# *N,N'*-Bis(trimethylsilyl)dicyandiamide

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*N,N'*-Bis(trimethylsilyl)dicyandiamide was prepared for the first time by the reaction of dicyandiamide with hexamethyldisilazane in boiling tetrahydrofuran. Thermal transformations of this compound were studied by DTA. The novel compound may be used in the synthesis of bis(trimethylsilyl)carbodiimide.

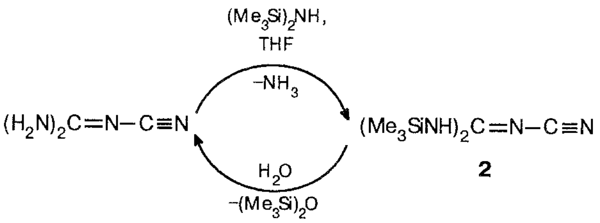
**Key words:** dicyandiamide; carbodiimide; organosilicon derivatives.

Previously[1—3] we developed an efficient method for preparing bis(trimethylsilyl)carbodiimide (**1**) as well as its organogermanium and organotin analogs based on reactions of dicyandiamide (DCDA) with hexamethyldisilazane (HMDSA) (catalyzed by ammonium sulfate), triethylgermyldiethylamine, or bis(tributylstannyl)oxide without a solvent. More recently,[4] the reaction of DCDA with a germylating mixture, $(Et_3Ge)_2O/(Me_3Si)_2NH[(NH_4)_2SO_4]$, was accomplished, which afforded bis(triethylgermyl)carbodiimide and $Et_3GeOSiMe_3$ in high yields. These chemical processes are likely to proceed *via* intermediate organometallic derivatives of DCDA, which are unstable under the reaction conditions and could not yet be isolated.

Attempts to silylate DCDA with trimethylchlorosilane in the presence of triethylamine in MeCN (55 °C, 4 h),[1] DMF, and HMPA[5] did not result in the formation of any individual dicyandiamide organosilicon derivative similar to the known *N*-tributylplumbylcyanoguanidine.[6] However, it has been suggested[5] that the difficultly separable mixture of reaction products contained such a compound and that it may be responsible for the absorption bands at 2200 and 2165 cm$^{-1}$ in the IR spectra.

In order to prepare *N,N'*-bis(trimethylsilyl)dicyandiamide (**2**) in the present work we used the conditions under which oganosilicon derivatives of urea, thiourea, biuret, thiobiuret, and triuret[7—10] have been previously prepared: the reaction of the corresponding nitrogen-containing compounds with HMDSA in the presence of $(NH_4)_2SO_4$ was carried out in boiling THF. Actually, by boiling crystalline DCDA with excess HMDSA (two- to four-fold) in the presence of the above-mentioned catalyst (66 °C, 8—14 h) we managed to obtain compound **2** in a yield of up to 80 % (Scheme 1).

**Scheme 1**



Compound **2** is a free-flowing white powder which is hydrolized in air. The IR spectrum recorded in vaseline oil exhibits the following main absorption bands, $\nu$/cm$^{-1}$: 3410, 3350, 3230, ($\nu$NH); 1640, 1570, 1520 ($\delta$NH, $\delta$CN); 2190, 2150 ($\nu$C≡N); 1250 ($\delta_s$Me in $Me_3Si$); 950 ($\nu_{as}$Si—N); 850, 760 ($\rho$Me in $Me_3Si$); 700, 685 ($\nu_{as}SiC_3$ + $\omega$NH). The IR spectra of the reaction mixtures and solutions of compound **2** in aprotic dipolar solvents (DMF, DMSO, or THF) each exhibit only two absorption bands due to the NH groups, at 3300 and 3150 cm$^{-1}$; the latter practically disappears after the THF solution is diluted. The $\nu$C≡N stretching region changes as well: the absorption band at 2150 cm$^{-1}$, which is the most intense in the spectrum of a suspension of compound **2** in vaseline oil, becomes in these solvents only a shoulder at the intense band at 2170 cm$^{-1}$. The IR spectra of solutions of compound **2** in hexane, benzene, or toluene differ little from those in vaseline oil, and in the region of the N—C≡N group vibrations they differ little from that of DCDA itself. The above-described changes in the IR spectra may be explained by the fact that the crystalline compound **2** can form various types of associates, which are successively destroyed, as compound **2** is dissolved and its concentration in aprotic dipolar solvents decreases. The fact that there is practically only one $\nu$N—H absorption band confirms the validity of the structure proposed for molecule **2**, which contains two identical $Me_3SiN$—H groups, and, like DCDA itself, is not a derivative of cyanoguanidine

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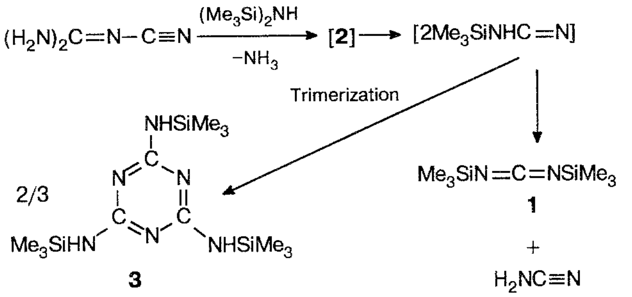
**Scheme 2**



[$Me_3SiNH-(Me_3SiN{=})C-NH-C{\equiv}N$].[11] In addition, we have shown that the monosubstituted derivative of the type $Me_3SiNH(NH{=})C-NH-C{\equiv}N$, analogous to known $Bu_3Pb$-cyanguanidine,[6] is not formed.

While examining the IR spectra and thermograms of **2** we found that an increase in the duration of the reaction (more than 10 h) results in the appearance of a side product, tris(trimethylsilyl)melamine (**3**) whose concentration increases with time; IR, $\nu$/cm$^{-1}$: 3230 (N—H); 1560, 1415, 560 (the *symm*-triazine ring); 1250, 860, 745 ($Me_3Si$) (see Ref. 12). This compound forms during thermal decomposition of **2** (170—180 °C), which was carried out to prepare carbodiimide **1** (yield ≤ 70 %). Among the products of rigorous thermolysis (T ≥ 240 °C), melamine and DCDA were also found. Thus, we carried out silylation of DCDA by the action of HMDSA according to the scheme reported by us previously.[13] The existence of intermediate compound **2** in the synthesis of **1** may thus be considered to be proved (Scheme 2).

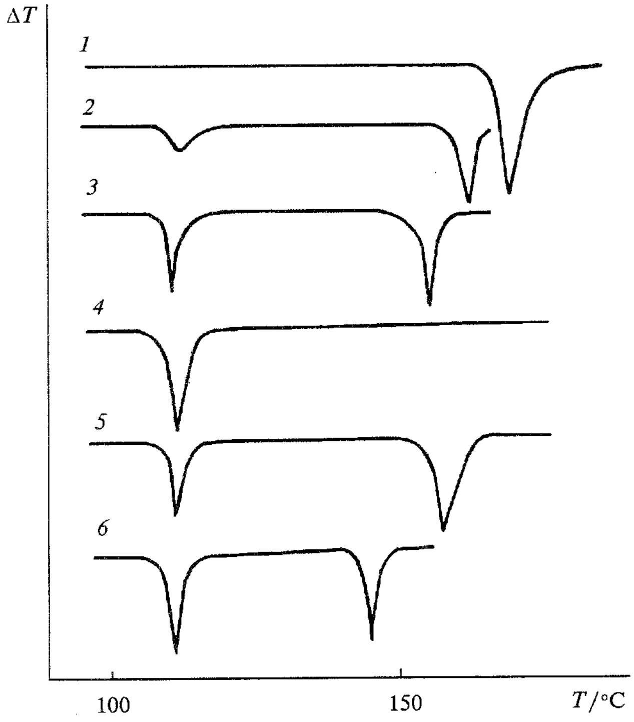


**Fig. 1.** DTA thermograms for various specimens of compound **2** (*1—3*), compound **3** (*4*), mixtures of compounds **2** and **3** in a ratio of 3:1 w/w (*5*) and 1:1 w/w (*6*).

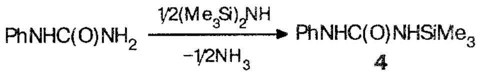
Thermal decomposition of compound **2** may be offered as an efficient method for preparing carbodiimide **1** containing no admixture of HMDSA that would be difficult to separate.[1,2] Compound **2** acts as a "latent" carbodiimide and offers obvious advantages over compound **1** with regard to its storage and transportation.

In order to confirm the scheme suggested for thermal transformations of **2** and to determine its melting point, we carried out its DTA (Fig. 1). Melting points for specimens of **2** prepared under various conditions were determined to lie within the interval 154—168 °C (thermograms *1—3*), which indicates that the pure compound has a m.p. of 168 °C. The specimens with lower melting points exhibited an additional endothermic effect in the range 100—120 °C, which is due to an admixture of melamine **3**. This was confirmed by the results of DTA of specimen **3** (thermogram *4*) and its mixtures with compound **2** (thermograms *5*, *6*). The specimens of compound **2** studied contain no DCDA admixture (m.p. 205 °C, according to DTA, *cf.* Ref. 14, m.p. 207—208 °C).

Compound **2** is hydrolized in air and under the action of aqueous MeOH or acetic acid to give DCDA, and the yield of hydrolysis products can be as high as 80—90 % (see Scheme 1). This reaction makes it possible to detect an admixture of compound **3** formed as a by-product, since under the action of water it is quantitatively converted into melamine,[12] which displays a very characteristic IR spectrum.

This method of the silylation of nitrogen compounds enables the preparation of a variety of organisilicon compounds which have been previously believed to be unstable and only recognized as intermediates. The method can be used as well for the synthesis of difficultly accessible derivatives, for example, *N*-trimethylsilyl-*N'*-phenylurea (**4**), which has been mentioned only once in Ref. 15 (a reference to an unpublished work of F. A. Heuglein and K. Linder). The conditions of performing the reaction according to Scheme 3 are similar to those given for Scheme 1. The yield of compound **4** is 83 %.

**Scheme 3**



$$PhNHC(O)NH_2 \xrightarrow[-1/2NH_3]{1/2(Me_3Si)_2NH} \underset{\mathbf{4}}{PhNHC(O)NHSiMe_3}$$

The IR spectrum of compound **4** exhibits the following absorption bands (vaseline oil), $\nu$/cm$^{-1}$: 3405, 3375, 3280, 3175 (N—H), 3110, 3050, 1580, 750 (Ph); 1630 (C=O); 1250, 850 ($Me_3Si$). The IR spectrum of a THF solution of compound **4** displays bands caused by the absorption of N—H groups which form H-complexes with the solvent (3320 and 3200 cm$^{-1}$), while the absorption bands of non-associated N—H groups (3420 and 3380 cm$^{-1}$) disappear. M.p. of **4** determined by DTA (146 °C) corresponds to the reported[15] value (147—148 °C).

The composition of compounds **2** and **4** has been confirmed by elemental analysis.

## Experimental

IR spectra for vaseline-oil suspensions placed between KBr plates or for THF solutions placed in 0.027 mm thick KBr cells were recorded on a Specord 75-IR spectrophotometer. The temperatures of the phase transitions were determined by DTA using a unit based on PRT-1000 M. The error of the measurements was not above 0.7 %, the rate of heating was 5 or 10 °C min$^{-1}$, the sensitivity of thermocouples was 6.9 mV cm$^{-1}$. All of the chemical operations were carried out in evacuated units or in an atmosphere of pure dry argon.

***N,N′*-Bis(trimethylsilyl)dicyandiamide (2).** A heterogeneous mixture of 4.2 g of DCDA, 16.1 g of HMDSA (fourfold excess), and 0.2 g of $(NH_4)_2SO_4$ in 50 mL of THF was refluxed at 66—67 °C for 14 h. When the evolution of ammonia was over, the resulting homogeneous solution was cooled, and some of compound **2** precipitated. Most of the product was isolated by removing THF. The overall yield of compound **2** was 9.15 g (80 %). Found (%): C, 41.54; H, 8.95; N, 24.65; Si, 22.90. $C_8H_{20}N_4Si_2$. Calculated (%): C, 42.06; H, 8.82; N, 24.52; Si, 24.59.

***N*-Trimethylsilyl-*N′*-phenylurea (4)** was prepared in a similar way from 2.72 g of phenylcarbamide, 1,61 g of HMDSA (molar ratio was 2:1), and 0.1 g of $(NH_4)_2SO_4$ (boiling for 8 h in 30 mL of THF) as a white solid. Yield 3.47 g (83 %). Found (%): C, 56,92; H, 7.32; Si, 13.25. $C_{10}H_{16}N_2OSi$. Calculated (%): C, 57.65; H, 7.74; Si, 13.48.

## References

1. I. A. Vostokov, Yu. I. Dergunov, and A. S. Gordetsov, *Zh. Obshch. Khim.*, 1977, **47**, 1769 [*J. Gen. Chem. USSR,* 1977, **47** (Engl. Transl.)].
2. USSR Pat. 583125, *Byul. izobret.*, 1977, 45 (in Russian).
3. A. S. Gordetsov, V. P. Kozyukov, I. A. Vostokov, S. V. Sheludyakova, Yu. I. Dergunov, and V. F. Mironov, *Usp. Khim.*, 1982, **51**, 848 [*Russ. Chem. Rev.*, 1982, **51** (Engl. Transl.)].
4. A. S. Gordetsov, A. P. Kozina, S. E. Skobeleva, Yu. I. Mushkin, R. P. Zakharova, and Yu. I. Dergunov, *Metalloorg. Khim.*, 1989, **2**, 1129 [*Organomet. Chem. USSR*, 1989, **2** (Engl. Transl.)].
5. I. A. Vostokov, *Khimiya elementoorgan. soedinenii* [*Chemistry of Organometallic Compounds*], Gor'kii, 1980, 103 (in Russian).
6. France Pat. 1525268, *Chem. Abstrs.*, 1969, **71**, 30588.
7. V. P. Kozyukov, G. I. Orlov, and V. F. Mironov, *Zh. Obshch. Khim.*, 1980, **50**, 1899 [*J. Gen. Chem. USSR,* 1980, **50** (Engl. Transl.)].
8. V. P. Kozyukov, E. V. Muzovskaya, and V. F. Mironov, *Zh. Obshch. Khim.*, 1983, **53**, 1096 [*J. Gen. Chem. USSR,* 1983, **53** (Engl. Transl.)].
9. A. S. Gordetsov, Yu. I. Mushkin, S. E. Skobeleva, N. P. Makarenko, S. V. Zimina, E. M. Moseeva, L. N. Martynova, and Yu. I. Dergunov, *Metalloorg. Khim.*, 1991, **4**, 1143 [*Organomet. Chem. USSR,* 1991, **4** (Engl. Transl.)].
10. A. S. Gordetsov, S. V. Zimina, L. N. Martynova, E. M. Moseeva, S. E. Skobeleva, T. K. Postnikova, V. L. Tsvetkova, and R. P. Zakharova, *Metalloorg. Khim.*, 1992, **5**, 811 [*Organomet. Chem., USSR,* 1992, **5** (Engl. Transl.)].
11. Yu. I. Mushkin, *Zh. Org. Khim.*, 1969, **5**, 235 [*J. Ogr. Chem. USSR,* 1969, **5** (Engl. Transl.)].
12. A. S. Gordetsov, I. A. Vostokov, V. A. Gal'perin, and Yu. I. Dergunov, *Zh. Obshch. Khim.*, 1976, **46**, 1654 [*J. Gen. Chem. USSR,* 1976, **46** (Engl. Transl.)].
13. A. S. Gordetsov and Yu. I. Dergunov, *Usp. Khim.*, 1985, **54**, 2076 [*Russ. Chem. Rev.*, 1985, **54** (Engl. Transl.)].
14. I. T. Goronovskii, Yu. P. Nazarenko, and E. F. Nekryach, *Kratkii spravochnik po khimii* [*Brief Handbook of Chemistry*], Naukova dumka, Kiev, 1987, 438 (in Russian).
15. V. Bazant, V. Chvalovský, and J. Rathouský, *Organosilicon compounds,* Prague, 1965, **2**(1), 387.

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