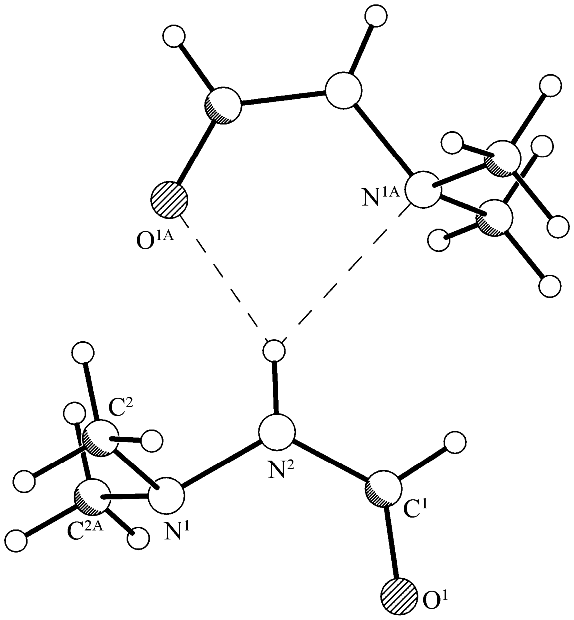


Fig. 2. Assocoation of molecules of *N,N*-dimethylcarbazine acid trimethylsilyl ester (**I**).

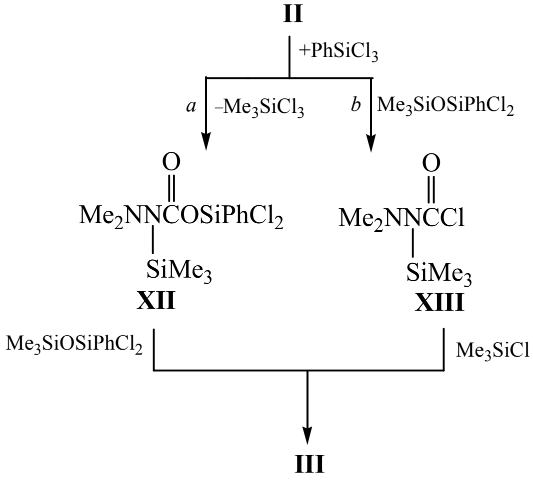
Nevertheless, despite the significant reduction of the process temperature, isolation of dimethylaminoisocyanate failed again, although undoubtedly it actually formed, as confirmed prolonged presence of strong absorption bands at 2300 cm^{-1} in the infrared spectrum. Moreover, among the reaction products were found unexpectedly organosiloxanes other than trimethyl-

Table 1. Principal bond lengths and bond angles in the structure **I**

Bond	*d*, Å	Bond angle	ω, deg
$Si^1–O^1$	1.694(1)	$O^1Si^1C^4$	109.47 (7)
$Si^1–C^4$	1.854(2)	$O^1Si^1C^2$	102.29 (7)
$Si^1–C^2$	1.856(2)	$C^4Si^1C^2$	111.47 (9)
$Si^1–C^3$	1.857(2)	$O^1Si^1C^3$	111.40 (7)
$O^1–C^1$	1.351(2)	$C^4Si^1C^3$	111.65 (8)
$O^2–C^1$	1.214(2)	$C^2Si^1C^3$	110.20 (8)
$N^1–N^2$	1.409(2)	$C^1O^1Si^1$	121.3(1)
$N^1–C^5$	1.467(2)	$N^2N^1C^5$	110.6(1)
$N^1–C^6$	1.465(2)	$N^2N^1C^6$	110.0(1)
$N^2–C^1$	1.342(2)	$C^5N^1C^6$	112.1(1)
		$C^1N^2N^1$	117.5(1)
		$O^2C^1N^2$	125.4(1)
		$O^2C^1O^1$	122.7(1)
		$N^2C^1O^1$	111.8(1)

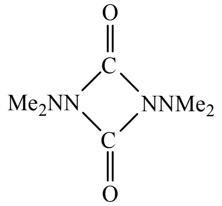
chlorosilane and phenyltrichlorosilane (Table 2), not forming in the similar processes studied earlier [10].

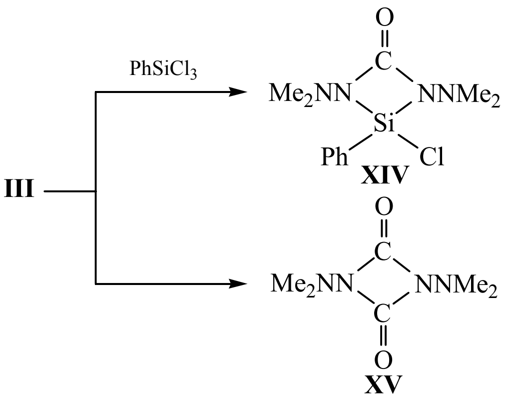
Analysis of the pyrolysis products (Table 2) allows us to conclude that there are two competing reactions involving Me_3SiO groups, that lead to the formation of a new, less stable *O*-silyluretane: without (*a*) and with (*b*) splitting of the SiO bond:



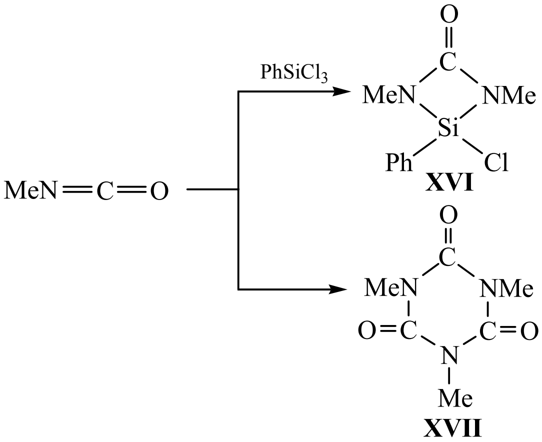
Attempt to separate these compounds from the dimer **IV** leads to an even more profound transformations with the removal of Me_2N, including formation of methylisocyanate and asymmetric dimers and trimers of the formed isocyanates (Table 3).

Table 2. The composition of the *O*-silyluretane **II** pyrolysis products determined by chromatography–mass spectrometry

Comp. no.	Formula	Content, %
IV		0.37
V	Me_3SiCl	1.31
VI	$Me_3SiOSiMe_3$	2.71
VII	$PhSiCl_3$	66.81
VIII	$PhSiCl_2OSiMe_3$	9.23
IX	$PhSi(OSiMe_3)_3$	0.81
X	$PhCl_2SiOSiPhCl_2$	17.38
XI	$PhCl_2SiOSiPhClOSiMe_3$	1.39

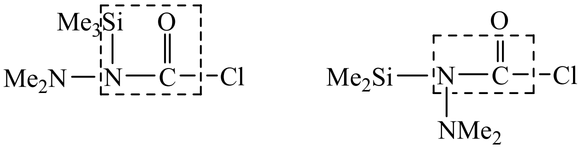


(1)

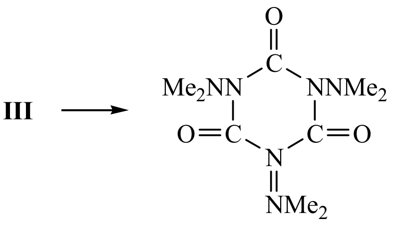


(2)

In connection with the common ideas about the propensity of the compounds **XII, XIII** to the β-elimination reactions, one would expect the formation of $Me_2NN{=}C{=}O$ as the main product [11]. In fact, the carbaminoyl chloride **XIII** molecule has two distinct electrophilic center: the silicon atom of the Me_3Si group and the carbon atom of the carbonyl group. Moreover, the reaction is complicated by the effects of the substituents neighboring to these centers, namely, Me_2N nitrogen atom and the chlorine atom at the carbon. Formally, there are two β-system:

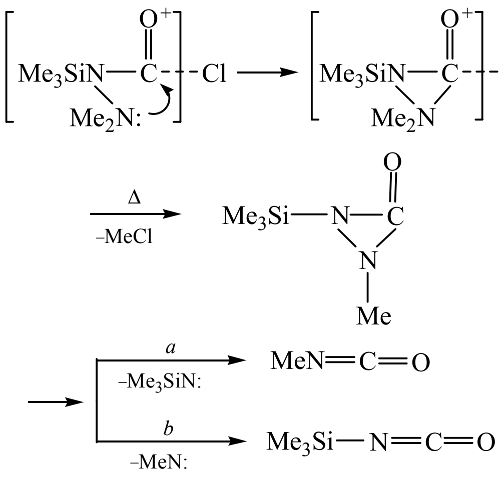


In the first case is possible an intramolecular quaternization at the nitrogen atom of the Me_2N group.



XVIII (3)

This is one of the versions for the appearance of MeNCO fixed as the products **XVI–XVIII** shown in Table 3.



Another parhway is confirmed experimentally [12]. It also implies the possibility of formation of two isocyanates:

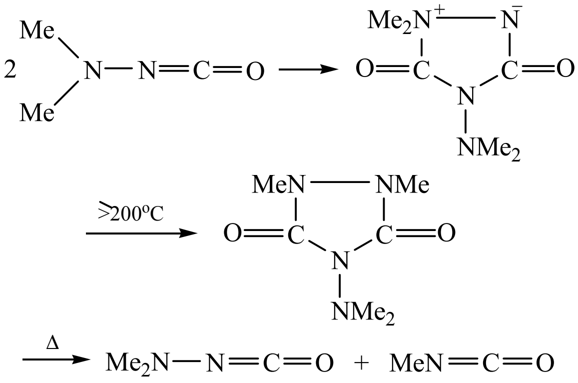
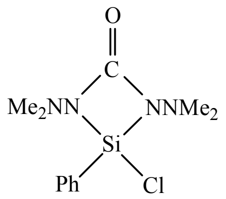
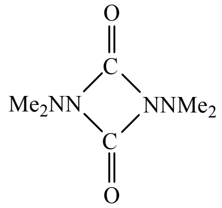
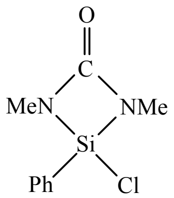
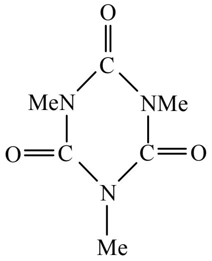
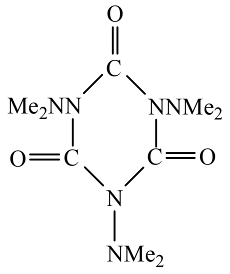


Table 3. The composition of the products of reactions (7)–(9) after separation, determined by chromatography – mass spectrometry

Comp. no.	Formula	Content, %
XIV		0.86
XV		97.48
XVI		0.28
XVII		1.06
XVIII		0.39

EXPERIMENTAL

The X-ray diffraction studies were performed on a Bruker SMART 1000 CCD diffractometer ($\lambda[\text{Mo}K_\alpha]$ = 0.71073 Å, ω-scan). The structure was solved by direct methods and refined by the full-matrix least squares method in anisotropic approximation over F^2hkl. Hydrogen atoms were located from difference Fourier syntheses of electron density and refined in the isotopic approximation. The main crystallographic data and refinement parameters are listed in Table 4. All calculations were performed using SHELXTL PLUS program package.

The study of composition of the *O*-silyluretane **II** pyrolysis products was carried out on a Thermo Focus

Table 4. The main crystallographic data and refinement parameters of structure **I**

Parameter	Value
Formula	$C_6H_{16}N_2O_2Si$
Molecular weight	176.30
T, K	120
Crystal system	Monoclinic
Space group	$P2_1/c$
Z	4
a, Å	11.7265(19)
b, Å	8.1556(13)
c, Å	11.5957(18)
β, deg	113.835(3)
V, Å^3	1014.4(3)
d_{calc}, g cm^{-3}	1.154
μ, cm^{-1}	1.94
F(000)	384
$2\theta_{\max}$, deg	60
Number of reflexes (total)	11415
Number of independent reflexes	2933
Number of reflexes with $I > 2\sigma(I)$	2138
Number of refined parameters	106
R_1	0.0450
wR_2	0.0974
$GOOF$	0.982
Residual electron density, e Å^{-3} ($\rho_{\min}/\rho_{\max}$)	0.552/–0.248

DSQ II gas chromatograph/mass spectrometer (gas chromatography: capillary column Supleco SPB-5ms, 15 m length, 0.25 mm inner diameter, phase thickness of 0.25 μm, carrier gas helium, operation mode: injector temperature 290ºC, the chromatograph initial oven temperature 60ºC, isothermal maintaining for 2 min, followed by heating 15ºC min^{-1} to 300ºC; mass spectrometer ionization energy 70 eV, source temperature 230ºC, scan range 10–800 Da at a rate of 1 scan s^{-1}, one unity resolution over the entire range of masses).

The sudy of composition of the *O*-silyluretane **II** pyrolysis products after separation of the reaction mixture was performed on a Finnigan MAT 95 XL gas chromatography/mass spectrometer (gas chromatography: capillary column Varian VF-5ms, 30 m length, inner diameter 0.25 mm, phase thickness 0.25 μm, carrier gas helium; chromatograph operation mode: injector temperature 270ºC, the chromatograph oven initial temperature 60ºC, heating at 15ºC min^{-1} to 270ºC; mass spectrometer operation: ionization energy 70eV, source temperature 230ºC, scan range 20–800 Da with rate of 1 s for a decade of mass, resolution 1500 FWHM).

The compounds **I** and **II** were synthesized by the method described in [1].

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