ELECTROCHEMICAL AND CHEMICAL REDUCTIVE SILYLATION OF ALIPHATIC NITRILES: A NEW ACCESS TO α -(SILYL)ALKYLAMINES^{1,2}

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Abstract : A general and efficient synthesis of the title amines (**6**) is described which consists in the electroreductive silylation of nitriles (**1**), followed, in a one pot process, by the protonolysis of the silazanes (**2**, **3**) and acylsilane enamines (**8**) formed and hydride reduction of the intermediate iminium salt. Formation of acylsilane enamines is interpreted as the result of the reductive silylation of the ketenimine form of the nitriles whereas formation of silazanes is interpreted as the result of the reductive silylation of the nitrile function itself. A preliminary study of the electroreductive silylation of a N-(trimethylsilyl)aldimine, yielding a title amine after protonolysis of the intermediate silazane, is also reported. Some of the silazanes presented particular nmr properties which were interpreted as being indicative of a conformationally locked structure.

INTRODUCTION

α -C-Silylated amines $\Sigma(\text{Me}_3\text{Si})\text{CH-NH}_2$ are very attractive compounds which have found uses in various domains of organic chemistry (α -azaanions⁵ and unprotected azomethine ylids,⁶ for example). Moreover, the Si-C-N framework seems to hold biological activity,⁷ this being attested by the appearance in the recent years of an increasing number of molecules including it. At the present time, Σ represents a proton or, to a less extent, an aryl group in most of the compounds described in the literature⁸. Very recently we synthesized bis(trimethylsilyl)methylamine, "BSMA"^{9,10} and showed that it could be a valuable tool in organic synthesis^{11,12}. Only a few molecules where Σ is an alkyl group (R) have been described, probably because their access is very tedious¹³. We have made efforts to develop synthetic methods for α -(trimethylsilyl)alkylamines, $\text{R}(\text{Me}_3\text{Si})\text{CH-NH}_2$ ("RSMA"), and have recently published their preparation through reduction of iminium salts of acylsilanes.¹⁴ This method gave access to RSMA in which R was a secondary or tertiary alkyl group.

However, in spite of the fact that starting materials were easily accessible from silyl-protected cyanohydrins, we have been looking for other possible precursors of RSMA and decided to explore the possibility of using N-silyl aldimines¹⁵ and nitriles. Though we got a positive result from one N-silyl aldimine, and because we have been facing the problem of a general synthesis of these imines (enolizable aldehydes do not give easily the corresponding N-silyl imines),^{16,17} we turned then our attention to the use of nitriles,^{18,19} a more readily accessible starting material.

We report here the results of our investigations on the reductive silylation of a N-(silyl)aldimine and nitriles R-CN where R is a primary, secondary or tertiary alkyl group.

EXPERIMENTAL

General data. Gas chromatographic (GC) analyses were performed on a Hewlett-Packard 5890 (series II) temperature programmable chromatograph equipped with capillary columns (CPSIL, 25 m x 0.25 μm). Infrared spectra (neat compounds) were obtained from a Perkin-Elmer

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1420 infrared spectrometer. A Nicolet Model 20 SXC GC instrument connected to a Carlo-Erba Model GC 6000 Vega chromatograph (PTE, 25 m x 0.25 mm capillary column) was used for FTIR studies. ^1H NMR spectra were obtained using a Hitachi R-1200 (60 MHz, solvent CCl_4 and CH_2Cl_2 at $\delta = 5.33 \text{ ppm}^{20}$ as internal reference) or a Bruker AC250 (250 MHz, solvent CDCl_3) or AC200 (200 MHz, solvent CDCl_3) spectrometer. These two last were also used for recording ^{13}C and ^{29}Si NMR spectra. To record mass spectra, a VG Micromass 16F (70 eV) mass spectrometer, coupled with an Intersmat IGC 121M (BPI 25 m x 0.25 mm capillary column) chromatograph, was used. Elemental analyses were performed at the Laboratoire Central de Microanalyse du CNRS (B.P. 22, 69390 Vernaison, France). We have given the observed values for Si even if they are out of the acceptable range : a loss of trimethylsilyl groups from compounds very susceptible to the mineralisation process used in the analysis could explain the lower values obtained.

Starting materials. Reagent-grade HMPA (Aldrich)²¹, THF, pivalaldehyde and $\text{N-Bu}_4\text{NBr}$ were used without purification. Trimethylsilyl chloride, kindly supplied by Rhône-Poulenc Co. (France), was distilled over magnesium turnings prior to use and kept under an argon atmosphere.

Pivalaldehyde N-(trimethylsilyl)imine. This imine was prepared following Hart's procedure.^{16b} Hexamethyldisilazane (54 mL, 260 mmol) was placed in a 250 mL three-necked round-bottomed flask, equipped with a pressure-equalizing dropping funnel, an argon inlet, an argon outlet and a magnetic stirring bar. A 2.5M solution of n-BuLi (100 mL) in n-hexane was added from the funnel under stirring over a period of 30 min. After 20 min stirring, solvent was evaporated under the reduced pressure of a water-pump until a white powder, i.e lithium bis(trimethylsilyl)amide, was obtained. The flask was kept in an ice bath and pivalaldehyde (21.5 g, 250 mmol) was introduced over a period of 15 min. After 3 h stirring at room temperature, the imine was distilled directly from the reaction mixture (26.4 g, 67% yield) and obtained as a single isomer (from GC and NMR analyses), probably the E isomer owing to the size of the substituents:

Pivalaldehyde N-(trimethylsilyl)imine: bp 82°C (20 mmHg); ^1H NMR δ 0.0 [s, 9 H, $\text{Si}(\text{CH}_3)_3$], 0.88 [s, 9 H, $\text{C}(\text{CH}_3)_3$], 8.13 [s, 1 H, $\text{N}=\text{CH}$]; ^{13}C NMR -1.3 ($\text{Si}-\text{CH}_3$), 26.8 ($\text{C}-\text{CH}_3$), 38.8 (CC_3), 180.5 ($\text{N}=\text{CH}$); IR 1642 cm^{-1} ($\text{C}=\text{N}$).

Electrochemical reductive silylation of pivalaldehyde N-(trimethylsilyl)imine. The electrolysis procedure has already been published.¹⁰ Using the equipment described (500mL undivided cell equipped with an aluminum-made sacrificial anode), the imine (150 mmol, 23.5 g) was mixed with THF (150 mL), trimethylsilyl chloride (2.3 M, 300 mL), HMPA (0.2 M, 40 mL) and tetrabutylammonium bromide (300 mg). After 4.4 faradays/mole were passed, pentane (200 mL) was added to the reaction mixture under stirring. Salts were thus precipitated (essentially the HMPA-AlCl_3 complex) and then separated by decantation. Low-boiling materials (pentane, THF and excess trimethylsilyl chloride) were evaporated on a rotatory evaporator leaving an oily residue which was dissolved in pentane (50 mL). This solution was washed with 0.1N HCl until neutrality, with water and finally dried over magnesium sulfate. Evaporation of pentane left a viscous liquid which has been identified as being the silazane **2a** (64% yield), after purification by distillation.

2,2-Dimethyl-1,N,N-tris(trimethylsilyl)propylamine (2a) : bp 78°C (0.05 mmHg); IR (cm^{-1}) 895 ($\nu_{\text{Si-N}}$); MS (70 eV) m/z (relative intensity) 246 (M-tBu , 54.3), 230 (96.1), 142 (31.4), 73 (100). Anal. Calc. for $\text{C}_{14}\text{H}_{37}\text{NSi}_3$: C, 55.37; H, 12.28; N, 4.61; Si, 27.74. Found: C, 55.29; H, 12.37; N, 4.46; Si, 27.46; ^1H NMR δ 0.14 [s, 9 H, $\text{CSi}(\text{CH}_3)_3$], 0.16 [s, 9 H, $\text{NSi}(\text{CH}_3)_3$], 0.21 [s, 9 H, $\text{NSi}(\text{CH}_3)_3$], 0.98 [s, 9 H, $\text{C}(\text{CH}_3)_3$], 2.25 [s, 1 H, NCHSi]; ^{13}C NMR δ 1.4 ($\text{CSi}(\text{CH}_3)_3$), 3.5 ($\text{NSi}(\text{CH}_3)_3$), 4.3 ($\text{NSi}(\text{CH}_3)_3$), 31.5 ($\text{C}(\text{CH}_3)_3$), 38.5 ($\text{C}(\text{CH}_3)_3$), 56.3 (NCH); ^{29}Si NMR δ 2.6 (SiC_3), $^2J_{\text{SiMe}_3} = 6.4 \text{ Hz}$, 9 H and $^3J_{\text{Si-CH}_3} = 12.2 \text{ Hz}$, 1 H), 3.2 (N-Si), $^2J_{\text{SiMe}_3} = 6.3 \text{ Hz}$, 9 H and $^3J_{\text{Si-N-CH}} = 7.4 \text{ Hz}$, 1 H), 7.9 [(N-Si), $^2J_{\text{SiMe}_3} = 6.4 \text{ Hz}$ (9 H) and $^3J_{\text{Si-N-CH}} = 11.4 \text{ Hz}$ (1 H)].

Partial electrochemical reductive silylation of pivalaldehyde N-(trimethylsilyl)imine. When the same experiment was stopped after 2.2 faradays per mole have been passed through the solution, GC analysis of the crude mixture before any acidic washing showed it to be an almost 1/1 mixture of silazane **2a** and the starting imine. There was also a variable significant amount of hexamethyldisilane.

Chemical reductive silylation of pivalaldehyde N-(trimethylsilyl)imine. Following a described procedure,⁹ the imine (7.8 g, 50 mmol) was reacted with 3.5 g lithium sand and trimethylsilyl chloride (250 mL) in a THF (125 mL) - HMPA (90 g) mixture at 0°C , giving rise, after normal work-up, to a viscous liquid which contained (GC/MS analysis) a mixture of silazane **2a**, starting

imine and hexamethyldisilane. Using a large excess of lithium (up to ten times) did not affect this result.

Electrochemical reductive silylation of pivalonitrile 1a. Using the equipment and procedure described above, 1a (100 mmol) was treated with trimethylsilyl chloride (1.6 M, 200 mL), in a THF-HMPA mixture (100 mL - 25 mL) in the presence of dry tetrabutylammonium bromide (200 mg). Work-up gave 24.3 g of a viscous liquid which was identified as 3a (60% yield) after distillation:

2,2-Dimethyl-1-N-bis(trimethylsilyl)-N-[(trimethylsilylmethyl)dimethylsilyl]propylamine (3a) : bp 108-110°C (0.05 mmHg); IR (cm⁻¹) 903 ($\nu_{\text{Si-N-Si}}$); MS (70 eV) *m/z* (relative intensity) 302 (M^+ -SiMe₃, 43.9), 202 (20), 145 (100), 142 (36), 73 (92.5). Anal. Calc. for C₁₇H₄₅NSi₄: C, 54.32; H, 12.07; N, 3.73; Si, 29.88. Found: C, 54.41; H, 12.05; N, 3.71; Si, 29.39; ¹H NMR δ 0.18, 0.28, 0.53 [3 s, 3 x 9 H, Si(CH₃)₃], 0.19, 0.24 [2 s, 2 x 3 H, NSi(CH₃)₂, non-equivalent methyl groups], 0.46 [s, 2 H, SiCH₂Si], 1.02 [s, 9H, C(CH₃)₃], 2.17 [s, 1 H, NCHSi]; ¹³C NMR δ 1.4, 2.8, 5.7 [Si(CH₃)₃], 4.8, 5.4 [NSi(CH₃)₂], 8.6 [SiCH₂Si], 30.2 [C(CH₃)₃], 37.2 [C(CH₃)₃], 58.9 [NCH]; ²⁹Si NMR δ -0.9 [Si_a, ²J_{SiMe3} = 6.5 (9H), ²J_{SiCH2} = 9.2 (2H)], 2.1 [Si_b, ²J_{SiMe3} = 6.3 (9H), ³J_{Si-N-CH} = 12.0 (1H)], 2.85 [Si_c, ²J_{SiMe3} = 6.3 (9H), ²J_{SiCH} = 12.4 (1H)], 8.4 [Si_d, ²J_{SiMe3} = 6.2 (3H), ²J_{SiMe3} = 6.2 (3H), ²J_{SiCH2} = 9.3 (2H), ³J_{Si-N-CH} = 7.0 (1H)]; ¹⁵N NMR δ -351.3 [C-NSi₂, ¹J_{NSi} = 13.2 and 11.3]; in contrast to 5,¹⁰ only one set of peaks was observed, indicating that only one rotamer has been formed. On the basis of the ³J_{Si-N-CH} coupling constants (respectively 12 Hz for Me₃Si_b and 7 Hz for Me₂Si_d) which are very similar to those of 5¹⁰ "trans", 3a also should probably have a "trans" configuration.

Labelling of silicon atoms in silazane 3a.

Chemical reductive silylation of pivalonitrile 1a. Using the procedure described above, 1a (100 mmol) was reacted at 0-5°C with trimethylchlorosilane (500 mL, 4 M) and lithium sand (7 g, 1 M) in a THF-HMPA mixture (300 mL, 180 mL). Work-up left a viscous liquid (27.3 g) which was analysed as a 18/19/63 mixture of 3a, 4, and 5 (74% total yield). Compounds 4 and 5 have been already described.⁹

Protonolysis of the silazanes 2a and 3a. Synthesis of 2,2-dimethyl-1-(trimethylsilyl)-propylamine or t.butyl(trimethylsilyl)methylamine (6a). In a 250 mL two-necked round-bottomed flask fitted with a 100mL pressure-equalizing dropping funnel and a condenser, and placed in an ice bath, was introduced 100 mmol of 2a (or 3a) and 40 mL of methanol. Trimethylsilyl chloride (30 mL) was then dropwise added from the funnel under magnetic stirring. After 15 min stirring at room temperature, low boiling materials (excess of methanol and silyl chloride, methoxysilanes) were evaporated under reduced pressure, and a white powder was obtained which was rapidly washed with dry ether on a sintered-glass filter, leaving pure 6a's hydrochloride (18.6 g). It was poured into a flask containing dry ether (100 mL) and solid sodium hydroxide (0.4 g), and kept under magnetic stirring for one hour. Separation of the solid residue and evaporation of the solvent left an amine-like characteristic odorous liquid identified as 6a:

2,2-Dimethyl-1-(trimethylsilyl)-propylamine (6a) : bp 56-59°C (25 mmHg); IR (cm⁻¹) 3300 (ν_{NH_2}); Anal. Calc. for C₈H₂₁NSi: C, 60.30; H, 13.28; N, 8.79; Si, 17.63. Found: C, 60.12; H, 12.95; N, 8.39; Si, 17.24; ¹H NMR δ 0.02 (s, 9 H, Si(CH₃)₃), 0.87 (s, 9H, C(CH₃)₃), 1.30 (s, 2H, NH₂, deuterium exchangeable), 1.83 (s, 1 H, NCHSi); ¹³C NMR δ -0.3 (Si(CH₃)₃), 28.7 (C(CH₃)₃), 35.3 (C(CH₃)₃), 53.2 (NCH); MS (70 eV) *m/z* 159 (0.9), 144 (8.1), 102 (45.1), 86 (76.1), 74 (100), 73 (40.2).

Obtention of imine 7. When an equimolar mixture of 2a or 3a and pivalaldehyde N-(trimethylsilyl)imine (50 mmol each) has treated with trimethylsilyl chloride (30 mL) in methanol (40 mL), a liquid compound, identified as imine 7, was obtained (72% yield). Imine 7 was also

obtained after work-up of the chemical and incomplete electrochemical reductive silylation of pivalaldehyde N-(trimethylsilyl)imine (see above). It has been synthesized by condensation of pivaldehyde and amine 6a in the presence of molecular sieves.¹²

(E)-2,2-Dimethyl-N-[2,2-dimethyl-1-(trimethylsilyl)propyl]propanimine (7) : bp 83°C (25 mmHg); IR (cm^{-1}) 1654 ($\nu_{\text{C=N}}$); ^1H NMR δ 0.0 [s, 9 H, $\text{Si}(\text{CH}_3)_3$], 0.92 [s, 9H, $\text{C}(\text{CH}_3)_3$], 1.05 [s, 9H, $\text{C}(\text{CH}_3)_3$], 2.36 [s, 1 H, NCHSi], 7.27 [s, 1 H, N=CH]; ^{13}C NMR δ -0.4 ($\text{Si}(\text{CH}_3)_3$), 27.3 ($\text{C}(\text{CH}_3)_3$), 29.2 ($\text{C}(\text{CH}_3)_3$), 34.8 ($\text{C}(\text{CH}_3)_3$), 36.2 ($\text{C}(\text{CH}_3)_3$), 75.3 (NCH), 167.1 (N=CH); MS (70 eV) m/z (relative intensity) 227 (M^+ , 1.2), 170 (100), 154 (61.6), 142 (15.8), 73 (84.9).

Electrochemical reductive silylation of nitriles 1b-d. These nitriles were reacted in the same way 1a was (4.4 F/mole). The crude product obtained after the work-up of the reaction was analysed by GC/MS and CG/IRFT and, in some instances, products were separated by distillation. Nitrile 1b. Starting from 10.3 g (150 mmol) of the nitrile, 35.3 g of a mixture of nitrile 1e,²² silazanes 2b and 3b, and enamine 8b was obtained in proportions and yields given in Table 2. Distillation did not allow separation of silazane 2b from enamine 8b. Nmr analysis of silazane 3b, isolated in pure state by distillation, showed it to be a one to one mixture of the two rotamers; nmr spectra were assigned through (^1H - ^{13}C) and (^1H - ^{29}Si) 2D correlations and coupling constants, measured from $\{^{29}\text{Si}$ - ^1H (^1H - ^{29}Si)} 2D correlations.⁹

2-Methyl-1,N,N-tris(trimethylsilyl)propylamine (2b) : IR (cm^{-1}) 908 ($\nu_{\text{Si-N-Si}}$); ^1H NMR δ 0.13, 0.14, 0.18 (3 x s, 3 x 9H, 3 $\text{Si}(\text{CH}_3)_3$), 0.90 (d, $^3J = 6.5$, 3H, CH_3), 0.93 (d, $^3J = 8.7$, 3H, CH_3), 1.96 (m, 1 H, Me_2CH), 2.19 (d, $^3J = 5.6$, 1H, SiCHN); MS (70 eV) m/z (relative intensity) 246 (M^+ -iPr, 3.2), 216 (100), 128 (27.4), 73 (64.2).

2-Methyl-N[(trimethylsilyl)methyl]dimethylsilyl-1,N-bis(trimethylsilyl)propylamine (3b) : bp 112°C (0.05 mm Hg); IR (cm^{-1}) 902 ($\nu_{\text{Si-N-Si}}$); MS (70 eV) m/z 318 (1.9), 288 (100), 202 (16.1), 145 (68.4), 73 (63.3). Anal. Calc. for $\text{C}_{16}\text{H}_{43}\text{NSi}_4$. C, 53.11; H, 11.98; N, 3.87; Si, 31.05. Found: C, 52.97; H, 11.93; N, 3.59; Si, 29.89.

3b trans²³ : ^1H NMR δ 0.00 (s, 2H, $\text{Si-CH}_2\text{-Si}$), 0.05 [s, 9H, $\text{Si}(\text{CH}_3)_3$], 0.15 [s, 9H, $\text{CH}_2\text{Si}(\text{CH}_3)_3$], 0.22 [s, 6H, $\text{NSi}(\text{CH}_3)_2$], 0.23 [s, 9H, $\text{NSi}(\text{CH}_3)_3$], 0.91 (d, $^3J = 6.3$, 3H, CH_3), 1.00 (d, $^3J = 6.5$, 3H, CH_3), 1.90-2.00 (m, 1H, Me_2CH), 2.23 [d, $^3J = 3.1$, 1H, NCHSi]; ^{13}C NMR δ 1.1 [$\text{Si}(\text{CH}_3)_3$], 1.5 [$\text{CH}_2\text{Si}(\text{CH}_3)_3$], 3.5 [$\text{NSi}(\text{CH}_3)_2$], 5.4 and 5.7 [$\text{Si}(\text{CH}_3)_2$], 7.7 [SiCH_2Si], 22.5 and 22.6 [CH_3], 31.9 (Me_2CH), 55.7 (NCHSi); ^{29}Si NMR δ -1.0 [CH_2SiMe_3 , $^2J_{\text{SiMe}_3} = 6.4$ (9H), $^2J_{\text{SiCH}_2} = 9.4$ (2H)], 2.5 [SiMe_3 , $^2J_{\text{SiMe}_3} = 6.3$ (9H), $^2J_{\text{SiCH}} = 11.6$ (1H), $^3J_{\text{Si-C-CH}} = 8.4$ (1H)], 3.3 [NSiMe_3 , $^2J_{\text{SiMe}_3} = 6.4$ (9H), $^3J_{\text{Si-N-CH}} = 11.2$ (1H)], 4.6 [NSiMe_2 , $^2J_{\text{SiMe}_2} = 6.3$ (6H), $^2J_{\text{SiCH}_2} = 9.8$ (2H), $^3J_{\text{Si-N-CH}} = 7.3$ (1H)].

3b "trans"

3b "cis"

3b cis²³ : ^1H NMR δ -0.03 (s, 2H, $\text{Si-CH}_2\text{-Si}$), 0.04 [s, 6H, $\text{NSi}(\text{CH}_3)_2$], 0.14 [s, 9H, $\text{Si}(\text{CH}_3)_3$], 0.18 [s, 9H, $\text{NSi}(\text{CH}_3)_3$], 0.20 [s, 9H, $\text{CH}_2\text{Si}(\text{CH}_3)_3$], 0.90 (d, $^3J = 6.5$, 3H, CH_3), 1.01 (d, $^3J = 6.5$, 3H, CH_3), 1.90-2.00 (m, 1H, Me_2CH), 2.28 [d, 1 H, NCHSi]; ^{13}C NMR δ 1.3 [$\text{Si}(\text{CH}_3)_3$], 1.5 ($\text{CH}_2\text{Si}(\text{CH}_3)_3$), 5.2 [$\text{NSi}(\text{CH}_3)_3$], 4.0 and 4.2 ($\text{Si}(\text{CH}_3)_2$), 9.0 [SiCH_2Si], 22.5 and 22.8 [CH_3], 32.2 (Me_2CH), 55.3 (NCHSi); ^{29}Si NMR δ 0.9 [CH_2SiMe_3 , $^2J_{\text{SiMe}_3} = 6.5$ (9H), $^2J_{\text{SiCH}_2} = 9.3$ (2H)], 2.2 [SiMe_3 , $^2J_{\text{SiMe}_3} = 6.3$ (9H), $^2J_{\text{SiCH}} = 11.6$ (1H), $^3J_{\text{Si-C-CH}} = 8.4$ (1H)], 3.4 [NSiMe_2 , $^2J_{\text{SiMe}_2} = 6.4$ (6H), $^2J_{\text{SiCH}_2} = 9.2$ (2H), $^3J_{\text{Si-N-CH}} = 12.1$ (1H)], 4.3 [NSiMe_3 , $^2J_{\text{SiMe}_3} = 6.4$ (9H), $^3J_{\text{Si-N-CH}} = 6.8$ (1H)].

2-Methyl-1-(trimethylsilyl)-1-bis(trimethylsilyl)amino]prop-1-ene (8b) : identified by comparison with an authentic sample.¹⁴

Nitrile 1c. Starting from 8.3 g (150 mmol) of the nitrile, were isolated 27.5 g of a complex mixture from which the following compounds were identified in proportions and yields were given in Table 2 : nitrile 1f,²² silazane 2c, enamines 8c and 8f. Silazane and enamines, which were not separated by distillation, were obtained in a 63% overall yield. Enamines were identified by comparison with authentic samples.¹⁴

2-Methyl-1,N,N-tris(trimethylsilyl)propylamine (2c) : IR (cm^{-1}) 921 (ν_{SiNSi}); MS (70 eV) m/z 218 (16.9), 202 (100), 114 (31.3), 73 (55.7).

Nitrile 1d. Starting from 6.15 g (150 mmol) of the nitrile, were isolated 21.3 g of a complex mixture from which the following compounds were identified in proportions and yields given in Table 2 : nitriles 1g²⁴ and 1h, silazanes 2g and 3g and enamines 8d and 8g. We have not been able to separate silazanes from enamines by distillation. Reactions performed at 40°C and above yielded tris(trimethylsilyl)amine 10 (up to 15% yield) as an extra product.

Bis(trimethylsilyl)acetonitrile (1h) : b.p. 89-92°C (20 mmHg); IR (cm^{-1}) 2227 ($\nu_{\text{C}\equiv\text{N}}$); ^1H NMR δ 0.00 [s, 18H, Si(CH₃)₃], 0.98 (s, H, CH); ^{13}C NMR δ -0.8 (Si(CH₃)₃), 7.0 (CH), 121.1 (C $\equiv$ N).

1,2,N,N-Tetrakis(trimethylsilyl)ethylamine (2a) : IR (cm^{-1}) 914 (ν_{SiNSi}); MS (70 eV) m/z 260 (100), 218 (15.3), 172 (27.7), 73 (73.9).

N-[Dimethyl(trimethylsilylmethyl)silyl]-1,2-N-tris(trimethylsilyl)ethylamine (3g) : IR (cm^{-1}) 922 (ν_{SiNSi}); MS (70 eV) m/z 332 (100), 202 (14.2), 172 (14.1), 145 (31.2), 73 (58.8).

1-[Bis(trimethylsilyl)amino]-1-trimethylsilylethylene (8d) : IR (cm^{-1}) 1580 ($\nu_{\text{C}=\text{C}}$), 948 (ν_{SiNSi}); MS (70 eV) m/z 259 (10.5), 244 (51.7), 186 (89.5), 170 (22), 73 (100).

(Z)-1,2-Bis(trimethylsilyl)-1-[bis(trimethylsilyl)amino]ethylene (8gZ) : IR (cm^{-1}) 1521 ($\nu_{\text{C}=\text{C}}$), 950 (ν_{SiNSi}); MS (70 eV) m/z 316 (2.5), 258 (100), 218 (14.4), 170 (19.2), 73 (73.9).

(E)-1,2-Bis(trimethylsilyl)-1-[bis(trimethylsilyl)amino]ethylene (8gE) : IR (cm^{-1}) 1539 ($\nu_{\text{C}=\text{C}}$), 929 (ν_{SiNSi}); MS (70 eV) m/z 316 (2.4), 258 (100), 218 (6.6), 170 (18.1), 73 (62.6).

Tris(trimethylsilyl)amine (10) : identified by comparison with an authentic sample.²⁵ It has already been emphasized that this compound, reputed to be difficult to hydrolyse (a property attributed to the complete delocalisation of the lone pair of the nitrogen onto the Si-C bonds), was completely transformed into methoxytrimethylsilane and ammonium chloride when treated with one equivalent of trimethylsilyl chloride in methanol at room temperature.¹⁰

Chemical reductive silylation of nitriles 1b-d. Using the same procedure as for 1a, 1b-d (100 mmol) were reacted at 0-5°C with trimethylchlorosilane (500 mL, 4 M) and lithium sand (7 g, 1 M) in a THF-HMPA mixture (300 mL, 180 mL). Work-up left a viscous liquid which was analysed by GC/MS. Beside compounds from the electrochemical process, were identified silazanes 4 and 5, present in 15 to 30% in the mixture, the overall yield being about 60% in each case.

Synthesis of RSMA, 6, from silazane/enamine mixtures. In a 100 mL Grignard flask, equipped with a magnetic stirrer, a condenser connected to a potash short column, a rubber septum and a 50 mL pressure equalizing dropping funnel, were introduced the silazane/enamine mixture resulting from the reductive silylation of 100 mmol of nitrile, NaBH₄ (100 mmol, 4.4 g) and methanol (50 mL). Then, trimethylsilyl chloride (100 mmol, 11 g) was dropwise added over a 2 hours period. After 4 hours stirring, volatile products (methanol, methoxysilanes, siloxanes, trimethylsilyl chloride in excess) were evaporated under vacuum and a solid residue was obtained, which was washed twice with pentane (5 mL). Sodium hydroxide pellets (4 g, 100 mmol) and diethyl ether (20 mL) were added. After 1 hour stirring, the ethereal solution was separated by filtration, ether was evaporated and the crude amine was purified by distillation. Thus the already described RSMA¹⁴ 6b and 6c were obtained in 57 and 42% yields respectively from the corresponding nitriles. However, only the original amine 6g (7% yield) was isolated from nitrile 1d.

1,2-Bis(trimethylsilyl)ethylamine (6g). Very volatile product; IR (cm^{-1}) 3307 (NH₂ absorptions); MS (70 eV) m/z 189 (0.9), 117 (10.1), 116 (100), 100 (13.7), 74 (85.9), 73 (47.9).

RESULTS AND DISCUSSION

Electrochemical and Chemical Reductive Silylation of Pivalic Aldehyde N-(Trimethylsilyl)imine. Synthesis of bis(trimethylsilyl)methylamine, BSMA, through reductive silylation of cyanides using either a chemical or an electrochemical process,^{9,10} was postulated to involve (Me₃Si)₂C=NSiMe₃, i.e a N-(trimethylsilyl)imine, as an intermediate. Looking for RSMA, we anticipated that applying the same reaction process to N-(trimethylsilyl)aldimines, the corresponding silazane, 2, would be formed, the protonolysis of which giving access to the desired amines, 6 (Scheme 1).

Scheme 1 : Strategy for synthesizing RSMA from N-silyl imines.

Pivalaldehyde N-(trimethylsilyl)imine ($R = \text{Me}_3\text{C}$), imine of a non-enolizable aldehyde, was selected as the model compound for testing this idea. This imine was submitted to the reductive silylation either under chemical or electrochemical conditions. Results differed on the technique employed.

Starting imine, trimethylsilyl chloride, hexamethylphosphoramide (HMPA)²⁶ and tetrahydrofuran (THF), were introduced into an electrochemical undivided cell equipped with an aluminum-made sacrificial anode.²⁷ After 4.4 faradays per mole have been passed through the mixture²⁸, reaction led to the formation of silazane **2a**.

It should be pointed out that this reaction has required 4.4 faradays per mole of imine instead of 2 from the theory. After 2.2 F/mole were passed,²⁸ chromatographic analysis (GC) of the reaction medium showed that almost 50% of the starting material was not transformed and a large amount of hexamethyldisilane was concurrently formed.²⁹ Apparently, the reduction potential of the starting imine should probably be close to that of trimethylsilyl chloride. At this stage, a non-hydrolytic work-up of the reaction medium afforded silazane 2a mixed with the starting aldimine.

When pivalaldehyde N-(trimethylsilyl)imine was treated with lithium sand and trimethylsilyl chloride in a HMPA/THF mixture at 0°C (according to the already described technique),¹⁰ a complex mixture of products was obtained. Among these products, the GC analysis of the reaction medium before the work-up revealed the presence, in addition to silazane 2a, of the starting compound in a significant amount, even when a large excess of lithium and TMSCl have been used. We believe that this result confirmed the reductive silylation of N-silyl imine as being particularly difficult.

Chemical and Electrochemical Reductive Silylation of Pivalonitrile : Synthesis of 2,2-Dimethyl-1-(trimethylsilyl)propylamine. It has been shown that aliphatic saturated nitriles having at least one hydrogen α with respect to the function led to the corresponding N-silylated ketene-imine when treated with lithium and trimethylsilyl chloride in THF as the solvent, in the absence of HMPA.²² As we wanted to know about the behavior of the nitrile functionality in the conditions of a chemical and an electrochemical²⁷ reductive silylation reaction (as above), we decided to test pivalonitrile, **1a**, first, in order to circumvent the eventual formation of the ketene-imine derivative.

Results were differing with the technique employed (Table 1). The chemical process gave a mixture of three silazanes **3a**, **4** and **5** (Scheme 2). Electrochemical process was more selective, **3a** being exclusively formed. Silazanes **4** and **5** have already been described as being the result of the reductive silylation of silyl cyanides, dimethyl cyanamide, trimethylsilyl isocyanate or N,N'-bis(trimethylsilyl)carbodiimide.^{9,10}

Scheme 2: Reductive silylation of pivalonitrile 1a.

process	% overall yield	4 %	5 %	3a %
electrochemical	60	-	-	100
chemical	74	18	19	63

Table 1 : Reductive silylation of pivalonitrile 1a.

Formation of **4** and **5** arised through elimination of the t.butyl group followed by the reductive silylation of the CN group, as it was the case with silyl cyanides.^{9,10} To this purpose, it is inte-

resting to note that Ingold et al.³⁰ have shown (Scheme 3) that a trimethylsilyl radical can add to **1a** to form an iminyl radical which eliminates the *t*-butyl group to give trimethylsilyl isocyanide, known to equilibrate rapidly with trimethylsilyl cyanide.³¹

Scheme 3 : Formation of Me₃Si-CN from *t*-Bu-CN.³⁰

This could be an explanation for our result. However, even if we cannot exclude completely the possibility of forming trimethylsilyl radicals from trimethylsilyl chloride, we should point out that the same iminyl radical could result from nucleophilic attack of the nitrogen anionic part of the intermediate radical-anion (resulting from the trapping of an electron by **1a**) to silyl chloride, in a mechanism parallel to that postulated in the case of silyl cyanides^{9,10}. (Scheme 4).

Scheme 4 : Alternate explanations for the formation of the intermediate iminyl radical.

In fact, elimination or not of the *t*.butyl group should be dependent on the conditions in the reaction medium more than on the nature of the source of electrons (lithium or anode).

Structure of silazanes 2a and 3a. NMR analysis of silazane **2a** revealed it is conformationally locked (no rotation around the C-N bond) as was the analogous silazane **4**.¹⁰

Scheme 5 : Blocked conformation of silazanes **2a** and **4**

Like silazane **5**,¹⁰ silazane **3a** also possessed a conformationally locked structure, one of the silyl groups linked to the nitrogen atom eclipsing the methine proton (Scheme 6). In contrast to **5**, which was obtained as a 1/1 mixture of both "cis" and "trans" rotamers, **3a** was obtained as the single rotamer, probably "trans"³² (see experimental).

"cis" and "trans" were defined from the respective positions of H and SiMe₃ on the C-N bond

Scheme 6 : Blocked conformation of silazanes **3a** and **5**

Synthesis of RSMA 6a. We have already described^{9,10,14} the preparation of amines from silazanes using a non-aqueous very mild and efficient process. Thus, protonolysis of silazanes **2a** and **3a**, with one equivalent of trimethylchlorosilane in methanol, yielded the corresponding free amine **6a** (61% yield from starting imine through **2a**; 58% yield from **1a**) after neutralization of the intermediate hydrochloride with solid sodium hydroxide³³ in diethyl ether (Scheme 7).

Scheme 7 : RSMA 6a from the protonolysis of silazanes 2a and 3a

When silazane 2a was protolysed in the same way in the presence of pivalaldehyde N-(silyl)imine (one equivalent), imine 7 was obtained (Scheme 8).

Scheme 8: Formation of imine 7

Evidently, this compound resulted from the condensation of pivalaldehyde released by protonolysis of starting imine, on the one hand, and amine 6a coming from protonolysis of 2a, on the other hand. That 7 survived hydrolytic conditions confirmed the already noted high stability of SMA imines.¹²

Access to RSMA from Nitriles $\text{R}'\text{R}''\text{HC-CN}$, 1b-d. This study was performed on the following nitriles, i-butyro- ($\text{R}' = \text{R}'' = \text{Me}$, 1b), propio- ($\text{R}' = \text{Me}$, $\text{R}'' = \text{H}$, 1c) and aceto- ($\text{R}' = \text{R}'' = \text{H}$, 1d) nitriles elected as model substrates for nitriles having at least one α -hydrogen atom. The electrochemical reductive silylation was used and the chemical process was tested for comparison.

Electrochemical process. The reaction led to a mixture of compounds which belong to three types of structures: α -trimethylsilylnitrile, silazane and acylsilane enamine. The following comments may be made on the results summarized in Table 2:

RR'HC-		nitriles 1 (yield%)	silazanes 2 (yield %)	silazanes 3 (yield %)	enamines 8 (yield %; Z/E)
Me ₂ HC-	b		2b (4)	3b (50)	8b (13.5; -)
MeH ₂ C-	c		2c (21)		8c(20.7; 80/20)
H ₃ C-	d				8d(13; -)
Me ₃ SiMe ₂ C-	e	1e (3.5)			
Me ₃ SiMeHC-	f	1f (9.8)			8f (14.5; 73/27)
Me ₃ Si H ₂ C-	g	1g(2.5)	2g(2.5)	3g(1)	8g(27; 70/30)
(Me ₃ Si) ₂ HC-	h	1h(5)			

1b $\rightarrow$ 1e + 2b + 3b + 8b (71%); 1c $\rightarrow$ 1f + 2c + 8c + 8f (66%); 1d $\rightarrow$ 1g + 1h + 2g + 3g + 8d + 8g (51%)

Table 2 : Electrochemical reductive silylation of nitriles 1b-d.

• - α) it is assumed that α -trimethylsilylnitriles 1e-h resulted from the substitution of the acidic α -hydrogen atom by a trimethylsilyl group, this proton being abstracted probably by any base present in the medium to form the corresponding α -cyano carbanion which is in equilibrium with the ketenimine azaanion (Scheme 9).

Scheme 9 : Formation of silylated nitriles 1e-h from nitriles 1b-d,g.

- - β) It can be proposed that acylsilane enamines **8b-d,f,g** (Scheme 10) resulted probably from the reductive silylation of the C=N bond of the N-silyl ketenimines **9b-d,f,g**.

Scheme 10 : Formation of Enamines **8** from Ketenimines **9**. Scheme 11 : Tentative Explanations for the Formation of Enamines **8** from Nitriles **1b-d** and Cyanohydrins

The Z isomer was preponderant in this reaction, whereas the E isomer was obtained as the major product in the reductive silylation of O-silyl-protected cyanohydrins.¹⁴ We suggested that these enamines were formed in each case by a specific pathway (i.e formation of enamines **8** from cyanohydrins would not occur through an intermediate ketenimine).³⁴ Taking into account the greater steric interaction of the trimethylsilyl group with a group linked to a β -carbon, than the planar³⁵ N,N-bis(trimethylsilyl)amino group,³⁶ on one side, and assuming that Me_3SiO^- could be eliminated via a trans antiperiplanar process, on other side, we proposed the following scheme where the decisive factor was the steric hindrance in the vinylic anion **B** on one side and in the carbanion **A** on the other (Scheme 11).

- - γ) Silazanes **2b,c,g** and **3b,g** have the same structures as silazanes **4**, **5**, **2a** and **3a**. They have been formed either directly from starting nitriles (**2b,c** and **3b**) or from transient silylated nitriles (**2g** and **3g**). While **3a** was obtained as a single rotamer ("trans"), both rotamers were formed in the case of **3b** and **3g**, result which was consistent with the smaller bulkiness of the i-propyl, ethyl and methyl group compare to t-butyl group.³²

• - δ) In one experiment made at 40°C with acetonitrile 1d, cleavage of the C-N bond took place at some stage in the process since formation of tris(trimethylsilyl)amine, 10 (up to 15%) was observed.

Chemical process. Using the same conditions as those defined with 1a, nitriles 1b-d were treated with lithium and trimethylsilyl chloride in THF/HMPA at 0°C. A very complex mixture of products was formed. Its analysis by GC/MS technique indicated the presence of the same products as those resulting from the electrochemical process, accompanied by silazanes 2 and 3. Overall yields were about 60% with 2+3 representing from 15% (from 1d) to 30% (from 1b) of the mixture. This result confirmed the one obtained from 1a, i.e. that the cleavage of the C-CN bond occurred during the chemical process, though the reaction was performed at 0°C. This illustrated the already underlined better selectivity of the electrochemical process.³⁷

Access to RSMA. The transformation of silazanes (*vide supra*) and acylsilane enamines,¹⁴ separately, into the corresponding α -(silyl)alkylamines has already been described. Protonolysis of the Si-N linkages of silazanes by trimethylsilyl chloride in methanol led to RSMA's hydrochloride, which released free RSMA on neutralization with solid sodium hydroxide³³ in diethyl ether. Protonolysis of the Si-N linkages of acylsilane enamines led to enaminium hydrochlorides and finally iminium hydrochlorides after slow isomerization. Reduction of these salts with sodium borohydride in methanol yielded the free RSMA.

We found that the silazanes/enamines mixtures can be treated in a one-pot process with trimethylsilyl chloride in methanol in the presence of sodium borohydride to lead to the corresponding RSMA in good overall yields, respectively 57% (6b) and 42% (6c) (Scheme 12 and Table 3):

Scheme 12 : α -(Silyl)alkylamines from nitriles R'R''HC-CN

Starting material	Resulting RSMA (% overall yield)
N-silyl aldimine	6a (61)
nitrile 1a	6a (58)
nitrile 1b	6b (57)
nitrile 1c	6c (42)
nitrile 1d	6g (7)

Table 3 : Recapitulation of synthesized RSMA and their origin.

It should be pointed out that a mixture of 6d (R'R''CH = CH₃) and 6g (R'R''CH = Me₃SiCH₂) was obtained from 1d, only 6g being isolated in low yield (7%), probably because of the high volatility of both compounds.

CONCLUSIONS

Electrochemical reductive silylation of alkanenitriles provides a new and efficient access to silazanes and acylsilane enamines, precursors of α -(trimethylsilyl)alkylamines (RSMA). The fact that the major isomer of acylsilane enamines was the E isomer when issued from silyl-protected cyanohydrins, and Z isomer when issued from nitriles has been explained in term of differentiated steric hindrance in the intermediates.

Electrochemical reductive silylation of pivalaldehyde N-(silyl)imine, followed by protonolysis of the intermediate silazanes, has also given rise to the desired corresponding RSMA in quite good yield. The scope of this synthesis starting from N-(silyl)imines will be extended to any kind of RSMA (R $\neq$ tertiary) when an efficient and general synthesis of N-(trimethylsilyl)aldimines will be possible. This is not the case actually in spite of the many attempts made by different authors.^{16 17}

However, considering the origin of the proton linked to functional carbon atom, the choice between imine and nitrile as the starting material will be of importance. In the last case, the proton originated from a trimethylsilyl group through an already described 1-5 hydrogen shift,¹⁰ although it

belonged to the starting material (aldiminyl proton) in the former case. Thus, the synthesis of deuterated RSMA, $R(\text{Me}_3\text{Si})\text{DCNH}_2$, can be envisioned from deuterated aldehydes $\text{RCD}=\text{O}$.

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