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STUDIES ON THE NITROSATION OF *N*-SILYLATED CYCLOPENTENYLAMINES

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The diazotization of *N*-silylated *N*-methyl- and *N*-phenylcyclopentenylamines affords products derived from intermediate methyl- and phenyldiazonium ions. However, when this method is applied to *N,N*-bissilylated cyclopentenylamines, the products obtained do not confirm the formation of a cyclopentenyl cation intermediate.

INTRODUCTION

Vinyl cations are an important class of organic intermediates which have attracted considerable theoretical and synthetic interest.[1,2] Vinyl cations can be generated through electrophilic addition to alkynes and allenes (the π-route)[3,4] or by solvolysis (the σ-route) of appropriate systems possessing super leaving groups such as perfluoroalkanesulphonates.[5] The deamination of vinylic amines is another method for the generation of vinyl cations but it is rarely employed because these amines are difficult to synthesise.[6] The nitrosation of mono- and bissilylated alkyl- and arylamines (**1**) has been shown to proceed with the formation of the corresponding diazonium salts. This represents a new procedure for the diazotization in non-aqueous media under mild conditions (Scheme 1).[7]

1

R = H, $SiMe_3$

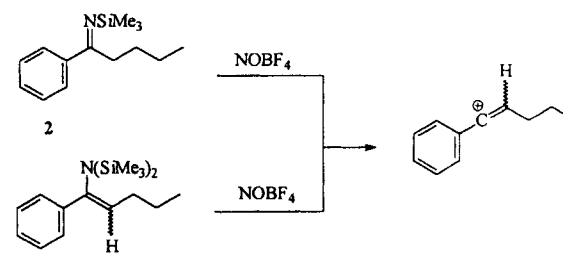
X = BF_4, Cl, Br, OTf

Scheme 1

In an earlier study[8] we investigated the reaction of silylated imines (**2**) and enamines (**3**) with different nitrosyl salts. The reaction affords products derived from intermediate vinyl cations (Scheme 2).

This method was also employed in attempts to generate an ethynyl cation from an *N,N*-bissilylated ynamine.[9] However, the diazotization of **4** does not lead to the expected ethynyl diazonium salt and its corresponding ethynyl cation (Scheme 3).

Several groups have attempted to generate the 1-cyclopentenylcation.[1,2] This cation has eluded its direct formation by solvolytic procedures.[10] The formation of the cyclopentenyl cation is restricted to the photolysis of 1-iodocyclopentene[11] and to the rearrangement which



2

3

Scheme 2

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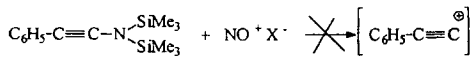


4

Scheme 3

takes place during the solvolysis of 1-cyclobutylidenethyl triflate.[10]

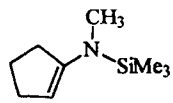
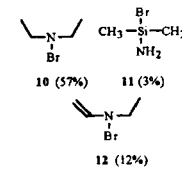
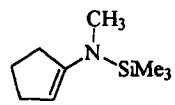
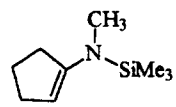
RESULTS AND DISCUSSION

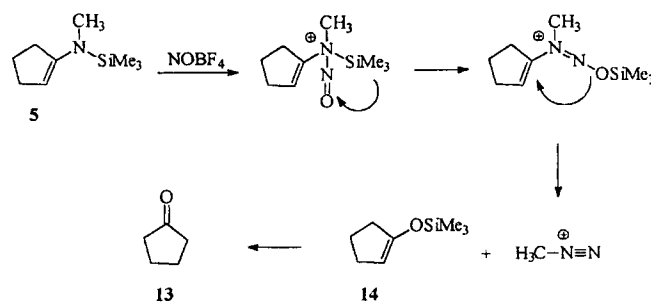
We have now investigated the reaction of *N*-methyl-*N*-trimethylsilyl-1- cyclopentenylamine (**5**), *N*-phenyl-*N*-trimethylsilyl-1-cyclopentenylamine (**6**), *N*,*N*-bis(trimethylsilyl)-1-cyclopentenylamine (**7**), 5-methyl-*N*,*N*-bis(trimethylsilyl)-1-cyclopentenylamine (**8**) and *N*,*N*-bis(trimethylsilyl)-2- norbornenylamine (**9**) with nitrosyl tetrafluoroborate in dichloromethane at −78 C. When the reaction mixture is quenched with different nucleophiles, a mixture of products is formed (Tables 1–3).

The results can be arranged into three different groups according to the substituents attached to the nitrogen atom. The product composition of each group was found to be dependent on the nucleophiles employed.

The reaction of **5** with $NOBF_4$ (Table 1) does not appear to proceed via an intermediate cyclopentenyl cation. With tetraethylammonium bromide as trapping agent the products are formed by a side reaction of the nucleophile. Cyclopentanone (**13**) appears to be the hydrolysis product of the starting material **5**. However, treatment of **5** with a 1:1 mixture of dichloromethane and water under the same reaction conditions (−78 °C, 2 h) affords the enamine without change. Moreover, cyclopentanone is the hydrolysis product from 1-cyclopentenyl trimethylsilyl ether (**14**) formed as an intermediate in the nitrosation of **5** (Scheme 4). In the

Table 1. Nitrosation of *N*-methyl-*N*-trimethylsily-1-cyclopentenylamine (**5**)

Starting material	Reaction conditions	Nucleophile	Products
 **5**	$NOBF_4$ / CH_2Cl_2 - 78°C	Et_4NBr / CH_3CN	 **10** (57%) **11** (3%) **12** (12%)
 **5**	$NOBF_4$ / CH_2Cl_2 - 78°C	D_2O	 **13** (5%)
 **5**	$NOBF_4$ / CH_2Cl_2 - 78°C	NaI / CH_3CN	 **13** (2%)



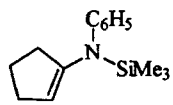
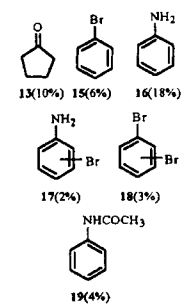
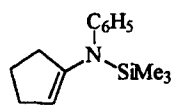
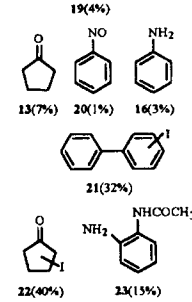
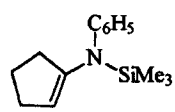
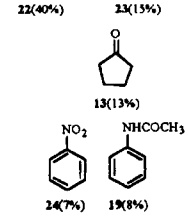
Scheme 4

reaction of silylated amines with nitrosyl reagents, intermediates and products are formed from the electrophilic attack of the nitrosyl salt at the nitrogen atom with subsequent generation of a diazonium salt.[7,8] No deuterated products were detected when D_2O was used as the nucleophile, indicating that cyclopentanone was formed before the reaction was quenched in deuterium oxide. Products derived from a reaction with sodium iodide or acetonitrile were not found. In this case, we can conclude that the mechanism proceeds through the formation of a methyldiazonium ion rather than the more unstable cyclopentenyldiazonium ion. The methyldiazonium salt reacts with the nucleophiles forming volatile and water soluble products (e.g. methanol) which are lost in the reaction work-up.

The nitrosation of **6** (Table 2) affords a complicated mixture of products in which aromatic compounds predominate. These products can be explained by the formation of a phenyldiazonium ion which loses nitrogen to form a phenyl cation that reacts with the different nucleophiles (Scheme 5). The reaction path favours the formation of the more stable phenyldiazonium ion over the cyclopentenyldiazonium ion. Aniline is formed in a concomitant reduction process of the phenyldiazonium ion generated. Iodinated products such as **21** and **22** are probably formed by a radical mechanism when sodium iodide is used as the trapping reagent.

In Table 3, the results for the nitrosation of the bissilylated enamines **7–9** are summarised. The ketones **13, 26** and **28** are the hydrolysis products of the corresponding enamines **7**, **8** and **9** via the corresponding silyl ethers (cf. Scheme 4). A DBF_4-catalysed (generated from D_2O and $NOBF_4$) deuterium exchange of the ketones **13**, **26** **28** formed as described above can explain the incorporation of deuterium to give the monodeuterated ketones **25**, **27** and **29**. However, when the enamines are dissolved in dichloromethane and cooled to −78 °C for 2 h, then shaken with D_2O at room temperature for 1 h, the silylated enamines are quantitatively recovered unchanged and no deuterated ketones

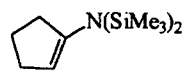
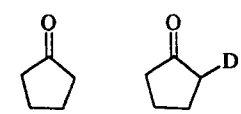
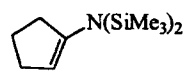
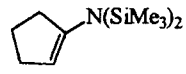
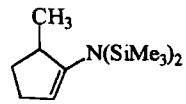
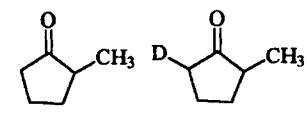
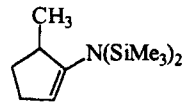
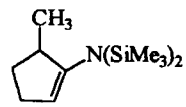
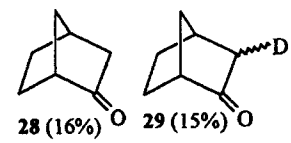
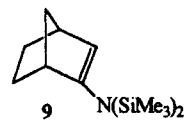
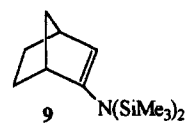
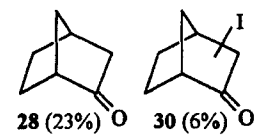
Table 2. Nitrosation of *N*-phenyl-*N*-trimethylsily-1-cyclopentenylamine (**6**)

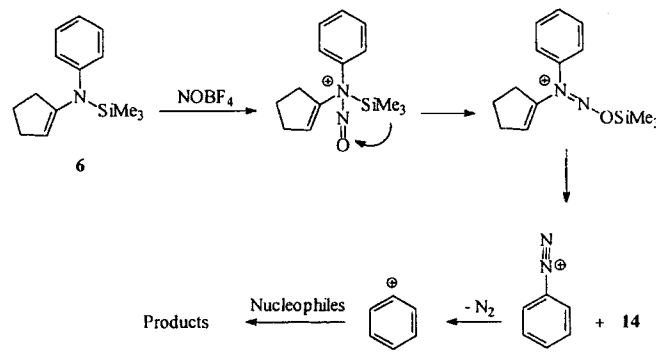
Starting material	Reaction conditions	Nucleophile	Products
 **6**	$NOBF_4$ / CH_2Cl_2 -78°C	Et_4NBr / CH_3CN	 **13**(10%) **15**(6%) **16**(18%) **17**(2%) **18**(3%) **19**(4%)
 **6**	$NOBF_4$ / CH_2Cl_2 -78°C	NaI / CH_3CN	 **13**(7%) **20**(1%) **16**(3%) **21**(32%) **22**(40%) **23**(15%)
 **6**	$NOBF_4$ / CH_2Cl_2 -78°C	CH_3CN	 **13**(13%) **24**(7%) **19**(8%)

are detected. Moreover, treatment of the ketones **13**, **26** and **28** with D_2O at room temperature affords the starting material without hydrogen–deuterium exchange. It is known, that these ketones exchange their α-hydrogen by reaction with deuterium oxide only under basic catalysis.[12] The iodinated 2-norbornanone **30** is formed by radical substitution when sodium iodide is used as nucleophile.

The tempting explanation that the monodeuterated ketones **25**, **27** and **29** are formed by the reaction of an

Table 3. Nitrosation of the bissilylated enamines **7**, **8** and **9**

Starting material	Reaction conditions	Nucleophile	Products
 **7**	$NOBF_4$ / CH_2Cl_2 -78°C	D_2O	 **13** (25%) **25** (5%)
 **7**	$NOBF_4$ / CH_2Cl_2 -78°C	Et_4NBr / CH_3CN	**13** (2%)
 **7**	$NOBF_4$ / CH_2Cl_2 -78°C	NaI /CH_3CN	**13** (13%)
 **8**	$NOBF_4$ / CH_2Cl_2 -78°C	D_2O	 **26** (38%) **27** (10%)
 **8**	$NOBF_4$ / CH_2Cl_2 -78°C	Et_4NBr / CH_3CN	**26** (40%)
 **8**	$NOBF_4$ / CH_2Cl_2 -78°C	NaI /CH_3CN	**26** (33%)
 **9**	$NOBF_4$ / CH_2Cl_2 -78°C	D_2O	 **28** (16%) **29** (15%)
 **9**	$NOBF_4$ / CH_2Cl_2 -78°C	Et_4NBr / CH_3CN	**28** (26%)
 **9**	$NOBF_4$ / CH_2Cl_2 -78°C	NaI /CH_3CN	 **28** (23%) **30** (6%)



Scheme 5

intermediate cyclopentenyl cation with deuterium oxide is invalidated by the fact that brominated compounds were not detected when tetraethylammonium bromide was used as the trapping reagent.

CONCLUSION

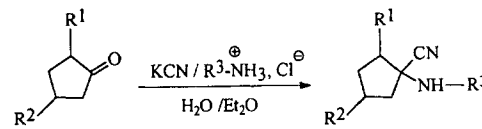
The nitrosation of silylated cyclopentenylamines affords products derived from a diazonium ion. The intrinsic instability of the cyclopentenyl diazonium ion and cyclopentenyl cation seems to control the reaction. A phenyl or a methyl group attached to the nitrogen atom of the enamines allows the formation of intermediate cations. However, the nitrosation of bissilylated cyclopentenyl- and norbornenylamines does not lead to the formation of products derived from a suspected cyclopentenyl cation.

EXPERIMENTAL

Melting points are uncorrected. NMR spectra were recorded on Varian XL- 300 and Bruker AC 250 spectrometers using $CDCl_3$ as solvent. Mass spectra were recorded by electronic impact ionization at 70 eV on an HP 5989A spectrometer. Infrared spectra were taken with a Perkin-Elmer Model 781 instrument.

The silylated enamines **5–9** were prepared from α-aminonitriles. The corresponding aminonitriles **31–35** were synthesised by a modified Strecker procedure (Scheme 6).[13]

Synthesis of α-aminonitriles; general procedure. To a cooled mixture of 0·1 mol of potassium cyanide and 0·1 mol of the corresponding amine chlorohydrate or ammonia solutions in 150 ml of water is added 0·1 mol of the corresponding ketone in 50 ml of diethyl ether at 0 °C. The mixture is stirred vigorously for 48 h at room temperature, then the organic layer is extracted with diethyl ether (3 × 50 ml), washed with water (2 × 50 ml) and dried over sodium carbonate. The solvent is removed *in vacuo* and the residue distilled (Kugelrohr) or recrystallized.



13, 26, 28 **31-35**

	R^1	R^2
13	H	H
26	CH_3	H
27	$-CH_2CH_2-$	

	R^1	R^2	R^3	Yield (%)
31	H	H	CH_3	70
32	H	H	C_6H_5	72
33	H	H	H	68
34	CH_3	H	H	53
35	$-CH_2CH_2-$		H	72

Scheme 6

1-Methylaminocyclopentanecarbonitrile (**31**) b.p. 80 °C (4 mbar); IR (film), ν 3340, 2220, 1320, 770 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1·45 (bs, 1H, NH), 1·90 (m, 4H, CH_2), 2.10 (m, 4H, CH_2), 2·50 (s, 3H, CH_3NH) ppm; ^{13}C NMR ($CDCl_3$) δ 23·54 (C-3, C-4), 32·06 (CH_3NH), 38·53 (C-2, C-5), 62·05 (C-1), 122·76 (CN) ppm; MS, *m/z* (%B) 124 (M^+, 1), 123 (M − H, 8), 109 (M − CH_3, 2), 97 (M − CNH, 22), 68 (100).

1-Phenylaminocyclopentanecarbonitile (**32**) m.p. 53–54 °C (hexane); IR (KBr), ν 3380, 2240, 1605, 1520, 1500, 1315, 750, 700 cm^{-1}; ^1H NMR ($CDCl_3$) δ: 1·85 (m, 4H, CH_2), 2·15 (m, 2H, CH_2), 2·35 (m, 2H, CH_2), 4·00 (bs, 1H, NH), 6·85 (m, 3H, arom.), 7·30 (m, 2H, arom.) ppm; ^{13}C NMR ($CDCl_3$) δ 23·82 (C-3, C-4), 40·17 (C-2, C-5), 57·43 (C-1), 122·39 (CN), 115·56, 119·74, 122·39, 129·31, 144·18 (arom) ppm; MS *m/z* (%B): 186 (M^+· 43), 185 (M-H, 62), 159 (M-CNH, 40), 130 (100), 77 (66), 51 (60).

1-Aminocyclopentanecarbonitrile (**33**) b.p. 90 °C (0.4 mbar); IR (film) ν 3360, 3300, 2220, 1600, 1340, 850 cm^{-1}; ^{13}C NMR ($CDC1_3$) δ: 23·70 (C-3, C-4), 40·88 (C-2, C-5), 54·39 (C-1), 125·28 (CN) ppm.

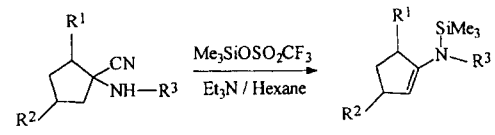
1-Amino-2-methylcyclopentanecarbonitrile (**34**) b.p. 90 °C (3 mbar); IR (film) ν 3380, 3300, 2230, 1620, 1380, 850 cm^{-1}. The ratio of *cis-trans* isomers of **34** (38 : 62) was determined by NMR; ^1H NMR ($CDCl_3$), δ 1.10 (d, 3H, J = 8 Hz, CH_3), 1·15 (d, 3H, J = 8 Hz, CH_3), 1·50 (bs, 4H, NH_2), 1·90–2·35 (m, 14H, CH_2, CH) ppm; ^{13}C NMR ($CDCl_3$) δ 12·65, 15·83 (CH_3), 20·78, 21·75 (C-4), 30·38, 31·53 (C-3), 39·94, 40·17 (C-5), 45·04, 45·96 (C-2), 56·45, 60·55 (C-1), 123·23, 124·75 (CN) ppm; MS, *m/z* (%B): 124 (M^+, 2), 109(M-CH_3, 4), 96(M-28, 10), 81(M-43, 40), 68(100), 41(55).

2-Amino-2-norbornanecarbonitrile (**35**) b.p. 11 °C (1.5 mbar), m.p. 54–55 °C; IR (film) ν: 3360, 3300, 2220, 1600, 1320 cm^{-1}; ^{13}C NMR spectra indicates that **35** is a 65 : 35 mixture of *endo* and *exo* isomers. ^{13}C NMR ($CDCl_3$), δ 21·09, 24·94, 27·92, 28·67, 35·48, 36·58, 37·17, 39·11, 45·86, 47·13, 47·80, 48·20, 54·63 (C-2), 55·35 (C-2), 124·92 (CN), 126·23 (CN) ppm; MS, *m/z* (%B) 136 (M^+, 4), 135 (M-H, 5), 109 (M-CNH, 28), 81(109-28, 32), 68 (100), 43 (68).

Synthesis of silylated enamines; general procedure. The preparation of silylated enamines **5–9** is carried out by treatment of the corresponding aminonitriles **31–35** with trimethylsilyl triflate according to the reported methods (Scheme 7).[13]

It is interesting to note the high regioselectivity of this process; thus, the reaction of **34** with trimethylsilyl triflate affords only the Hoffmann elimination product **8** and not the Saytzeff product (Scheme 7).

To a solution or suspension of 10 mmol of the appropriate aminonitrile and 40 mmol of triethylamine



31-35 **5-9**

	R^1	R^2	R^3	Yield (%)
5	H	H	CH_3	80
6	H	H	C_6H_5	85
7	H	H	$SiMe_3$	58
8	CH_3	H	$SiMe_3$	79
9		$-CH_2CH_2-$	$SiMe_3$	67

Scheme 7

in 50 ml of anhydrous hexane at room temperature and under an argon atmosphere are added 32 mmol of trimethylsilyl triflate in one portion. After 24 h, the upper layer is isolated by decantation and the hexane removed *in vacuo*. The residue is distilled at low pressure (Kugelrohr), affording the silylated enamine.

N-(Methyl)-*N*-(trimethylsilyl)-1-cyclopentenylamine (**5**) b.p. 25 °C (0·05 mbar); IR (film) ν 3070, 1620, 1415, 1260, 850 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0·22 (s, 9H, CH_3Si), 1·90 (q, J = 6·6 Hz, CH_2), 2·30 (m, 2H, CH_2), 2·45 (m, 2H, CH_2), 2·68(s, 3H, CH_3N), 4·32 (m, 1H, =CH) ppm; ^{13}C NMR ($CDCl_3$) δ 1·48 (CH_3Si), 23·49 (C-4), 29·58 (C-3), 34·03 (C-5), 35·29 (CH_3N), 95·96 (C-2), 151·23 (C-1); MS, *m/z* (%B): 169 (M^+, 50), 168 (M- H, 76), 154 (M-CH_3, 27), 73 [$(CH_3)_3Si^+$, 100].

N-(Phenyl)-*N*-(trimethylsilyl)-1-cyclopentenylamine (**6**) b.p. 120 °C (0.7 mbar); IR (film), ν 1620, 1580, 1480, 1250, 840 cm^{-1}; ^1H NMR ($CDCl_3$), δ 0·18 (s. 9H, CH_3Si), 1·88 (q, 2H, J = 6·3 Hz), 2·3 (m, 4H, CH_2), 4·39 (t, 1H, J = 4 Hz, =CH), 7·10 (m, 3H, arom), 7·30 (m, 2H, arom) ppm; ^{13}C NMR ($CDCl_3$) δ 1·19 (CH_3Si), 22·69 (C-4), 30·09 (C-3), 33·78 (C-5), 104·38 (C-2), 123·99, 127·77, 128·55, 147·19 (arom), 149·63 (C-1) ppm; MS, *m/z* (%B) 231 (M^+, not observed), 165 (35), 150 (100), 73 [$(CH_3)_3Si^+$, 12].

N,N-Bis(trimethylsilyl)-1-cyclopentenylamine (**7**) b.p. 20 °C (0·1 mbar); IR (Film) v: 3070, 1640, 1260, 970, 845 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0·18 (s, 18H, CH_3Si), 1·70 (q, 2H, J = 7 Hz, CH_2), 2·00 (m, 2H, CH_2), 2·15 (m, 2H, CH_2), 4·90 (m, 1H, =CH); ^{13}C NMR ($CDCl_3$) δ: 1·97 (CH_3Si), 22·85 (C- 4), 30·31 (C-3), 38·43 (C-5), 119·50 (C-2), 148·87 (C-1) ppm; MS, *m/z* (%B) 227 (M^+, 26), 212 (M-CH_3, 77), 73[$(CH_3)_3Si^+$, 100], 45 (50).

5-Methyl-*N*, *N*-bis(trimethylsilyl)-1-cyclopentenylamine (**8**) b.p. 60 °C (0·1 mbar); IR (film) ν 3050, 1630, 1370, 1255, 950, 845 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0·10 (s, 18H, CH_3Si), 0·80 (d, 3H, J = 7 Hz, CH_3CH),

1·80–2·15 (m, 4H, CH_2), 2·35 (m, 1H, C*H*CH_3), 4·80 (m, 1H, =CH) ppm; ^{13}C NMR ($CDCl_3$), δ 2·45 (CH_3Si), 18·16 (CH_3), 27·85 (C-4), 31·58 (C-3), 42·06 (C-5), 117·36 (C-2), 152·56 (C-1) ppm; MS, *m/z* (%B): 241 (M^+, 29), 226(M- CH_3, 100), 73 [$(CH_3)_3Si^+$, 70], 45 (31).

N,N-Bis(trimethylsilyl)-2-norbornenylamine (**9**) b. p. 60 °C (1·5 mbar); IR (film) ν 3075, 1600, 1260, 940, 850 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0·10 (s, 18H, CH_3Si), 0·85 (d, 1H, J = 8 Hz), 1·00 (m, 2H, CH), 1·20 (m, 1H, CH), 1·40 (m, 1H, CH), 1·50 (m, 1H, CH), 2·40 (m, 1H, CH), 2·60 (m, 1H, CH), 4·80 (d, 1H, J = 3 Hz, =CH) ppm; ^{13}C NMR ($CDCl_3$), δ: 2·60 (CH_3Si), 23·39 (C-6), 27·99 (C-5), 41·77 (C-7), 46·28 (C-4), 48·68 (C-1), 116·53 (C3), 153·27 (C-2) ppm; MS, *m/z* (%B): 253 (M^+, 20), 238 (M-CH_3, 15), 225 (M-28, 89), 73 [$(CH_3)_3Si^+$, 100], 45 (48).

Nitrosation reaction; general procedure. Nitrosyl tetrafluoroborate (Merck) is used without purification. To a suspension of nitrosyl salt (1 mmol) in anhydrous dichloromethane (5 ml) under an argon atmosphere at −78 °C is added dropwise the corresponding silylated enamine. After 2 h at −78 °C, the reaction mixture is quenched with various nucleophiles and then maintained for 1 h at room temperature. The mixture is washed with water, dried over magnesium sulphate and analysed.

The compositions of the reaction products reported in Tables 1, 2 and 3 were determined by GC–MS and the products were identified by comparison of their properties with those of commercial samples or with samples prepared according to literature methods.

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