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AMINOMERCURATION-DEMERCURATION OF DIMETHYL(CHLOROALKYL)ALKENYLSILANES AS A ROUTE TO AZASILACYCLOALKANES

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Summary

3,3-Dimethyl-1-phenyl-1-aza-3-silacyclopentane and 3,3,5-trimethyl-1-phenyl-1-aza-3-silacyclopentane were obtained by the reaction of dimethyl(chloromethyl)vinylsilane and dimethyl(chloromethyl)allylsilane with aniline in THF in the presence of mercury acetate followed by reduction with sodium borohydride. Aminomercuration-demercuration of dimethyl(3-chloropropyl)vinylsilane and dimethyl(3-chloropropyl)allylsilane results in the corresponding 3-chloropropylphenylaminoalkyl derivatives. Dimethyl(3-chloropropyl)(2-phenylaminopropyl)silane undergoes cyclization under the same reaction conditions giving 2,4,4-trimethyl-1-phenyl-1-aza-4-silacycloheptane in low yield. Competitive nucleophilic substitution of the chloroalkyl group of initial silanes by aniline affords dimethyl(phenylaminoalkyl)alkenylsilanes.

Introduction

Bifunctional organosilicon compounds of the type $Cl(CH_2)_nR_2Si(CH_2)_mXH$ (X = O, S) are highly versatile precursors for the synthesis of organosilicon heterocycles containing Si and X-atoms in the ring [1–4]. Up to now analogous compounds with X = NR′ have been unknown, although these compounds do seem to be the intermediates of the reaction of dialkyl(chloromethyl)chloroalkylsilanes with primary amine leading to the corresponding 1-aza-3-silacyclohexanes [1,3] or 1-aza-3-silacycloheptane [2].

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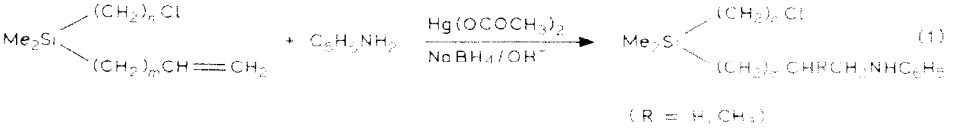
Results and discussion

We now report on a general method for the synthesis of dimethyl(chloroalkyl) aminoalkylsilanes and the corresponding azasilacycloalkanes.

With this aim in mind, dimethyl(chloroalkyl)alkenylsilanes were used as starting compounds. A simple convenient route of conversion of alkenylsilanes to the corresponding aminoalkylsilanes is aminomercuration-demercuration of the double bond [5].

We assumed that the interaction of aniline with dimethyl(chloroalkyl)alkenylsilanes in THF in the presence of mercury acetate followed by reduction with sodium borohydride in an alkaline medium would occur according to eq. 1.



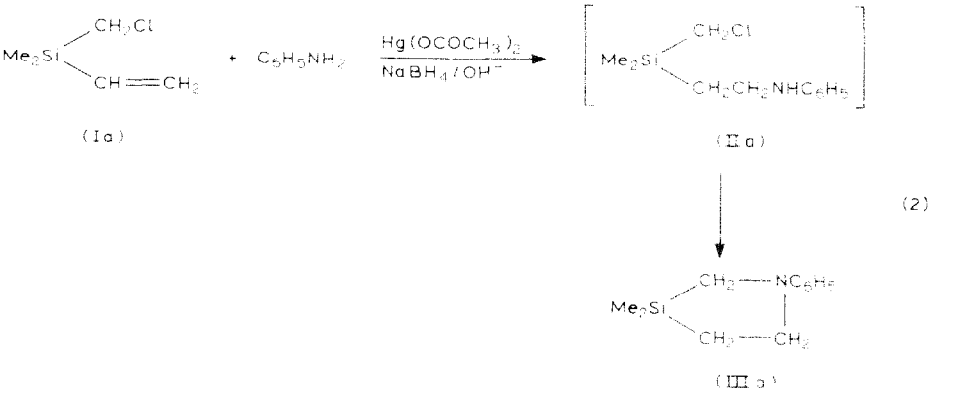
(1)

(R = H, CH_3)

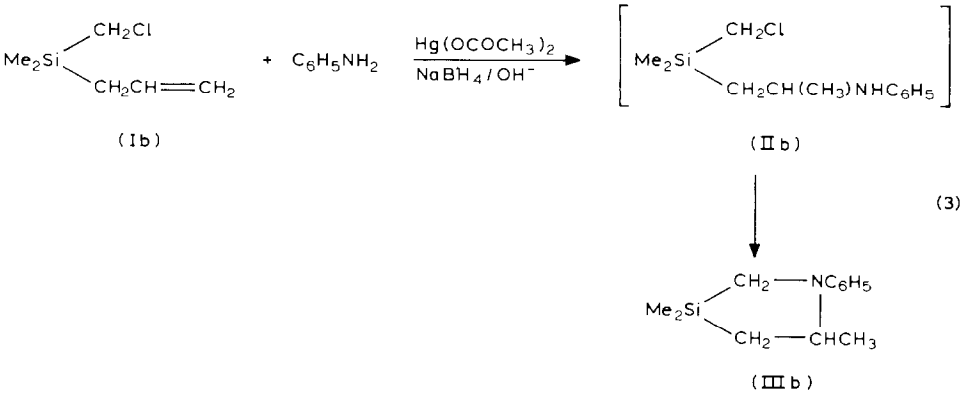
However, it was found that the reaction products depend on the nature of the initial compounds. Interaction of dimethyl(chloromethyl)vinylsilane (Ia, $n = 1$, $m = 0$) with aniline affords 3,3-dimethyl-1-phenyl-1-aza-3-silacyclopentane (IIIa) as major product. The intermediate compound (IIa) cyclizes readily to IIIa with an excess of aniline (eq. 2).

When dimethyl(chloromethyl)allylsilane (Ib, $n = 1$, $m = 1$) is treated with aniline in the presence of mercury acetate the only volatile reaction product is 3,3,5-trimethyl-1-phenyl-1-aza-3-silacyclopentane (IIIb). Conversion of Ib into the intermediate adduct (IIb) follows the Markovnikov rule (eq. 3).

Increasing the distance between the reactive NH and CH_2Cl groups results in a greater stability of the dimethyl(chloroalkyl)phenylaminoalkylsilanes formed and decreases the rate of cyclization. Thus, the reaction of dimethyl(3-chloropropyl)-vinylsilane (Ic) with aniline/mercury acetate affords the corresponding acyclic phenylaminoalkyl derivative (IIc) in 33% yield (eq. 4).



(2)



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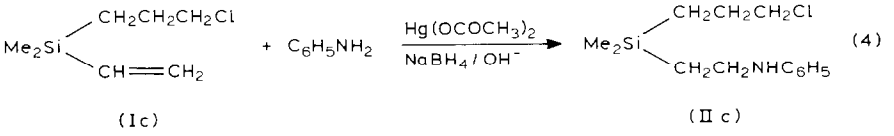
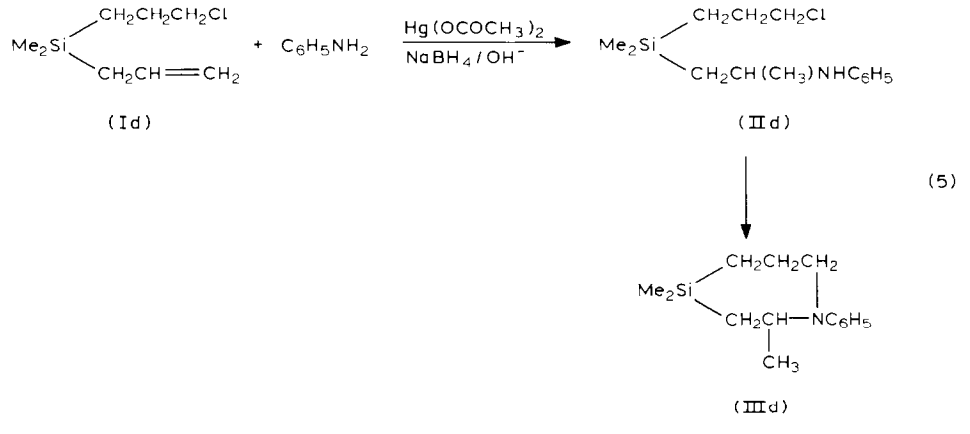


(4)

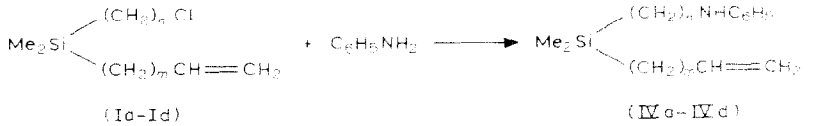
Dimethyl(3-chloropropyl)(2-phenylaminopropyl)silane (IId) and 2,4,4-trimethyl-1-phenyl-1-aza-4-silacycloheptane (IIId) were obtained by aminomercuration-demercuration of dimethyl(3-chloropropyl)allylsilane (Id) in a ratio of 8.4 : 1. The presence of a neighbouring methyl group near the reaction site probably favours the cyclization of IId in comparison with IIc (the Thorpe–Ingold effect) (eq. 5).

Thus, the main routes of conversion of dimethyl(chloroalkyl)alkenylsilanes (Ia-Id) in the $C_6H_5NH_2/Hg(OCOCH_3)_2/THF$ system involving the double bond are illustrated by eqs. 2–5.

However the possibility of competitive nucleophilic substitution of chloroalkyl group by aniline could not be excluded. In this case the reaction would follow eq. 6.



(5)



(6)

(Ia–Id) (IVa–IVd)

In fact, dimethyl(phenylaminomethyl)vinylsilane (IVa) and dimethyl(3-phenylaminopropyl)vinylsilane (IVc) are by-products of reactions 2 and 4. The time variation of the aminomercuration and reduction steps did not affect the IIIa : IVa ratio, which remained at 2.5 : 1.

It should be noted that the interaction of Ia with aniline in THF at room temperature, i.e., under conditions similar to those of the aminomercuration step proceeds very slowly. No formation of IVa was observed for 7 h. After stirring of the reaction mixture for 7 d, IVa was obtained in 23% yield. In contrast to substituted vinylsilanes, phenylaminoalkylallylsilane derivatives were not detected in reactions 3 and 5. This is probably due to transformation of dimethyl(phenylaminomethyl)allylsilane (IVb) and dimethyl(2-phenylaminopropyl)allylsilane (IVd) into the corresponding heterocycles (IIIb) and (IIId) since alkenylamines undergo electrophilic ring closure in the presence of mercury acetate [6]. The possibility of such intramolecular cyclizations occurring will be studied in the future. Treatment of azasilacyclopentane derivatives, IIIa and IIIb, with methyl iodide leads to the corresponding ammonium salts $[Me_2Si(CH_2)CH_2CHRN(C_6H_5)CH_3]^+ I^-$ (Va, R = H; Vb, R = CH_3).

The structure of the compounds obtained was confirmed by ^1H NMR and mass spectroscopy.

The mass spectrum of each compound contains a molecular ion peak which is intense only for compounds IIIa and IVc. Loss of a methyl radical from the parent ion is a common feature of the spectra of the compounds studied. Fragmentation by initial fission of an CH_3–C bond is more likely than rupture of a CH_3–Si bond, resulting in base peak $[M-CH_3]^+$, for compounds IIIb and IIId. The most important fragmentation pathway leading to the corresponding base and/or most intense ions is the loss of methylene, ethylene or propylene followed by the formation of Si–N or Si–Cl bonds.

The major ions of interest are listed in Table 1. The stoichiometric composition of most ions was confirmed by their agreement of the isotopic maximum intensities with calculated data (within 1–2%).

Experimental

Tetrahydrofuran was dried by a standard method and distilled over $LiAlH_4$ before use.

Analytical gas chromatography (GLC) was carried out on a LCHM-8MD instrument with a catharometer having a stainless steel 2.0 m × 3 mm column packed with 10% Lukopren G-1000 on 45-60 mesh Chromaton N-AW-HMDS. High boiling point compounds were analyzed on a Varian 2700 gas chromatograph equipped with a flame ionization detector. The column (1.5 m × 3 mm) was packed with 1.5% OV-101 on Chromosorb G (100-120 mesh).

Gas chromatography-mass spectrometry (GC-MS) was carried out with a Varian MAT 311 A gas chromatograph with a column similar to that described above, and

coupled to a Varian MAT 311 A mass spectrometer. The accelerating voltage was 3 kV, the emission current was 200 A, the electron energy was 70 eV. The temperature of the injector was 250 °C, and that of the separator and the ion source was 200 °C. Column temperature was programmed to increase from 100 °C to 250 °C at 4 °C/min.

Mass spectra and isotope distribution were analyzed on a Varian SS-100 MS computer.

^{1}H NMR spectra were obtained on a JEOL spectrometer operating at 90 MHz. All samples were recorded for solutions in CCl_4 or $CDCl_3$. Cyclohexane was used as internal standard.

Preparation of starting compounds

Dimethyl(chloromethyl)vinylsilane (Ia) was prepared by standard Grignard synthesis from dimethyl(chloromethyl)chlorosilane and vinyl magnesium bromide; yield 43%, b.p. 118–120 °C, n_D^{20} 1.4384. Ref. [7], b.p. 119–120 °C, n_D^{25} 1.4382.

Dimethyl(chloromethyl)allylsilane was obtained by a standard method [8]: yield 58%, b.p. 148–150 °C, n_D^{23} 1.4489. Ref. [8], b.p. 146–148 °C, n_D^{20} 1.4492.

Dimethyl(3-chloropropyl)vinylsilane (Ic) and dimethyl(3-chloropropyl)allylsilane (Id) were prepared in 30–40% yield by standard Grignard synthesis from dimethyl-(3-chloropropyl)chlorosilane and the corresponding Grignard reagent.

Ic, b.p. 58–60 °C (10 mmHg), n_D^{20} 1.4481. Found: C, 51.13; H, 9.26; Si, 17.82; Cl, 22.44. $C_7H_{15}SiCl$ calc: C, 51.66; H, 9.29; Si, 17.26; Cl, 21.79%. ^{1}H NMR δ ($CDCl_3$): 0.08 (s, 6H, Me_2Si); 0.65 (m, 2H, CH_2Si); 1.77 (m, 2H, CCH_2C); 3.48 (t, 2H, CH_2Cl); 5.53–6.35 (m, 3H, $CH{=}CH_2$).

Id, b.p. 73–76 °C (13 mm), n_D^{20} 1.4560. Found: C, 54.85; H, 9.79; Si, 15.64; Cl, 19.70. $C_8H_{17}SiCl$ calc: C, 54.36; H, 9.69; Si, 15.89; Cl, 20.06%. ^{1}H NMR δ (CCl_4): 0.025 (s, 6H, Me_2Si); 0.55 (m, 2H, CH_2Si); 1.49 (d, 2H, $CH_2C{=}$), 1.74 (m, 2H, CCH_2C); 3.41 (t, 2H, CH_2Cl); 4.77 (m, $=CH_2$); 5.61 (q.t, CH=).

Aminomercuration-demercuration of dimethyl(chloromethyl)vinylsilane (Ia)

To a stirred solution of Ia (5.00 g, 0.037 mol) and aniline (24.00 g, 0.220 mol) in THF (120 ml). was added mercury acetate (11.80 g, 0.037 mol) in small portions. Stirring was continued for 2 h at room temperature. Aqueous sodium hydroxide (0.5 *N*, 185 ml) was then added, followed by a solution of sodium borohydride (0.94 g, 0.025 mol) in 2.5 *N* aqueous sodium hydroxide (25 ml). After 15 min ether (50 ml) was added to the black reaction mixture and stirred for 30 min. After the precipitated mercury(0) had been filtered off, the THF/ether phase was separated, washed with brine and dried (Na_2SO_4). Removal of solvent in vacuo and vacuum distillation afforded 2.26 g of a fraction, b.p. 93–100 °C (1 mmHg), containing 84% of 3,3-dimethyl-1-phenyl-1-aza-3-silacyclopentane (IIIa, yield 23%) and 10% of dimethyl(phenylaminomethyl)silane (IVa, yield 3%). Compound IIIa, however, was contaminated by an unidentified impurity (M^+; m/z 193) which could not be resolved with GLC either with Lukopren G-1000 or with Carbowax 20M columns. However, the impurity can be detected easily at a 5% level in IIIa by GLC-MS. Compound IIIa isolated by GLC (Lukopren C-1000 column, 170 °C) was 95% pure. Found: C, 68.90; H, 9.21; Si, 13.71; N, 7.74. $C_{11}H_{17}SiN$ calc: C, 69.05; H, 8.96; Si, 14.67; N, 7.32%. ^{1}H NMR δ (CCl_4): 0.30 (s, 6H, Me_2Si); 1.06 (m, 2H, CH_2Si); 2.53 (s, 2H, NCH_2Si); 3.46 (m, 2H, CH_2N); 6.55–7.25 (m, 5H, C_6H_5).

The analytical sample of IVa was collected by GLC (Lukopren G-1000 column, 170 °C) and its structure was confirmed by comparison of spectral data and GLC retention time with those of an authentic sample prepared as described below.

To a solution of aniline (16.50 g, 0.177 mol) in THF (40 ml) was added Ia (8.00 g, 0.060 mol) and the mixture was stirred at room temperature for 7 d. Ether was then added to the reaction mixture and the insoluble aniline hydrochloride (1.77 g, 23%) was filtered off. After removal of the solvent the residue on distillation afforded IVa (0.73 g), b.p. 90–92 °C (2 mmHg). Found: C, 69.05; H, 8.89; Si, 14.31; N, 7.57. $C_{11}H_{17}SiN$ calc: C, 69.05; H, 8.96; Si, 14.67; N, 7.32%. ^{1}H NMR δ ($CDCl_3$): 0.21 (s, 6H, Me_2Si); 2.56 (s, 2H, CH_2N); 4.02 (s, 1H, NH); 5.65–6.26 (m, 3H, $CH{=}CH_2$); 6.72–7.19 (m, 5H, C_6H_5).

Besides, IVa was obtained by general procedure as described below. Yield 48%.

Aminomercuration-demercuration of dimethyl(chloromethyl)allylsilane (Ib)

This was carried out using the AM-DM procedure as described for Ia with the exception that the periods for mercuration and for reduction were 40 min and 22 h, respectively. 2.02 g of 3,3,5-trimethyl-1-phenyl-1-aza-3-silacyclopentane (IIIb, yield 29%) was obtained from dimethyl(chloromethyl)allylsilane (5.00 g, 0.034 mol), mercury acetate (10.07 g, 0.034 mol) and aniline (18.72 g, 0.201 mol). IIIb was isolated by distillation in vacuo, b.p. 120–124 °C (7 mmHg), n_D^{20} 1.5160. Found: C, 70.33; H, 9.60; Si, 13.15; N, 6.93. $C_{12}H_{19}SiN$ calc: C, 70.18; H, 9.33; Si, 13.67; N, 6.82%. ^{1}H NMR δ ($CDCl_3$): 0.23 (s, 3H, CH_3Si); 0.35 (s, 3H, CH_3Si); 0.74–1.26 (m, 2H, CH_2Si); 1.02 (d, 3H, CH_3), ^3J(CH_3–CH) 6.4 Hz; 2.35 (d, 2H, NCH_2Si), 2.66 (d, 2H, NCH_2Si), $^2J_{gem}$ 13.4 Hz; 4.52 (m, 1H, CH); 6.57–7.31 (m, 5H, C_6H_5). The presence of the chiral ring carbon atom causes inequivalence of chemical shifts of the methyl groups at the silicon and NCH_2 group protons.

Aminomercuration-demercuration of dimethyl(3-chloropropyl)vinylsilane (Ic)

To a solution of Ic (5.00 g, 0.031 mol) and aniline (17.22 g, 0.185 mol) in THF was added (115 ml) mercury acetate (9.80 g, 0.031 mol) with stirring. After further stirring for 7 h at room temperature, the reaction mixture was treated with 0.5 *N* NaOH (160 ml), then $NaBH_4$ (0.81 g, 0.031 mol) dissolved in 2.5 *N* NaOH (21.3 ml) and worked-up in the usual manner. The solvents were removed and residue was distilled. The distillate (3.22 g), b.p. 110–137 °C (0.06 mmHg) contained 80% of dimethyl(3-chloropropyl)(2-phenylaminoethyl)silane (IIc, 33% yield) and 10% of dimethyl(3-phenylaminopropyl)vinylsilane (IVc, 5% yield). IIc was isolated by repeated vacuum distillations, b.p. 147–160 °C (1 mmHg), n_D^{22} 1.5175. Found: C, 60.30; H, 8.88; Si, 11.55; N, 5.36; Cl, 12.91. $C_{13}H_{22}SiNCl$. Calc: C, 61.03; H, 8.67; Si, 10.97; N, 5.47; Cl, 13.86%. ^{1}H NMR δ ($CDCl_3$): 0.02 (s, 6H, Me_2Si); 0.59 (m, 2H, $SiCH_2CCCl$); 0.88 (m, 2H, $SiCH_2CN$); 1.71 (m, 2H, CCH_2C); 3.10 (m, 2H, NCH_2); 3.45 (t, 2H, CH_2Cl); 4.19 (s, 1H, NH); 6.65–7.14 (m, 5H, C_6H_5).

Compound IVc was identified by comparison of GLC retention time with that of an authentic sample obtained by the usual method, as described below.

Aminomercuration-demercuration of dimethyl(3-chloropropyl)allylsilane (Id)

To a solution of Id (5.00 g, 0.028 mol) and aniline (15.61 g, 0.168 mol) in THF (100 ml) was added mercury acetate (9.04 g, 0.028 mol) and the resulting mixture was stirred at room temperature for 2.5 h. The solution was treated with 0.5 *N*

TABLE 1

MASS SPECTRAL DATA

Ion	IIIa		IIIb		IIId		IIc		IId		IVa		IVc	
	m/z	(I_{rel}) [a]	m/z	(I_{rel})	m/z	(I_{rel})	m/z	(I_{rel})	m/z	(I_{rel})	m/z	(I_{rel})	m/z	(I_{rel})
$M^{+\cdot}$	191	(65)	205	(28)	233	(6)	255	(5)	269	(3)	191	(20)	219	(61)
$M-H$	190	(17)	–	–	–	–	–	–	–	–	–	–	218	(3)
$M-Me$	176	(9)	190	(100)	218	(100)	–	–	–	–	–	–	–	–
$M-CH_2CH_2$	163	(7)	–	–	–	–	–	–	–	–	–	–	191	(8)
$M-CH_2CHCH_3$	–	–	163	(8)	–	–	–	–	–	–	–	–	–	–
$M-CH_2CH_2CH_2$	–	–	–	–	–	–	–	–	–	–	–	–	177	(100)
$Me_2SiNHC_6H_5$	150	(4)	150	(19)	150	(2)	150	(71)	150	(8)	150	(34)	150	(6)
$M-Me-CH_2CH_2$	148	(31)	–	–	190	(3)	–	–	–	–	–	–	–	–
$M-Me-(CH_2)_3$	–	–	–	–	176	(5)	–	–	–	–	–	–	–	–
$MeHSiNC_6H_5$	136	(100)	136	(33)	136	(6)	136	(6)	136	(4)	–	–	136	(13)
$H_2SiNHC_6H_5$	122	(15)	–	–	122	(3)	122	(3)	–	–	–	–)	122	(3)
$C_2H_5NC_6H_5$	–	–	–	–	–	–	120	(4)	120	(14)	–	–	–	–
$CH_3NC_6H_5$	–	–	106	(7)	106	(4)	106	(80)	106	(9)	106	(100)	106	(8)
HNC_6H_5	92	(3)	92	(43)	–	–	–	–	–	–	–	–	92	(3)
C_6H_6	78	(20)	78	(20)	78	(9)	78	(61)	78	(13)	78	(14)	78	(11)
Me_2SiNH_2	–	–	–	–	74	(5)	–	–	74	(7)	–	–	–	–
Me_2HSi	59	(35)	–	–	59	(51)	59	(35)	59	(5)	59	(18)	59	(13)
$M-Me-CH_2CHNHC_6H_5$	–	–	–	–	57	(5)	135	(29)	135	(6)	–	–	85	(5)
Me_2SiCl	–	–	–	–	–	–	93	(100)	93	(100)	–	–	–	–
$MeClSiNHC_6H_5$	–	–	–	–	–	–	170	(6)	170	(3)	–	–	–	–

[a] Values are given as a percentage of base in each case.

NaOH (142 ml) and $NaBH_4$ (1.07 g, 0.028 mol) dissolved in 2.5 *N* NaOH (20 ml). Then, the reaction mixture was worked up as described above. The solvents were removed in vacuo and the residue was distilled. The fraction collected (2.35 g) contained dimethyl(3-chloropropyl)(2-phenylaminopropyl)silane (IId, yield 18%), 2,4,4-trimethyl-1-phenyl-1-aza-4-silacycloheptane (IIId, yield 3%) and some unidentified compounds (18%), b.p. 122–132°C (0.1 mmHg). Compound IId was purified by vacuum distillation, b.p. 150–165°C (1 mmHg). n_D^{20} 1.5177. Found: C, 60.97; H, 9.12; Si, 10.49; N, 5.27; Cl, 13.60. $C_{14}H_{24}SiNCl$ calc: C, 62.30; H, 8.96; Si, 10.41; N, 5.19; Cl, 13.14%. ^1H NMR δ ($CDCl_3$): 0.04 (s, 6H, Me_2Si); 0.63 (m, 2H, $SiCH_2$); 0.91 (m, 2H, $SiCH_2CH$); 1.23 (d, 3H, CH_3); $^3J(CH_3–CH)$ 7.0 Hz; 1.74 (m, 2H, CCH_2C); 3.47 (t, 2H, CH_2Cl); 3.57 (m, 1H, CH); 4.26 (s, 1H, NH); 6.66–7.17 (m, 5H, C_6H_5).

Compound IIId was assigned by mass spectral data (Table 1).

General method for the synthesis of dimethyl(phenylaminoalkyl)alkenylsilanes (IVa–IVd)

A mixture of dimethyl(chloroalkyl)alkenylsilane and aniline (1 : 6) was heated for 7 h at 100°C in a sealed ampoule. The precipitated aniline hydrochloride was filtered off and washed with dry ether. The residue, after removal of the solvent and the excess of aniline under vacuum, afforded the desired dimethyl(phenylaminoalkyl)alkenylsilane in 30–40% yield.

Dimethyl(phenylaminomethyl)allylsilane. (IVb), b.p. 97–100°C (1 mm), n_D^{20} 1.5160. Found: C, 70.46; H, 9.33; Si, 13.74; N, 6.69%. $C_{12}H_{19}SiN$ calc: C, 70.18; H, 9.33; Si, 13.67; N, 6.82%. ^1H NMR δ ($CDCl_3$): 0.11 (s, 6H, Me_2Si); 1.63 (d, 2H, $CH_2C=$); 2.52 (s, 2H, $SiCH_2N$); 3.46 (s, 1H, NH); 4.91 (m, 2H, $CH_2=$); 5.76 (q.t, 1H, CH =); 6.67–7.16 (m, 5H, C_6H_5).

Dimethyl(3-phenylaminopropyl)vinylsilane. (IVc), b.p. 120°C (1 mm), n_D^{25} 1.5175. Found: C, 71.51; H, 9.83; Si, 12.71; N, 6.25. $C_{13}H_{21}SiN$ calc.: C, 71.17, H, 9.65; Si, 12.80; N, 6.38%. ^1H NMR δ ($CDCl_3$): 0.02 (s, 6H, Me_2Si); 0.53 (m, 2H, CH_2Si); 1.51 (m, 2H, CCH_2C); 2.99 (t, 2H, NCH_2); 3.68 (s, 1H, NH); 5.50–6.40 (m, $CH=CH_2$); 6.53–7.08 (m, C_6H_5).

Dimethyl(3-phenylaminopropyl)allylsilane. (IVd), b.p. 132–137°C (1 mm), n_D^{25} 1.5175. Found: C, 71.34; H, 9.77; Si, 12.05; N, 5.67. $C_{14}H_{23}SiN$ calc: C, 72.04; H, 9.93; Si, 12.03; N, 6.00%. ^1H NMR δ ($CDCl_3$): 0.12 (s, 6H, Me_2Si); 0.63 (m, 2H, CH_2Si); 1.57 (m, 2H, CCH_2C); 3.12 (t, 2H, NCH_2); 3.64 (s, 1H, NH); 4.89 (m, 2H, $=CH_2$); 5.83 (m, 1H, CH); 6.72–7.20 (m, 5H, C_6H_5).

3,3-Dimethyl-1-phenyl-1-aza-3-silacyclopentane methiodide (Va)

A solution of 3,3-dimethyl-1-phenyl-1-aza-3-silacyclopentane (0.01 g, 0.0524 mmol) and CH_3I (0.05 g, 0.352 mmol) in ether (1 ml) was allowed to stand for 2 d at 5°C. After removal of the solvent and unchanged methyl iodide, the yellow oil obtained was dissolved in ethanol. To this solution was added ether and the precipitate was recrystallized from ethanol/ether (1 : 3) to give (Va), m.p. 122°C. Found: C, 43.08; H, 6.24; Si, 7.68; N, 4.20; I, 38.23. $C_{12}H_{20}SiNI$ calc: C, 43.25; H, 6.01; Si, 8.43; N, 4.21; I, 38.03%. ^1H NMR δ (DMSO-d_6): 0.14, 0.44 (s, 3H, MeSi); 1.22 (q.t, 2H, $SiCH_2C$); 3.44 (s, 3H, NCH_3); 4.29 (t, 2H, NCH_2); 7.62–7.98 (m, 5H, C_6H_5).

3,3,5-Trimethyl-1-phenyl-1-aza-3-silacyclopentane methiodide (Vb)

Vb was obtained similarly, from IIIb, m.p. 133–134°C. Found: C, 44.75; H, 6.21; Si, 8.03; N, 4.39; I, 36.74. $C_{13}H_{22}SiNI$ calc: C, 44.96; H, 6.38; Si, 8.09; N, 4.04; I, 36.73%. ^1H NMR δ (DMSO-d_6): 0.43, 0.49, 0.52 (s, MeSi); 0.92 (d), 1.10 (d, CH_3); 1.39–1.89 (m, $SiCH_2C$): 2.80 (d), 3.18 (d, $SiCH_2N$); 3.37 (s), 3.49 (s, NCH_3); 4.18, 5.01 (m, NCH); 7.61 (m), 7.95 (m, C_6H_5). The presence of the chiral ring carbon and nitrogen atoms causes inequivalence of chemical shifts of the Me_2Si, $SiCH_2C$ and $SiCH_2N$ group protons.

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