Reaction of Anhydrides of Mono-, Di-, and Tetracarboxylic Acids with Hexamethyldisilazane: A New Method for Synthesis of N-Trimethylsilylamides and -Imides

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Received October 24, 2002

Previously, we found that the reaction of hexamethyldisilazane (HMDS) with carboxylic acids [1] or their ammonium salts [2] resulted in the corresponding trimethylacyloxysilanes.

Continuing this research, we showed that the reaction of anhydrides of monocarboxylic acids with HMDS resulted in the formation of their *N*-trimethylsilylamides and trimethylacyloxysilanes:

$$(RCO)_2O + Me_3SiNHSiMe_3$$

$$\sim RCONHSiMe_3 + RCOOSiMe_3.$$
(1)

The yields of the products of reaction (1) are close to quantitative. In contrast to this, the reaction of HMDS with dicarboxylic acid anhydrides gives cyclic *N*-trimethylsilylimides:

Y = cis-CH=CH, cis-ClC=CCl, and 1,2-C₆H₄. Tetracarboxylic acid anhydrides react analogously:



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The yields of cyclic *N*-trimethylsilylimides are 50–99%. All these compounds are yellowish crystalline substances, which are readily soluble in common organic solvents.

The cyclic anhydrides of 1,2-alkanedicarboxylic acids, as well as phthalic anhydride derivatives with electronegative substituents (Cl, NO₂), react with HMDS to produce acyclic 1-(trimethylsiloxycarbonyl)-2-(trimethylsilylaminocarbonyl) derivatives rather than cyclic imides:

$$Y[< C > O] + (Me_3Si)_2NH$$

$$U = O$$

$$(4)$$

$$\rightarrow \text{Me}_3\text{SiOCOYCONHSiMe}_3,$$

$$= -\text{CHCH}_2-, \qquad \begin{array}{c} \text{Cl} \\ \text{Cl} \\ \text{Cl} \end{array}, \text{ and } \\ O_2\text{N} \end{array}$$

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In the above reactions, 1,1,3,3-tetramethyldisilazane can be used along with HMDS. Thus, for example, the former reacts with phthalic anhydride according to the scheme

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Table 1. Physicochemical constants and elemental analysis data for N-trimethylsilylimides of di- and tetracarboxylic acids

Compound	Yield, %	$T_{\rm m}$, °C	Found	, wt %	Empirical formula	Calculated, wt %		
Compound			С	Н		С	Н	
I. C ₂ H ₂ (CO) ₂ NSiMe ₃	42	_	50.01	6.72	C ₇ H ₁₁ NO ₂ Si	49.67	6.55	
II. C ₂ Cl ₂ (CO) ₂ NSiMe ₃	87	_	35.07	4.10	C7H9NO2Cl2Si	35.31	3.81	
III. $C_6H_5(CO)_2NSiMe_3^*$	99	66–67	60.32	6.03	C ₁₁ H ₁₄ NO ₂ Si	60.24	5.98	
IV. $O[C_6H_3(CO)_2NSiMe_3]_2^{**}$	98	126–128	58.84	5.18	$C_{22}H_{24}N_2O_5Si_2$	58.40	5.30	
V. $CO[C_6H_3(CO)_2NSiMe_3]_2^{***}$	97	120–122	_	_	-	_	_	

* Bp 120(1)°C. IR (v, cm⁻¹): 1700 (C=O); 1295 (C–N); 1070 (Si–N).

** IR (v, cm⁻¹): 1700, 1710 (C=O); 1300 (C–N); 1070 (Si–N).

*** IR (v, cm⁻¹): 1680, 1720 (C=O); 1070 (Si–N). MS, *m/z* (intensities, % of maximum): 464(1) M⁺; 449(57) (M–Me); 376(27) (M–NHSiMe₃)⁺; 348(19) (M–CO–NHSiMe₃)⁺; 73(100) (SiMe₃⁺).

Table 2. Physicochemical constants and elemental analysis data for O,N-bis(trimethylsilyl) derivatives of monoamides of dicarboxylic acids Me₃SiOC(O)YC(O)NHSiMe₃

Com- pound	Y	Yield, %	T _b , °C	Found, wt %				Empirical	Calculated, wt %			
				C	Н	N	Si	formula	C	Н	Ν	Si
VI	$CH_2CH_2^*$	96	110(1)	45.90	8.63	5.68	21.42	C ₁₀ H ₂₃ NO ₃ Si ₂	54.197	8.81	5.36	21.40
VII	C ₆ H ₃ (NO ₂)**	90	63 (mp)	47.02	6.27	7.40	15.80	$C_{14}H_{22}N_2O_5Si_2$	47.45	6.21	7.90	15.80
VIII	$C_6 Cl_4^{***}$	96	147–9 (1)	_	_	_	_	_	_	—	_	_

* d_4^{20} 1.0036; n_D^{20} 1.4525. IR (v, cm⁻¹): 3418 (N–H); 2955 (CH₃); 1716(C(O)–O); 1682 (C(O)–N); 1450, 1370 (CH₃); 1250, 850, 755 (Si–CH₃); 1055 (Si–O).

** ¹H NMR (δ, ppm): 0.27 (Me₃SiO); 0.48 (Me₃SiNH); 7.58 (C₆H₃NO₂); IR (ν, cm⁻¹): 3420 (N–H); 2960 (CH₃); 1728 (C(O)–C); 1718 (C(O)–N); 1600 (C₆H₃); 1450, 1345 (CH₃); 1245, 840, 755 (Si–CH₃); 1055 (Si–O).

*** ¹H NMR (δ , ppm): 0.22 (Me₃SiO); 0.28 (Me₃SiNH). MS, *m*/z (intensities, % of maximum): 445(3) M⁺; 430(20) (M–Me)⁺; 357(19)

 $(M-NHSiMe_3)^+$; 146(100) Me_3SiNHSiMe_2^+.

The primary act in the reaction of HMDS with carboxylic acid anhydrides is the cleavage of one anhydride C–O bond. In the case of acyclic anhydrides, this reaction is the final one, which is shown in Eq. (1). For cyclic anhydrides of di- and tetracarboxylic acids (for example, phthalic), this stage is described by the scheme



The intermediate 1-(trimethylsiloxycarbonyl)-2-(trimethylsilylaminocarbonyl)benzene undergoes further cyclization, with elimination of trimethylsilanol:



The yields of the obtained *N*-trimethylsilylamides and -imides, their physical constants, and analytical data are summarized in Tables 1 and 2, respectively.

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Their structures were confirmed by ¹H NMR and IR spectroscopy (the parameters are shown in the same tables) and by mass spectrometry.

The anhydrides and HMDS were taken in a 1:1 or 1:2 molar ratio. The reactions were carried out at $130-140^{\circ}$ C. The mixtures were stirred for 2-3 h (in the case of the solid aromatic anhydrides, until they completely dissolved). The liquid reaction products

were isolated by distillation, and the solid ones, by recrystallization.

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