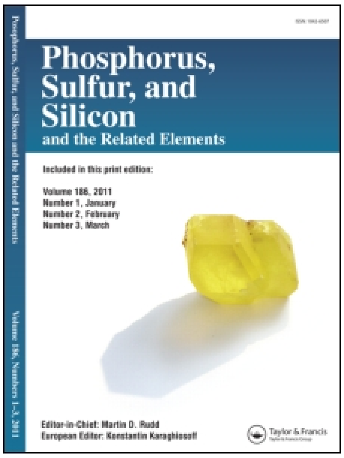

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CONTRIBUTIONS TO THE CHEMISTRY OF ORGANIC SILICON-NITROGEN-COMPOUNDS, I

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CONTRIBUTIONS TO THE CHEMISTRY OF ORGANIC SILICON-NITROGEN-COMPOUNDS, I. SYNTHESIS OF N,N-BIS-(TRIMETHYLSILYL)AMINES

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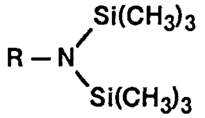
The preparation of N,N-bis-(trimethylsilyl)amines 1 has been investigated. Three convenient methods are reported: A, Transfer of (catalytically) activated Tms-groups to amines starting from N-silylated carbonamides, B, silylation of amines with trimethylsilylchloride 5/NEt_3 in the presence of $TiCl_4$, C, silylation of primary amines 4 or mono-(trimethylsilyl)amines 16 with CF_3SO_3 Tms/NEt_3 or TmsI/NEt_3. Methods A and B are limited to the silylation of (ar)alkylamines which have no branched α-position.

Key words: N,N-bis-(trimethylsilyl)amines; N,N-bis-silylamines; N-silylamines; N-silylcarbonamides.

INTRODUCTION

N,N-Bis-(trimethylsilyl)-amines[1] 1 are not yet thoroughly investigated although their properties make them interesting tools in organic synthesis as is demonstrated with some examples in literature. In that way, for instance, they react with benzoyl chloride in the presence of zinc chloride to bis-benzoyl amines[2] or with aldehydes or ketones forming Schiff bases.[3] The reaction with nitrosyl compounds constitutes a nucleophile excluding diazotization technique leading to diazonium salts.[4] On the other hand the bis-(trimethylsilyl)amino moiety can be used as a protecting group with Grignard reactions[5] or with deprotonation and subsequent nucleophilic addition.[6]

In monosilylated amines 2 a back-bonding of the (d ← p) π-type contributes considerably to the Si-N-bond.[7,8] For that reason the nucleophilic attack to the Si-atom is rendered more difficult. The addition of a second silyl group to the N-atom results in the extension of the conjugated system. As a consequence the Si-N-Si-angle in disilylamines 3 is widened, the N-atom is plain,[9] and the nucleophilic attack to the Si-atoms is made still more difficult. Thus these derivatives 3 are easily hydrolysed only by aqueous acids but in contrast to monosilylamines are largely stable to water or alcohols under neutral or alkaline conditions at room temperature.[2,10]



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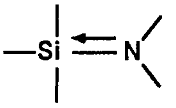

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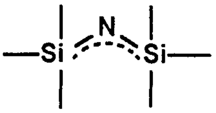

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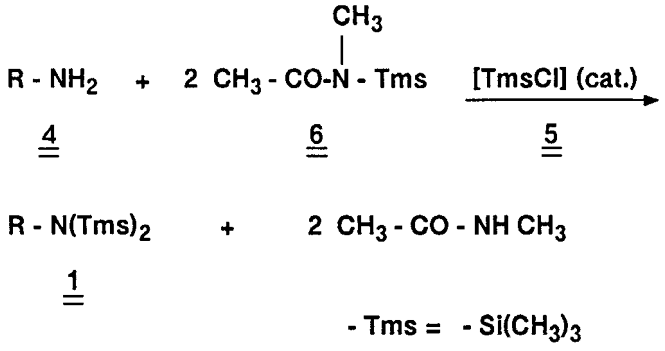
These properties created our interest in N,N-bis-(trimethylsilyl)amines as intermediates in organic synthesis. In this way we were urged to revise several synthetic procedures described in literature and to develop improved methods making this class of compounds more easily available.

A). N,N-Bis(trimethylsilyl)-alkylamines (1, R = alkyl or aralkyl) have been prepared by alkylation of alkalimetal salts of hexamethyldisilazane.[2,11] The method can be modified by using chlorodimethylether[12,13] or chlorodimethylthioether[14] as alkylating agents and subsequent reaction with a Grignard compound removing the methoxy or methyl-thio group by an alkyl chain.

Usual silylation of primary amines even with excess of trimethylsilylchloride (5) in the presence of a tertiary amine results generally in the formation of monosilylated amines.[15] Only in few cases[15,16] isolation of traces of disilylamine is mentioned. In order to achieve addition of a second silyl group to the nitrogen with this reagent deprotonation of the monosilylamine is required. That can be reached by reaction with sodium and styrol,[16] with butyllithium[17] or a Grignard compound.[15]

Another widely used method of amine silylation is the transfer of a trimethylsilyl group to an amine from either diethyltrimethylsilylamine[18] or N-methyl-N-trimethylsilylacetamide (6).[19] Again it generally ends up in the formation of N-monosilylamines. With both reagents, however, also preparation of disilylamines could be managed in the presence of specific catalysts. In the case of diethyltrimethylsilylamine J. Hils, V. Hagen, H. Ludwig and K. Rühlmann[20] succeeded with ammonium sulfate whereas L. Birkhofer and D. Brokmeier[21] worked with 6 in the presence of trimethylsilyl chloride (5). With both methods disilylation is limited to amines not branched at the α-C-atom.



$$\underset{\underline{\underline{4}}}{R\text{-}NH_2} + 2\ \underset{\underline{\underline{6}}}{CH_3\text{-}CO\text{-}\overset{\displaystyle CH_3}{\overset{|}{N}}\text{-}Tms} \xrightarrow[\underline{\underline{5}}]{[TmsCl]\ (cat.)}$$

$$\underset{\underline{\underline{1}}}{R\text{-}N(Tms)_2} + 2\ CH_3\text{-}CO\text{-}NH\,CH_3$$

$$\text{-}Tms = \text{-}Si(CH_3)_3$$

We studied scope and limitation of the preparation of disilylamines 1 according to L. Birkhofer and D. Brokmeier[21] starting with primary amines as well as with monotrimethylsilylamines and came to the following results which are summarized in Table I: a, It could be confirmed that following this method only α-unbranched amines are disilylated. b, No disilylamine was formed in the absence of a catalyst, as e.g. 5. c, Only monosilylamines were obtained, too, even in the presence of 5, on using N-trimethylsilylacetamide (7) or N-trimethylsilylpyrrolidinone (8) as Tms-suppliers. d, On the other hand in disilylation we could successfully replace 6 by other N-alkylated or aralkylated N-silylcarbonamides, but not by silylated N-arylsubstituted carbonamides. e, Contrary to G. Mischer[22] who in a special instance has reported formation of disilylamines by silylation with N,O-bistrimethylsilyl-

TABLE I

N,N-Bis(trimethylsilyl)amines by silylation with N-trimethylsilylamides

	amine	silylating agent	cat.	temp(°C)	time (h)	yield (%)
1a	4a	6	5	25	2	65
1a	4a	6	-	25	2	0
1a	4a	7	5	25	3	0
1a	4a	8	5	25	2	0
1b	4b	6	5	25	2	77
1a	4a	9	5	25	2	57
1b	4b	9	5	25	15	58
1b	4b	9	5	80	7	75
1b	4b	9	-	25	24	0
1b	4b	10	5	25	24	20
1b	4b	11	5	80	6	74
1b	4b	12	5	80	6	63
1b	4b	13	5	80	6	0
1a	4a	14	-	25	2	60
1a	4a	14	5	25	2	76
1b	16b	15	-	80	8	0
1b	16b	15	5	80	6	0
1b	4b	6	$SiCl_4$	80	6	47
1b	4b	6	$TiCl_4$	80	6	50
1b	4b	6	CF_3SO_3Tms	80	6	47
1b	4b	6	CF_3SO_3H	80	6	45
1b	4b	14	5	80	3	76
1b	16b	8	CF_3SO_3Tms	80	6	0
1b	16b	8	$TiCl_4$	25	4	10a)
1c	4c	9	5	80	4	0
1c	4c	14	5	80	3	0
1d	4d	6	5	80	6	0
1e	b)	9c)	5	80	6	66

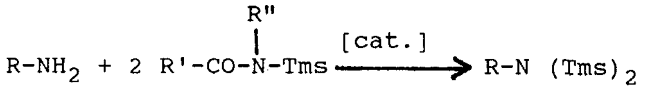
a) in methylenchloride solution

b) glycine

c) 3 mol

acetamide (15), this reagent failed in our hands. f, The reaction studied was also catalysed by Lewis acids different from 5. Using $TiCl_4$ small yields of disilylamine were observed even with 8 or 15 as Tms-supplier. g, No catalyst was necessary when disilylation was effected with N-methyl-N-trimethylsilyltrifluoroacetamide (14). h, According to Birkhofer and Brockmeier[21] the reaction generally is accompanied by temporary rise of temperature to about 50°C. In order to complete conversion we found subsequent heating to be advisable.

method A_1:



$$\text{R-NH}_2 + 2\ \text{R'-CO-}\overset{\text{R''}}{\overset{|}{\text{N}}}\text{-Tms} \xrightarrow{[\text{cat.}]} \text{R-N (Tms)}_2$$

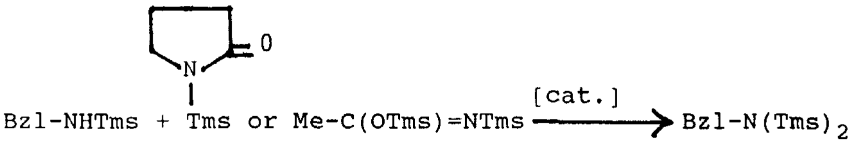
4 1

	R'	R''
6	Me	Me
7	Me	H
8	-$(CH_2)_3$-	
9	Ph	Me
10	4-FC_6H_4	Me
11	Me	Et
12	Me	Bzl
13	Me	Ph
14	CF_3	Me

	R
1a	n-C_5H_{11}
1b	Bzl
1c	C_6H_{11}
1d	Ph
1e	$TmsOCOCH_2$

15: Me-C(OTms)=NTms

method A_2:



$$\text{Bzl-NHTms} + \text{8 or Me-C(OTms)=NTms} \xrightarrow{[\text{cat.}]} \text{Bzl-N(Tms)}_2$$

16b 8 15 1b

These results show that the stabilized Si-N-Si-system can be formed by Tms-transfer from a silylated carbonamide to a monosilylamine. However, one basic requirement of that reaction is the activation of the Tms-group by means of reducing the π-share to the Si-*N*-bond of the silylcarbonamide. It can be attained by influence of a Lewis acid or by strong electronegative substitution of the underlying acid (as in 14). That activation, however, is normally neutralized by electrons of the carbonyl oxygen interfering with the Si-atom, as is obvious with compounds like 7 and 8. Anew, this influence is avoided by steric hindrance with N-alkyl substituents (com-

TABLE II

N,N-Bis(trimethylsilyl)amines by silylation with trimethylsilyl chloride

	R	cat	time(h)	yield(%)
1b	Bzl	$TiCl_4$	4	88
1b	Bzl	$SiCl_4$	3	58
1b	Bzl	$Ti(OiPr)_4$	3	50
1b	Bzl	CF_3SO_3H	5	54
1f	Pr-CH(CH_3)-	$TiCl_4$	6	0
1f	Pr-CH(CH_3)-	CF_3SO_3H	5	0
1d	Ph	$TiCl_4$	3	0
1g	Ph-$(CH_2)_2$	$TiCl_4$	6	84
1h	4-ClC_6H_4-CH_2	$TiCl_4$	6	85
1i	Ph_2CH-$(CH_2)_2$	$TiCl_4$	6	83
1k	4-$OCH_3C_6H_4$-CH_2	$TiCl_4$	6	77
1l	3,4-$(OCH_3)_2C_6H_3$-$(CH_2)_2$	$TiCl_4$	5	81
1m	3-$CF_3C_6H_4$--CH_2	$TiCl_4$	6	50
1n	2-Pyridylmethyl	$TiCl_4$	3	82
1o	Ph-CH(OTms)-CH_2	$TiCl_4$	5	76[a)]
1p	CH_2=CH-CH_2	$TiCl_4$	4	83
1q	Ph-CH=CH-CH_2	$TiCl_4$	5	85
1r	Ph-CH_2-O	$TiCl_4$	4	70
1s	-$(CH_2)_6$-	$TiCl_4$	9	78[b)]

a) from Ph-CH(OH)-CH_2NH_2 with 3 mol 5/NEt_3

b) from H_2N-$(CH_2)_6NH_2$ with 4 mol 5/NEt_3

pounds 9–12 and 14), but provided, free (ar)alkyl groups not integrated into a ring system together with the carbonamide group (as in 8) are involved.

B). N. Wiberg and F. Raschig[23] explain difficulties which they had in preparing N-halogen silylamines, with the observation that methyltrimethylsilylamine decomposes into methylamine and methyl-bistrimethylsilylamine as soon as being dissolved in methylenechloride. With several other monosilylamines we were not able to see any disproportionation under these conditions.

Therefore, we speculated the solvent used by Wiberg and Raschig may have been polluted with any catalytically active impurity. For obvious reasons we considered traces of acidic compounds or Lewis acids to be responsible for starting disproportionation. However, neither with dry HCl nor with 5 or CF_3SO_3Tms reactions could be seen. Only by adding a small amount of $TiCl_4$ to methylenchloride solutions of monosilylamines, we really could isolate the corresponding disilyl-amines in good yields.

By combining this disproportionation reaction with usual monosilylation we were able to develop a simple method for the preparation of disilylamines starting with primary amines: 2,2 mol each of trimethylsilylchloride ($\underline{\underline{5}}$) and triethylamine are added to a boiling methylenechloride solution of the amine containing catalytical amounts of $TiCl_4$. Also $SiCl_4$ and CF_3SO_3H have been found to be active but less effective catalysts. In principle the system $\underline{\underline{5}}/NEt_3$ can be replaced by $\underline{\underline{15}}$, but yields are lower.

Again this method is defined to (ar)alkylamines unbranched in α-position. The results are summarized in Table II.

$$\underset{\underline{\underline{4}}}{\text{R-NH}_2} + 2\text{NEt}_3 + 2\ \underset{\underline{\underline{5}}}{\text{TmsCl}} \xrightarrow[\text{CH}_2\text{Cl}_2]{[\text{cat}]} \underset{\underline{\underline{1}}}{\text{R-N(Tms)}_2} + 2\text{NEt}_3\text{H}^+\text{Cl}^-$$

C). Both methods mentioned above are limited to the preparation of α-unbranched disilylamines. The reason is that activation of the trimethylsilyl group to be transferred is connected with the formation of a bulky complex, which can be taken up only to monosilylamines not sterically hindered by α-substituents. This problem should be overcome with compounds which make available a more or less "nude" activated trimethylsilyl moiety, as it is known from trimethylsilyl triflate (CF_3SO_3Tms).

Although its Si-O bond is covalent (rather than ionic), the Si atom is endowed with eminent electron deficiency and close to a cryptocation in nature.[24] Indeed, we found that primary amines as well as N-monosilylamines can be reacted with CF_3SO_3Tms and Et_3N to form N,N-disilylamines in high yields irrespective of the substituents' structure. Even aromatic amines are within the reach of the reaction. Some silylesters of other sulfonic acids like bistrimethylsilyl sulfate can also be used, but give lower yields.

Whereas in the triflate ester the strong electron-withdrawing triflate moiety gives rise to the formation of a crypto-silylcation, in trimethylsilyl iodide (TmsI) a similar effect is produced by the wide radius of the iodide atom resulting in a big Si-I distance. For that reason we could well effect the same reaction with TmsI as silylating agent and, with some restrictions, even with Tms-Br (see Tables III and IV).

$$\underset{\underline{\underline{16}}}{\text{R-NHTms}} + \text{TmsX} + \text{NEt}_3 \longrightarrow \underset{\underline{\underline{1}}}{\text{R-N(Tms)}_2}$$

$$\underset{\underline{\underline{4}}}{\text{R-NH}_2} + 2\ \text{TmsX} + 2\ \text{NEt}_3 \longrightarrow \underset{\underline{\underline{1}}}{\text{R-N(Tms)}_2}$$

According to G. A. Olah, S. C. Narang, B. G. B. Gupta and R. Malhotra[25] the ether cleavage reaction, which was originally reported by T. L. Ho and G. A. Olah[26] to be effective only with TmsI, can be performed in acetonitrile solution with $\underline{\underline{5}}$ in the presence of NaI. The authors interpret the effect by the temporary formation of an acetonitrile-TmsI complex, whereas NaCl is precipitated. We made

TABLE III

N,N-Bis(trimethylsilyl)amines by silylation with trimethylsilyl iodide or triflate

	R	X	solvent	temp. (°C)	time (h)	yield (%)
1b	Bzl	CF_3SO_3	-	80	6	85
1b	Bzl	I	$(MeOCH_2)_2$	80	6	73
1b	Bzl	a)	-	80	5	29
1d	Ph	CF_3SO_3	-	80	6	50
1f	Pr-CH(CH_3)	CF_3SO_3	-	80	6	69
1f	Pr-CH(CH_3)	I	$(MeOCH_2)_2$	80	7	35
1t	TmsO$(CH_2)_2$	CF_3SO_3	-	80	6	79
1u	4-BrC_6H_4	CF_3SO_3	-	80	7	67
1c	C_6H_{11}	I	$(MeOCH_2)_2$	80	6	40
1c	C_6H_{11}	I	CH_3CN	80	5	23
1c	C_6H_{11}	Br	$(MeOCH_2)_2$	80	6	24
1c	C_6H_{11}	I	$CHCl_3$	60	5	65
1c	C_6H_{11}	I	CH_2Cl_2	20	20	58
1c	C_6H_{11}	I	hexane	80	5	0
1c	C_6H_{11}	I	toluene	80	5	64[b]

a) TmsX = ½ $SO_2(OTms)_2$

b) When TmsI is added to a solution of N-mono-trimethylsilyl-cyclohexylamine (**16 c**) in toluene a white precipitate is formed. It has to be regarded as an addition product of the crypto-silyl-cation to the nitrogen. From the solid (without seperation) the disilyl derivative is formed by HI-elimination with Et_3N or in lower yields with other bases, e.g. $NaNTms_2$, or aqueous solutions of sodium carbonate or sodium hydroxyde in the presence of a phase transfer catalyst.

TABLE IV

N,N-Bis(trimethylsilyl)amines by silylation with trimethylsilyl iodide

	R	X	solvent	temp. (°C)	time (h)	yield (%)
1b	Bzl	I	$(MeOCH_2)_2$	80	5	48
1b	Bzl	Cl(cat. NaI/CH_3CN)	$CHCl_3$	60	6	70
1c	C_6H_{11}	Cl(cat. NaI/CH_3CN)	$CHCl_3$	60	6	0
1v	TmsOCO-CH(CH_3)	I	CH_2Cl_2	20	6	62[a]

a) from alanin with 3 mol TmsI/NEt_3

use of this observation by analogy. In the presence of catalytic amounts of NaI and acetonitrile benzylamine (4b) was silylated with 2 mol 5 and 2 mol Et_3N in boiling chloroform solution yielding 70% 1b. Contrary to the reaction with TmsI, however, this silylation variant, again, does not allow preparation of α-branched N,N-disilylamines, which has to be considered as a consequence of the "bulky" form of the activated silyl complex.

TABLE V

Physical and spectroscopic properties of bis(trimethylsilyl)amines, 1

	amine(4)	yield		b.p.	n_D^{20}
	(g)	(g)	(%)	(°C/Torr)	
1b	53.55	111.3	88.5	83-85°/0.3	1.4910
1g	60.55	112.2	84.4	113-115°/0.65	1.4889
1h	70.8	121.3	84.7	116-118°/0.3	1.5043
1i	105.65	148.2	83.3	148-150°/0.15	1.5272
1k	68.6	108.5	77.1	127-129°/0.85	1.4995
1l	90.6	132.4	81.3	140-142°/0.5	1.5020
1m	88.03	79.2	49.6	71-73°/0.4	1.4574
1n	54.17	103.9	82.3	80-82°/0.5	1.4898
1o	68.58[a]	134.7	76.2	98-102°/0.45	
1p	28.55	83.9	83.2	71-72°/19-20	1.4409
1q	66.67	117.6	84.7	94-95°/0.2	1.5132
1r	61.53	94.2	70.3	87-88°/0.5	
1s	58.10[b]	158.8	78.4	148-152°/0.7	1.4562

	^{1}HNMR (δ)
1b	0.11 (s, 18H, $Si(CH_3)_3$, 4.06 (s, 2H, CH_2), 7.15 (s, 5H, aromatic)
1g	0.21 (s, 18H, $Si(CH_3)_3$, 2.43-3.20 (m,4H, $(CH_2)_2$) 7.16 (s, 5H aromatic)
1h	0.16 (s, 18H, $Si(CH_3)_3$), 4.10 (s, 2H, CH_2), 7.23 (s, 4H, aromatic)
1i	0.06 (s, 18H, $Si(CH_3)_3$), 1.80 - 2.83 (m, 4H, $(CH_2)_2$), 3.73 (t, J = 7 Hz, 1H, CH), 7.16 (s, 10H, aromatic)
1k	0.20 (s, 18H, $Si(CH_3)_3$), 3.85 (s, 3H, OCH_3), 4.10 (s, 2H, CH_2), 6.76 - 7.31 (m, 4H, aromatic)
1l	0.20 (s, 18H, $Si(CH_3)_3$), 2.38 - 3.18 (m, 4H, $(CH_2)_2$), 3.90 (s, 6H, OCH_3), 6.61 - 6.81 (m, 3H, aromatic)
1m	0.10 (s, 18H, $Si(CH_3)_3$), 4.13 (s, 2H, CH_2), 7.35 (s, 3H, aromatic), 7.48 (s, 1H, aromatic)
1n	0.10 (s, 18H, $Si(CH_3)_3$), 4.13 (s, 2H, CH_2), 6.71 - 7.85 (m, 3H, aromatic), 8.16 - 8.35 (m, 1H, aromatic)

TABLE V (*Continued*)

1o	0 - 0.38 (m, 27H, $Si(CH_3)_3$), 2.83 - 3.08 (m, 2H, CH_2), 4.35 - 4.60 (m, 1H, CH), 7.28 (s, 5H, aromatic)
1p	0.10 (s, 18H, $Si(CH_3)_3$), 3.30 - 3.50 (m, 2H, $-CH_2-$), 4.78 - 5.21 (m, 2H, $CH_2=$), 5.40 - 6.05 (m, 1H, CH)
1q	0.11 (s, 18H, $Si(CH_3)_3$), 3.50 - 3.68 (m, 2H, CH_2), 6.05 - 6.40 (m, 2H, CH=CH), 7.23 (s, 5H, aromatic)
1r	0.21 (s, 18H, $Si(CH_3)_3$), 4.60 (s, 2H, CH_2), 7.33 (s, 5H, aromatic)
1s	0.20 (s, 36H, $Si(CH_3)_3$), 1.26 - 1.66 (m, 8H, $(CH_2)_4$), 2.66 - 3.06 (m, 4H, NCH_2)

a) 0.5 mol 2-amino-1-phenylethanol were reacted with 166.8 (1.65 mol) NEt_3 and 179.1 g (1.65 mol) 5

b) 0.5 mol 1,6-diaminohexane were reacted with 222.4 g (2.2 mol) NEt_3, 2 ml $TiCl_4$, 238.9 g (2.2 mol) 5 and 650 ml CH_2Cl_2

EXPERIMENTAL

All solvents used have been dried; distillations have been performed under dry nitrogen. Boiling points are uncorrected. The ^{1}H-NMR spectra were recorded with Varian T60 spectrometer in $CDCl_3$. Silylating agents are commercially available (Wacker Chemie GmbH, Aldrich-Chemie GmbH or Lancaster Synthesis GmbH) or were prepared according to published instructions (11,[27] 9 and 13,[28] 10 Kp 84–86°C/0,3 Tor analogous to 9); the monosilylamines 16 were synthesized following a procedure given for 16b.[29]

N-Benzyl-N-trimethylsilylacetamide (12): 216.7 g (2 mol) 5 dropped at 80°C to a solution of 149.4 g (1 mol) N-benzylacetamide and 101.0 g (1 mol) NEt_3 in 500 ml toluene. Heating to 80°C and stirring was maintained for 8 hours. Then 102.3 g $NEt_3 \cdot HCl$ were separated by suction and the filtrate was evaporated and distilled in vacuo: yield 146.0 g (65.9%); b.p. 100–104°C/0.4 Torr; n_D^{20} = 1.4920.

Method A_1

N,N-Bis(trimethylsilyl)pentylamine (1a): A mixture of 35 g (0.24 mol) N-methyl-N-(trimethylsilyl)acetamide (6) and 1.16 ml trimethylsilylchloride (5) was slowly added to 9.58 g (0.11 mol) pentylamine (4a). The temperature rose to 60°C; at the same time two layers appeared. After stirring for another hour at room temp. the upper layer was separated and distilled; yield 16.6 g (65.3%), b.p. 86–87°C/10 Torr; n_D^{25} = 1.4361; ^{1}HNMR: δ = 0.15 (s, 18H, $Si(CH_3)_3$), 0.78–1.60 (m, 9H, $CH_3(CH_2)_3$), 2.58–2.93 (m, 2H, NCH_2).

To 8.71 g (0.1 mol) 4a a mixture of 43.53 g (0.21 mol) N-methyl-N-(trimethylsilyl)benzamide (9) and 1 ml 5 was slowly added. A solid formed and temperature rose to 60°C. After two hours stirring at room temp. the precipitate was separated by suction and washed with 100 ml hexane: 24.3 g (0.18 mol) N-methylbenzamide. The filtrate was distilled: yield 13.2 g (57%).

22.6 g (0.1 mol) N-methyl-N-(trimethylsilyl)trifluoroacetamide (88 per cent) (14) dropped to 4.35 g (0.05 mol) 4a whereby temp. rose to 48°C and a precipitate formed. The mixture was stirred at room temp. for two hours and was then diluted with 50 ml hexane. By suction 5.6 g N-methyltrifluoroacetamide (m.p. 51–53°C), were isolated. The filtrate was washed with water, dried with Na_2SO_4 and distilled, yield 6.9 g (59.6%).

When 14 was first of all mixed with 0.5 ml 5 and then dropped to 4a 13.2 g N-methyltrifluoroacetamide and 8.8 g (76%) 1a were isolated.

N,N-Bis(trimethylsilyl)benzylamine (1b): A mixture of 31.94 g (0.219 mol) 6 and 1 ml 5 dropped to 10.7 g (0.1 mol) 4b. The temp. rose to 50°C and two layers formed. After stirring at room temp. for two hours 50 ml saturated $NaHCO_3$-solution and 50 ml H_2O were added and the mixture was extracted with about 100 ml diethylether. The extract was washed with water, dried with Na_2SO_4, evaporated and distilled: yield 19.4 g (77.2%); b.p. 83–85°C/0.3 Torr; n_D^{20} = 1.4910; ^{1}HNMR: δ = 0.11 (s, 18H, $Si(CH_3)_3$), 4.06 (s, 2H, CH_2), 7.15 (s, 5H, aromatic).

Instead of 5 0.5 ml $SiCl_4$, 0.5 ml $TiCl_4$, 0.5 ml CF_3SO_3Tms or 0.5 ml CF_3SO_3H have been used. Also 34.9 g (0.219 mol) N-ethyl-N-(trimethylsilyl)acetamide (11) replaced 6. Reaction temp., time and yield can be seen from Table I.

22.8 g (0.11 mol) 9 and 0.5 ml 5 were mixed and dropped to 5.36 g (0.05 mol) 4b. The temp. rose to 49°C. The reaction mixture was stirred at 80°C for 7 hours and then diluted with 50 ml hexane. 14.2 g N-methylbenzamide were isolated by filtration. The filtrate was washed with water, dried with Na_2SO_4, evaporated and distilled: yield 9.4 g (74.7%).

In this procedure 9 could be replaced by 24.34 g (0.11 mol) N-benzyl-N-(trimethylsilyl)acetamide (12) or 26.63 g (0.11 mol) 14 (80 per cent). Yields see Table I.

N,N-Bis(trimethylsilyl)glycine trimethylsilylester (1e): 57.4 g (0.276 mol) 9 and 0.86 ml 5 were mixed and added to 6.45 g (0.086 mol) glycine. The reaction mixture was stirred at 80°C for 7 hours and then diluted with 70 ml hexane. 36 g N-methylbenzamide were isolated by suction. The filtrate was evaporated and distilled: yield 18.2 g (72.8%); b.p. 130–133°C/30 Torr; n_D^{20} = 1.4320; ^{1}HNMR: δ = 0.08 (s, 18H, $NSi(CH_3)_3$), 0.26 (s, 9H, $OSi(CH_3)_3$), 3.41 (s, 2H, CH_2).

Method A_2

N,N-Bis(trimethylsilyl)benzylamine (1b): A solution of 17.9 g (0.1 mol) N-trimethylsilylbenzylamine (16b) was slowly mixed with 0.5 ml $TiCl_4$ and stirred at room temp. for two hours. Then a solution of 15.7 g (0.1 mol) N-trimethylsilylpyrrolidinon (8) in 20 ml CH_2Cl_2 was added. The reaction mixture was stirred at room temp. for two hours, then evaporated and the residue was treated with diethylether and water. The organic layer was washed with water, dried with Na_2SO_4 and distilled: yield 2.5 g (9.9%).

Method B

Standard procedure: 0.5 mol primary amine 4 and 111.2 g (1.1 mol) NEt_3 were dissolved in 500 ml CH_2Cl_2 and slowly mixed with 1 ml $TiCl_4$. After 45 min. stirring at room temp. 119.45 g (1.1 mol) 5 were added dropwise, whereby temp. rose to b.p. of the solvent. Stirring under reflux was continued for 3–6 hours, followed by evaporation of the solvent. In order to precipitate $NEt_3 \cdot HCl$ the residue was mixed with 500 ml diethylether or diisopropylether, then filtered by suction, again evaporated and distilled. In case of absence of any group to be hydrolysed the ether solution can be washed with saturated $NaHCO_3$-solution and water before evaporation and distillation.

Method C

N,N-Bis(trimethylsilyl)aniline (1d): 22.22 g (0.1 mol) CF_3SO_3Tms dropped to a mixture of 16.53 g (0.1 mol) N-trimethylsilylaniline (16d) and 10.1 g (0.1 mol) NEt_3. The temp. rose to 70°C and two layers formed. After stirring for 6 hours at 80°C the reaction mixture was diluted with 100 ml diethylether and treated with 50 ml saturated $NaHCO_3$-solution and 50 ml water. The organic phase was washed with water, dried with Na_2SO_4, evaporated and distilled: yield 11.8 g (49.6%); b.p. 109–110°C/18 Torr; n_D^{20} = 1.4845; ^{1}HNMR: δ = 0.15 (s, 18H, $Si(CH_3)_3$), 6.75–7.35 (m, 5H, aromatic).

Likewise the following compounds were prepared: 2-N,N-Bis(trimethylsilyl)aminopentane (1f) from 16.07 (0.1 mol) 2-N-trimethylsilylaminopentane (16f); yield 16.0 g (69.1%); b.p. 98–99°C/18 Torr; n_D^{20} = 1.4435; ^{1}HNMR: δ = 0.2 (s, 18H, $Si(CH_3)_3$), 0.75–1.58 (m, 10H, $CH_3(CH_2)_2$, CH_3), 2.81–3.35 (m, 1H, CH).

N,N,O-Tris(trimethylsilyl)-2-aminoethanol (1t) from 20.63 g (0.1 mol) N,O-Bis(trimethylsilyl)-2-aminoethanol (16t); yield 22.0 g (79.4%); b.p. 112–113°C/18 Torr; ^{1}HNMR: δ = 0.23 (s, 27H, $Si(CH_3)_3$), 2.75–3.70 (m, 4H, $(CH_2)_2$).

4-Bromo-N,N-bis(trimethylsilyl)aniline (1u) from 24.42 g (0.1 mol) 4-bromo-N-trimethylsilylaniline (16u); yield 21.1 g (66.6%); b.p. 112–113°C/0.6 Torr; n_D^{20} = 1.5158; ^{1}HNMR: δ = 0.11 (s, 18H, $Si(CH_3)_3$), 6.61–7.38 (m, 4H, aromatic).

N,N-Bis(trimethylsilyl)cyclohexylamine (1c): 17.13 g (0.1 mol) N-Trimethylsilylcyclohexylamine (16c) and 10.1 g (0.1 mol) NEt_3 were dissolved in 75 ml 1,2-dimethoxyethane. Then 20.01 g (0.1 mol) TmsI were added dropwise. After stirring at 80°C for 6 hours the solvent was evaporated in vacuo and the residue was treated with 100 ml diethylether, 50 ml saturated $NaHCO_3$-solution and 50 ml water. The ether phase was washed with water, dried with Na_2SO_4 and distilled: yield 9.8 g (40%); b.p. 121–122°C/18 Torr; n_D^{20} = 1.4641; ^{1}HNMR: δ = 0.20 (s, 18H, $Si(CH_3)_3$), 0.95–1.88 (m, 10H, CH_2), 2.45–3.01 (m, 1H, CHN). This reaction was performed with different solvents; the influence to the yield is shown in Table III.

N,N-Bis(trimethylsilyl)benzylamine (1b): 21.42 g (0.2 mol) 4b, 40.4 g (0.4 mol) NEt_3 and 5 ml acetonitrile were dissolved in 150 ml chloroform. Then 21.72 g (0.2 mol) 5 were added dropwise. After 30 min. stirring at room temp. 0.5 g NaI were added and another 21.72 g (0.2 mol) 5 dropped in. The reaction mixture was stirred under reflux for 6 hours and evaporated in vacuo. The residue was dissolved in 100 ml diethylether and 100 ml water, the ether layer washed with water, dried and distilled: yield 35.2 g (69.9%).

N,N-Bis(trimethylsilyl)alanine trimethylsilylester (1v): 60.03 g (0.3 mol) TmsI dropped to a solution of 8.9 g (0.1 mol) alanine and 20.22 g (0.2 mol) NEt_3 in 90 ml methylenechloride. The temp. rose to the b.p. of the solvent. After stirring at room temp. for 30 min. another 10.11 g (0.1 mol) NEt_3 were added slowly. The temp. again increased and a precipitate formed. The reaction mixture was stirred at room temp. for 6 hours, evaporated in vacuo and the residue was treated with 250 ml diisopropylether. The precipitated $NEt_3 \cdot HI$ was separated by filtration and the solution was evaporated and distilled: yield 18.8 g (61.5%); b.p. 128–130°C/21–22 Torr; ^{1}HNMR: δ = 0.25 (s, 18H, $NSi(CH_3)_3$), 0.40 (s, 9H, $OSi(CH_3)_3$), 1.35–1.55 (d, 3H, CH_3), 3.55–3.95 (q, 1H, CH).

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