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Reaction of Hexamethyldisilazane with Cyclic Anhydrides of Organic Acids: A New Route to *N*-Trimethylsilylimides of Di- and Tetracarboxylic Acids

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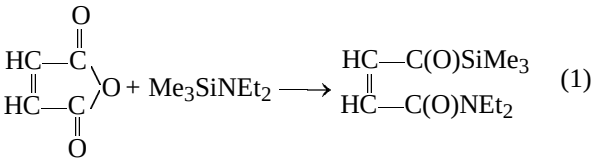
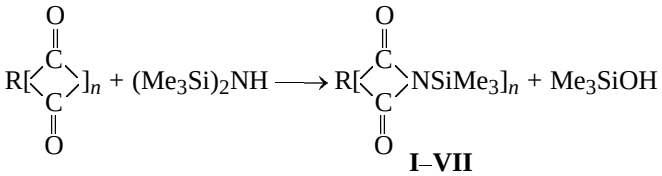
Abstract—Cyclic anhydrides of di- and tetracarboxylic acids react with hexamethyldisilazane to give the corresponding *N*-trimethylsilylimides in 90–96% yields. However, cyclic anhydrides of succinic, 4-nitrophthalic, and tetrachlorophthalic acids react differently, giving acyclic trimethylsilyl esters of mono-*N*-trimethylsilylamides of these acids in 90–93% yields. The ^{1}H NMR, IR, and mass spectra of the compounds synthesized were studied.

It is known [1] that cyclic anhydrides of dicarboxylic acids react with trimethylsilyl(diethyl)aminosilane [scheme (1)] to give acyclic trimethylsilyl esters of mono-*N*,*N*-diethylamides of the corresponding acids.



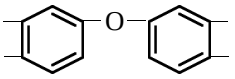
(1)

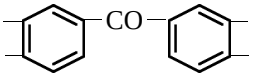
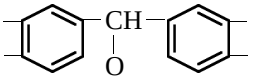
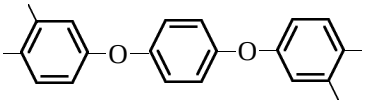
We found that hexamethyldisilazane reacts with cyclic anhydrides of dicarboxylic acids differently [reaction (2)].



(2)

I–**VII**

n = 1 (**I**–**III**), **2** (**IV**–**VII**); R = –CH=CH– (**I**), –CCl=CCl– (**II**),  (**III**),  (**IV**),

 (**V**),  (**VI**),  (**VII**).

Cyclic anhydrides of tetracarboxylic acids react with hexamethyldisilazane similarly to form the corresponding *N*,*N*'-bis(trimethylsilyl)diimides. Reaction (2) is performed by heating to 130–140°C a mixture of hexamethyldisilazane with an equimolar amount of a di- or tetracarboxylic acid anhydride with stirring for 2–3 h, until the anhydride fully dissolves. The target product precipitates on cooling. Compounds **I**–**VI** (Tables 1, 2) are yellowish crystalline substances soluble in the majority of organic solvents. Compound **VII** is a viscous liquid.

The new reaction is the simplest route to imides of di- and tetracarboxylic acids. The yields of *N*-trimethylsilylimides synthesized by this route (90–96% in most cases), their physicochemical constants, and ana-

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Table 1. Physicochemical constants and analytical data for *N*-trimethylsilylimides of di- and tetracarboxylic acids **I**–**VII**

Comp. no.	Compound	Yield, %	mp, °C	Found		Formula	Calculated	
				C	H		C	H
I	$C_2H_2(CO)_2NSiMe_3$	42	–	50.01	6.72	$C_7H_{11}NO_2Si$	49.67	6.55
II	$C_2Cl_2(CO)_2NSiMe_3$	87	–	35.07	4.10	$C_7H_9Cl_2NO_2Si$	35.31	3.81
III	$C_6H_4(CO)_2NSiMe_3$ [a]	99	66–67	60.32	6.03	$C_{11}H_{13}NO_2Si$	60.24	5.98
IV	$O[C_6H_3(CO)_2NSiMe_3]_2$ [b]	98	126–128	58.84	5.18	$C_{22}H_{24}N_2O_5Si_2$	58.40	5.30
V	$CO[C_6H_3(CO)_2NSiMe_3]_2$ [c]	97	120–122	–	–	–	–	–
VI	$Me_3SiOCH[C_6H_3(CO)_2NSiMe_3]_2$	99	112–115	57.69	6.25	$C_{26}H_{34}N_2O_5Si_3$	57.99	6.31
VII	$C_6H_4[OC_6H_3(CO)_2NSiMe_3]_2$	99	92–95	61.53	5.04	$C_{28}H_{28}N_2O_6Si_2$	61.76	5.14

[a] bp 120°C (1 mm Hg). IR spectrum, ν, cm^{-1}: 1700 (C=O), 1295 (C–N), 1070 (Si–N). [b] IR spectrum, ν, cm^{-1}: 1700, 1710 (C=O), 1300 (C–N), 1070 (Si–N). [c] IR spectrum, ν, cm^{-1}: 1680, 1720 (C=O), 1070 (Si–N).

Table 2. Mass spectra of *N*-trimethylsilylimides of di- and tetracarboxylic acids $R[(CO)_2NSi(CH_3)_3]_n$, *m/z* (I_{rel}, %)

Ion	R						
	C_2H_2 [a] (*n* = 1)	C_6H_4 [b] (*n* = 1)	C_2Cl_2 [c] (*n* = 1)	$(C_6H_3)_2O$ [d] (*n* = 2)	$(C_6H_3)_2CO$ [e] (*n* = 2)	$(C_6H_3)_2CH(OSiMe_3)$ [f] (*n* = 2)	$(C_6H_3O)_2C_6H_4$ [g] (*n* = 2)
$[M]^+$	169 (1)	219 (1)	237 (1)	452 (9)	464 (1)	538 (5)	544 (13)
$[M - Me]^+$	154 (44)	204 (100)	222 (67)	437 (100)	449 (57)	523 (20)	529 (84)
$[M - SiMe_3]^+$	96 (48)	146 (2)	164 (8)	379 (1)	–	465 (4)	475 (6)
$[M - NHSiMe_3]^+$	–	131 (64)	–	365 (17)	376 (27)	450 (100)	
$[M - CO - NHSiMe_3]^+$	–	103 (52)	121 (9)	–	348 (19)	–	
$[SiMe_3]^+$	73 (58)	73 (2)	73 (33)	73 (33)	73 (100)	73 (100)	73 (100)

Note: Other ions: [a] 143 (47), 130 (21), 126 (15) $[M - Me - CO]^+$, 75 (100). [b] 160 (74) $[M - Me - CO_2]^+$, 77 (4) $[C_6H_5]^+$. [c] 147 (24), 93 (100) $[M - NHSiMe_3 - 2CO]^+$, 88 (41) $[Me_3SiNH]^+$, 75 (21). [d] 424 (2) $[M - CO]^+$, 393 (8) $[M - Me - CO_2]^+$, 323 (4) $[M - SiMe_3 - 2CO]^+$. [e] 246 (2) $[M - C_6H_3(CO)_2NHSiMe_3]^+$. [f] 449 (70), 380 (30), 360 (16), 351 (12), 287 (18), 220 (18), 96 (16), 94 (15), 75 (30). [g] 490 (4), 400 (9) $[M - NHSiMe_3 - 2CO]^+$, 385 (10), 382 (7), 340 (4), 327 (8), 313 (6), 258 (12), 147 (100).

lytical and spectroscopic (^1H NMR, IR) data are given in Table 1; the mass spectra are given in Table 2.

However, cyclic anhydrides of succinic, 4-nitrophthalic, and tetrachlorophthalic acids do not form *N*-trimethylsilylimides in the reaction with hexamethyldisilazane. Instead, reaction of type (1) occurs, and acyclic trimethylsilyl esters of mono-*N*-trimethylsilylamides of these acids ($Me_3OOCRCONHSiMe_3$, **VIII**–**X**) are formed. Their yields (90–93%), physicochemical constants, and analytical and spectroscopic (^1H, NMR) data are given in Table 3; the mass spectra are given in Table 4.

EXPERIMENTAL

The mass spectra were taken on a Varian MAT-212 gas chromatograph–mass spectrometer (ionizing electron energy 70 eV, Varian-3700 chromatograph, carrier gas He, SE-54 phase). The IR spectra were taken on a Specord IR-75 spectrometer in the range 400–4000 cm^{-1} (thin films). The ^1H NMR spectra were measured on a Tesla BS-497 spectrometer (100 MHz, 10–30% solutions in CCl_4, internal reference TMS). The chemical shifts are given in the δ scale.

Trimethylsilylphthalimide III. A mixture of 29.6 g of phthalic anhydride and 32.2 g of hexamethyldisilazane was heated with stirring at 130–140°C until the anhydride fully dissolved. The reaction products, trimethylsilanol (17.5 g, 97%) and trimethylsilylphthalimide (43.3 g, 99%) were distilled in a vacuum.

Table 3. Physicochemical constants and analytical data for *O*,*N*-bis(trimethylsilyl) derivatives of dicarboxylic acid monoamides $Me_3SiOC(O)RC(O)NHSiMe_3$ (**VIII**–**X**)

Comp. no.	R	Yield, %	bp, °C (*p*, mm Hg) or mp, °C	Found				Formula	Calculated			
				C	H	N	Si		C	H	N	Si
VIII	CH_2CH_2[a]	96	110 (1)	45.90	8.63	5.68	21.42	$C_{10}H_{23}NO_3Si_2$	46.19	8.81	5.36	21.40
IX	$C_6H_3(NO_2)$-4[b]	90	63	47.02	6.27	7.40	15.80	$C_{14}H_{22}N_2O_5Si_2$	47.45	6.21	7.90	15.80
X	C_6Cl_4[c]	96	147–149 (1)	–	–	–	–	–	–	–	–	–

[a] d_4^{20} 1.0036, n_4^{20} 1.4525. IR spectrum, ν, cm^{-1}: 3418 (N–H), 2955 (CH_3), 1716 [C(O)–O], 1682 [C(O)–N], 1450, 1370 (CH_3), 1250, 850, 755 (Si–CH_3), 1055 (Si–O). [b] ^1H NMR spectrum, δ, ppm: 0.27 (Me_3SiO), 0.48 (Me_3SiNH), 7.58 ($C_6H_3NO_2$). IR spectrum, ν, cm^{-1}: 3420 (N–H), 2960 (CH_3), 1728 [C(O)–C], 1718 [C(O)–N], 1600 (C_6H_3), 1450, 1345 (CH_3), 1245, 840, 755 (Si–CH_3), 1055 (Si–O). [c] ^1H NMR spectrum, δ, ppm: 0.22 (Me_3SiO), 0.28 (Me_3SiNH).

Table 4. Mass spectra of acyclic trimethylsilyl esters of dicarboxylic acid mono-*N*-trimethylsilylamides $Me_3OC(O)\cdot RC(O)NHSiMe_3$, *m/z* ($I_{rel}$, %)

Ion	R		
	C_2H_4[a]	$C_6H_3NO_2$[b]	C_6Cl_4[c]
$[M]^{+\cdot}$	261 (7)	354 (1)	445 (3)
$[M - Me]^+$	246 (7)	339 (42)	430 (20)
$[M - CO_2]^{+\cdot}$	217 (1)	310 (5)	–
$[M - NHSiMe_3]^+$	173 (4)	266 (3)	357 (19)
$[M - Me - Me_3SiOH]^+$	–	234 (2)	340 (10)
$[Me_3SiNHSiMe_2]^+$	146 (70)	146 (100)	146 (100)
$[M - CO_2SiMe_3]^+$	144 (17)	–	–
$[Me_3Si]^+$	73 (100)	73 (44)	73 (76)

Note: Other ions: [a] 231 (2), 130 (15) $[M - CH_2CO_2SiMe_3]^+$. [b] 161 (3). [c] 415 (4), 329 (9) $[M - CONHSiMe_3]^+$, 321 (7), 268 (9) $[Cl_4C_6(CO)_2]^+$.

The reactions of hexamethyldisilazane with anhydrides of other di- and tetracarboxylic acids were performed similarly.

REFERENCES

1. Itoh, K., Sakai, S., and Ishii, Y., *J. Org. Chem.*, 1966, vol. 31, no. 12, p. 3948.