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SHORT COMMUNICATION

Reactivity of heterocyclic α-aminomethylsilanes with alcohols

Krzysztof Pypowski[1]*, Mariusz Mojzych[1]

[1] *Faculty of Natural Science, Siedlce University of Natural Sciences and Humanities, 54 3 Maja St., Siedlce 08-110, Poland; e-mail: pypowski@uph.edu.pl*

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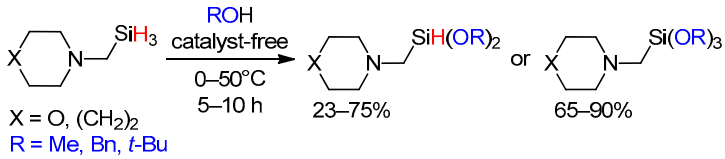


Alkoxylation of *N*-substituted heterocyclic aminomethylsilyl moieties was studied using primary and tertiary alcohols. The reaction of 4-(silylmethyl)morpholine and 1-(silylmethyl)azepane under catalyst- and solvent-free conditions leads to the formation of dialkoxy- and trialkoxyaminomethylsilyl derivatives. The methanolysis of 4-(silylmethyl)morpholine resulted in trimethoxyaminomethylsilane formation as the main product and two byproducts, i.e., tetramethoxysilane and *N*-methylmorpholine.

Keywords: aminomethylalkoxysilane, aminomethylsilane, dehydrocondensation, solvent-free.

The chemistry of compounds with the N–CH_2–Si framework is a rapidly growing area of organosilicon chemistry[1] and it is also the subject of many publications concerning α-silicon effect[2] and its use in the design of new and more reactive α-aminomethylsilanes.[3,4] Their specific chemical nature is the result of Si and N atoms connection to the same methylene group.[2a,5] An amino group present in α-position increases the reactivity of Si–O bonds, particularly in reactions with nucleophiles.[6] The interactions of this type of organosilicon compounds are called α-effect.[7] α-Aminomethylsilanes are used in the industrial production of polymers, cosmetics,[8,9] and some of the derivatives found their application in the synthesis of new compounds with anticancer, neurotropic, or antibacterial activity.[10,11] These compounds are convenient substrates for the synthesis of hypercoordinated organosilicon derivatives such as five-coordinated silicon compounds: silatranes[12] and zwitterionic spirocyclic λ^5 Si-silicates with an SiX_4C (X = O or S) skeleton.[13]

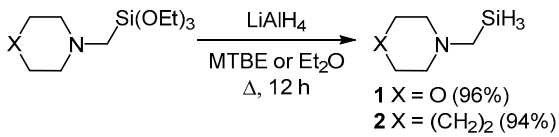
The most convenient method for the synthesis of trialkoxy-α-aminoalkylsilane derivatives is based on the catalyzed or noncatalyzed reaction of amine with haloalkyltrialkoxysilanes (R_3SiCH_2X), in which R is alkoxy group and X is Br or Cl atom.[14] Another group of silane derivatives are aminomethylhydrosilanes obtained by reduction of trihalo- or trialkoxysilane derivatives.[15]

The reaction of hydrosilanes with alcohols usually occurs in the presence of alkaline[16] or acid catalysts,[17] as well as in the presence of numerous metal salts.[18] Moreover, the use of transition metal complexes,[19] simple inorganic compounds,[20] and organocatalysts[1d,20b] in the reaction of primary, secondary, and tertiary silanes with aliphatic and aromatic alcohols is the subject of many present studies. Such catalytic processes are called dehydrogenative coupling and can be selectively realized in the homo- and heterogeneous media.[21]

The purpose of this paper is to investigate the ability of aminoalkylsilanes, with general formula $R_2NCH_2SiH_3$, to undergo dehydrogenative coupling with alcohols in catalyst- and solvent-free conditions. It is known that the reactivity of aminoalkylsilanes $Me_2N(CH_2)_nSiRH_2$ with alcohols decreases with the increase of quantity of methylene groups between N and Si atoms.[17] To date, only a few examples of hydrosilane alcoholysis without the use of catalysts and solvents were described in the literature.[17]

For the reactivity study of α-aminomethylsilanes with primary and tertiary alcohols, two silanes **1** and **2** with aminoheterocyclic moiety were selected as model substrates. Morpholin-4-ylmethylsilane (**1**) and azepan-4-ylmethylsilane (**2**) were obtained in the reduction of triethoxysilanes with $LiAlH_4$ in methyl *t*-butyl ether (MTBE) or Et_2O furnishing silanes **1** and **2** in high yields of 96% and 94%, respectively (Scheme 1).[22,23] The structures of both obtained aminomethylsilanes **1** and **2** were confirmed by ^1H, ^{13}C NMR and mass spectra.

Scheme 1



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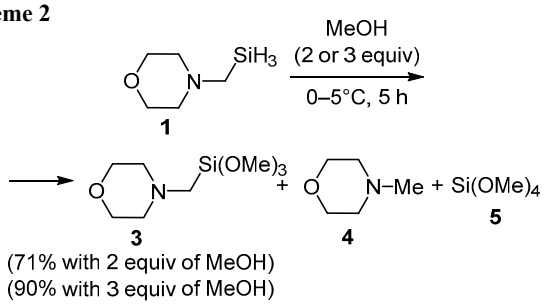
First, the reaction of the obtained morpholin-4-ylmethylsilane (**1**) with an excess of anhydrous MeOH was investigated at 0–5°C within 5 h. The progress of the reaction was monitored by spectroscopic methods and was indicated by the disappearance of the signal of SiH_3 group protons at 3.58 ppm. Analysis of the reaction mixture by GC/MS confirmed the formation of 4-[(trimethoxysilyl)-methyl]morpholine (**3**), *N*-methylmorpholine (**4**), and tetramethoxysilane (**5**) during the process (Scheme 2). Thus, silane **3** was the major product obtained in good yield of 71% (2 equiv of MeOH) or 90% (3 equiv of MeOH), while *N*-methylmorpholine (**4**) and tetramethoxysilane (**5**) were isolated in equal molar ratio with 14.5 and 5.5% yields, respectively.

Scheme 2



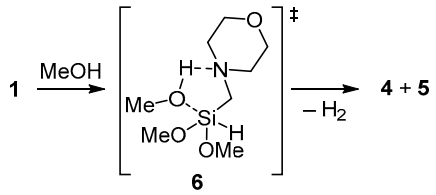
The formation of *N*-methylmorpholine (**4**) and $(MeO)_4Si$ (**5**) is explained by the cleavage of the Si–C bond in α-amino-methylmethoxysilane which is commonly observed in silicon chemistry.[24] It should be emphasized that the type of substituent effects the induction of a partial positive charge on the silicon atom,[25] and the heterolytic cleavage of the Si–C bond may occur catalyzed by both Lewis acids[26] or Lewis bases[27] and in the presence of *n*-BuLi that leads to the rearrangement of α-amino functional silanes to alkylaminosilanes (aza-Brook rearrangement).[28]

However, there is no data on the cleavage of the Si–C bond during alcoholysis of hydrosilanes under mild reaction conditions. Only the case described by Lazareva et al.[29] presents the Si–C bond cleavage under autocatalytic transesterification of *N*,*N*-bis[ethoxy(methyl)silylmethyl]-amines with phenol.

Alcoholysis of α-aminomethylsilanes with autocatalytic capacity is well documented in the literature.[17] These reactions are usually carried out in electron-donating solvent such as *N*,*N*-dimethylacetamide which probably is involved in the intermediate stabilization of dehydro-condensation products (solvent effect).[17] We assume that due to the hydrogen bond formation between alcohol and amine moiety[30] and the significant basicity of the nitrogen atom in the NCH_2–Si moiety[25,31] the interaction of morpholin-4-ylmethylsilane (**1**) with MeOH occurs through a cyclic five-coordinated silane transition state **6** (Scheme 3), and further the Si–C bond breaks in the presence of MeOH leading to the formation of *N*-methylmorpholine (**4**) and $(MeO)_4Si$ (**5**) (Scheme 3).

The control of the reaction progress by ^{1}H NMR revealed the appearance of singlets at 2.25 ppm, which is associated with N–CH_3 moiety, and at 3.56 ppm which is typical for $(MeO)_4Si$ (**5**). This excluded the possible

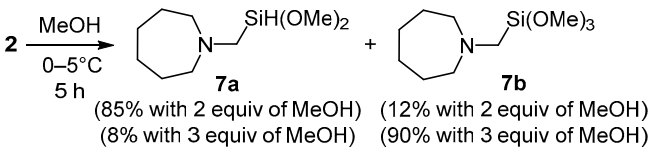
Scheme 3



cleavage of the Si–C bond in the formed silane **3**, especially in the case of MeOH deficiency. The NCH_2–Si proton signal at 2.01 ppm associated with intermediate **6** was also observed. The broad Si–H singlet of intermediate **6** is labile and was observed in the range from 3.49 to 3.60 ppm. To explain this behavior, it should be added that the formation of the Si–O bond is thermodynamically more favorable than the Si–C bond, and Si–O bond has dissociation energy 530 kJ/mol comparing to 360 kJ/mol of Si–C bond.[15]

Similarly, azepan-1-ylmethylsilane (**2**) reacted with 2 equiv of MeOH at 0°C. Dimethoxy(azepan-1-ylmethyl)silane (**7a**) and trimethoxy(azepan-1-ylmethyl)silane (**7b**) were isolated in the yield of 85% and 12%, respectively. Meanwhile, the reaction of silane **2** with 3 equiv of MeOH at 5°C resulted in the formation of product **7b** in 90% yield (Scheme 4). The control of the reaction progress by ^{1}H NMR did not reveal the presence of Si–C bond cleavage products.

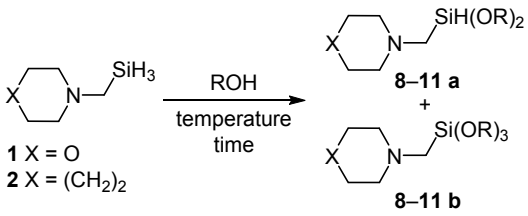
Scheme 4



In the next step, silanes **1** and **2** were submitted to the reaction with sterically hindered *t*-BuOH and BnOH. The appropriate dialkoxysilanes and trialkoxysilanes were formed. Optimal reaction conditions and the amount of formed products are shown in Table 1. However, it should be clarified that the amount of products has been calculated on the basis of ^{1}H NMR spectrum.

The reaction of morpholin-4-ylmethylsilane (**1**) with 2 equiv of *t*-BuOH was carried out at 35°C for 5 h. ^{1}H NMR spectroscopic analysis revealed the presence of di-*tert*-butoxy(morpholin-4-ylmethyl)silane (**8a**), tri-*tert*-butoxy(morpholin-4-ylmethyl)silane (**8b**), and a large amount of unreacted starting material **1** (52% of compound **1** was recovered, Table 1, entry 1). Under the same reaction conditions, silane **2** underwent dehydrocondensation, and tri-*tert*-butoxy(azepan-1-ylmethyl)silane (**10b**) was obtained as the main product (Table 1, entry 5). However, increasing the amount of *t*-BuOH to 3 equiv and the temperature to 50°C, trialkoxy-substituted silanes **8b** and **10b** were obtained in good yields (Table 1, entries 2, 6). Silane **1** in the reaction with BnOH (2 equiv) formed dibenzyloxy-(morpholin-4-ylmethyl)silane (**9a**) in 30% yield (Table 1, entry 3). Silane **2**, in similar reaction conditions formed disubstituted derivative **11a** as the main product of this transformation (Table 1, entry 7). However, the use of threefold excess of BnOH and prolonged reaction time (10 h)

Table 1. Reaction conditions and yields of products **8**–**11**



Entry	Silane	R	ROH, equiv	Temperature, °C	Time, h	Product (yield,* %)	
1	**1**	*t*-Bu	2	35	5	**8a** (46)**	**8b** (2)**
2	**1**	*t*-Bu	3	50	5	**8a** (6)	**8b** (90)
3	**1**	Bn	2	50	5	**9a** (30)	**9b** (62)
4	**1**	Bn	3	50	10	**9a** (21)	**9b** (70)
5	**2**	*t*-Bu	2	35	5	**10a** (23)	**10b** (60)
6	**2**	*t*-Bu	3	50	5	**10a** (8)	**10b** (78)
7	**2**	Bn	2	50	5	**11a** (75)	**11b** (10)
8	**2**	Bn	3	50	10	**11a** (20)	**11b** (65)

* NMR yield using TMS as an internal standard.
** Conversion of compound **1** was 48%.

allowed to obtain trisubstituted products **9b** (Table 1, entry 4) and **11b** (Table 1, entry 8) in good yields.

It was also observed that carrying out the reaction of silanes **1** or **2** with BnOH at temperature above 50°C led to a mixture of mainly Si–C bond cleavage products, i.e., tetrabenzyloxysilane and compound **4** or 1-methylazepane, respectively.

Thus, the optimal reaction conditions for the synthesis of alkoxy derivatives of heterocyclic α-aminomethylsilanes without the use of catalyst and solvent have been developed. It was shown that due to α-effect morpholin-4-ylmethylsilane possesses significantly higher reactivity in the dehydrocondensation reaction with MeOH than azepan-1-ylmethylsilane. The cleavage of the Si–C bond was observed although the process was carried out under mild reaction conditions and led to the formation of *N*-methylmorpholine and tetramethoxysilane. It should be noted that the steric effect of the *t*-BuOH suppresses the formation of trialkoxy derivative of morpholin-4-ylmethylsilane at 35°C although at the higher temperature (50°C), tri-*tert*-butoxy(morpholin-4-ylmethyl)silane was isolated in very good yield of 90%. The obtained result proves that it is possible to synthesize dibenzyloxy derivative of 1-(silylmethyl)azepane with a satisfactory yield of 75%.

Experimental

^{1}H and ^{13}C NMR spectra were recorded on a Bruker DRX-300 spectrometer (300 and 75 MHz, respectively) in $CDCl_3$ solutions using TMS as internal standard. Assignment of the ^{13}C NMR data was supported by DEPT 135 experiments. Low-resolution mass spectra were recorded on a Shimadzu GC/MS-QP5050A mass spectrometer (EI, 70eV) with a Shimadzu GC-17A gas chromatograph equipped with a Phenomenex DB 5 ms column (30 m × 0.25 mm i. d. × 0.25 μm). High-resolution mass spectra were recorded on an AMD 604 S mass spectrometer with electrospray ionization. All reactions were carried out under dry Ar atmosphere.

Methyl *t*-butyl ether (MTBE) and alcohols were dried and purified according to standard procedures and stored under N_2.

4-(Silylmethyl)morpholine (1) was prepared according to the literature procedure.[22]

1-(Silylmethyl)azepane (2). A solution of triethoxy(azepan-1-ylmethyl)silane (4.41 g, 16 mmol) in MTBE (20 ml) was added to the suspension of $LiAlH_4$ (1.22 g, 32 mmol) in MTBE (100 ml) at 0°C within 1 h under Ar atmosphere. The resulting mixture was stirred overnight at reflux. The solvent was removed under reduced pressure, and the residue was distilled under reduced pressure. Yield 4.31 g (94%), colorless liquid, bp 58°C (16 mmHg). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.59 (8H, br. s, CH_2); 2.38 (2H, q, *J* = 3.7, NCH_2Si); 2.62–2.68 (4H, m, $C\underline{H}_2NCH_2Si$); 3.55 (3H, t, *J* = 3.7, $^1J(^1H–^{29}Si)$ = 196.0, SiH_3). ^{13}C NMR spectrum, δ, ppm: 26.7; 27.6 (CH_2); 40.8 ($N\underline{C}H_2Si$); 58.6 ($\underline{C}H_2NCH_2Si$). Mass spectrum, *m*/*z* (I_{rel}, %): 143 $[M]^+$ (3), 127 (60), 112 (45), 98 (21), 84 (33), 71 (22), 56 (41), 49 (22), 42 (100). Found, *m*/*z*: 144.1213 $[M+H]^+$. $C_7H_{18}NSi$. Calculated, *m*/*z*: 144.1210.

Synthesis of compounds 3, **7**–**10** (General method). Silane **1** (0.5 g, 3.81 mmol) or **2** (0.55 g, 3.84 mmol) (1 equiv) was placed into a pressure tube with a safety valve filled with argon. Anhydrous alcohol (2 or 3 equiv) was added portionwise over 30 min. The reaction was carried out for 5–10 h at 0–50°C (for the conditions, see Schemes 2 and 3 and Table 1). After completion of the reaction, the residual alcohol was distilled off and the remaining mixture was analyzed by ^{1}H NMR and GC/MS.

4-[(Trimethoxysilyl)methyl]morpholine (3). Yields 0.6 g (71%) with 2 equiv of MeOH and 0.76 g (90%) with 3 equiv of MeOH, colorless liquid. Spectral data were in a good agreement with the reported.[13b] Mass spectrum, *m*/*z* (I_{rel}, %): 221 $[M]^+$ (5), 206 (1), 189 (3), 190 (9), 176 (3), 164 (24), 162 (45), 150 (12), 137 (5), 121 (32), 100 (100), 91 (28). Found, *m*/*z*: 222.1161 $[M+H]^+$. $C_8H_{20}NO_4Si$. Calculated, *m*/*z*: 222.1161.

1-[(Dimethoxysilyl)methyl]azepane (7a). Yields 0.66 g (85%) with 2 equiv of MeOH and 0.06 g (8%) with 3 equiv of MeOH, colorless liquid. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.48–1.56 (8H, m, CH_2); 2.35 (2H, d, *J* = 3.7, NCH_2Si); 2.58–2.69 (4H, m, $C\underline{H}_2NCH_2Si$); 3.38 (1H, t, *J* = 3.7, SiH); 3.46 (6H, s, OCH_3). ^{13}C NMR spectrum, δ, ppm: 26.8 (CH_2); 27.0 (CH_2); 44.3 (NCH_2Si); 50.7 (OCH_3); 57.2 ($\underline{C}H_2NCH_2Si$). Mass spectrum, *m*/*z* (I_{rel}, %): 203 $[M]^+$ (2), 190 (8), 176 (5), 164 (11), 150 (2), 148 (4), 134 (3), 121 (8), 112 (100), 91 (11), 84 (12), 75 (4), 70 (3), 61 (7). Found, *m*/*z*: 204.1426 $[M+H]^+$. $C_9H_{22}NO_2Si$. Calculated, *m*/*z*: 204.1420.

1-[(Trimethoxysilyl)methyl]azepane (7b). Yields 0.11 g (12%) with 2 equiv of MeOH and 0.81 g (90%) with 3 equiv of MeOH, colorless liquid. ^{1}H NMR spectrum, δ, ppm: 1.48–1.56 (8H, m, CH_2); 2.17 (2H, s, NCH_2Si); 2.58–2.69 (4H, m, $C\underline{H}_2NCH_2Si$); 3.48 (9H, s, CH_3). ^{13}C NMR spectrum, δ, ppm: 26.8; 27.0 (CH_2); 47.6 (NCH_2Si); 50.5 (CH_3); 58.0 ($\underline{C}H_2NCH_2Si$). Mass spectrum, *m*/*z* (I_{rel}, %): 233 $[M]^+$ (6), 218 (2), 204 (5), 190 (8), 176 (5), 164 (10), 148 (4), 134 (3), 121 (7), 112 (100), 84 (13), 59 (9). Found, *m*/*z*: 234.1529 $[M+H]^+$. $C_{10}H_{24}NO_3Si$. Calculated, *m*/*z*: 234.1525.

4-[(Di-*tert*-butoxysilyl)methyl]morpholine (8a). Yields 0.48 g (46%) with 2 equiv of *t*-BuOH and 0.06 g (6%) with 3 equiv of *t*-BuOH, colorless liquid. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.28 (18H, s, CH_3); 1.89 (2H, d, *J* = 3.6, NCH_2Si); 2.42–2.48 (4H, m, CH_2 morpholine); 3.57 (1H, t, *J* = 3.6, SiH); 3.63–3.69 (4H, m, CH_2 morpholine). ^{13}C NMR spectrum, δ, ppm: 31.1 (CH_3); 50.1 (NCH_2Si); 56.9 ($N\underline{C}H_2CH_2O$); 67.2 ($NCH_2\underline{C}H_2O$); 72.6 (C). Mass spectrum, *m*/*z* (I_{rel}, %): 274 $[M–H]^+$ (6), 216 (21), 176 (11), 133 (18), 100 (68), 84 (22), 77 (99), 75 (14), 59 (100). Found, *m*/*z*: 298.1823 $[M+Na]^+$. $C_{13}H_{29}NNaO_3Si$. Calculated, *m*/*z*: 298.1814.

4-[(Tri-*tert*-butoxysilyl)methyl]morpholine (8b). Yields 0.03 g (2%) with 2 equiv of *t*-BuOH and 1.19 g (90%) with 3 equiv of *t*-BuOH, colorless liquid. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.31 (27H, s, CH_3); 1.84 (2H, s, NCH_2Si); 2.43–2.48 (4H, m, CH_2 morpholine); 3.67–3.72 (4H, m, CH_2 morpholine). ^{13}C NMR spectrum, δ, ppm: 31.5 (CH_3); 49.2 (NCH_2Si); 57.0 ($N\underline{C}H_2CH_2O$); 67.1 ($NCH_2\underline{C}H_2O$); 72.8 (C). Mass spectrum, *m*/*z* (I_{rel}, %): 347 $[M]^+$ (9), 332 (10), 290 (17), 274 (27), 234 (3), 218 (6), 178 (15), 162 (20), 148 (9), 135 (60), 121 (5), 100 (100), 86 (11), 79 (52), 57 (93). Found, *m*/*z*: 348.2576 $[M+H]^+$. $C_{17}H_{38}NO_4Si$. Calculated, *m*/*z*: 348.2576.

4-{[Bis(benzyloxy)silyl]methyl}morpholine (9a). Yields 0.39 g (30%) with 2 equiv of BnOH and 0.27 g (21%) with 3 equiv of BnOH, colorless liquid. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 2.01 (2H, d, *J* = 3.6, NCH_2Si); 2.35–2.41 (4H, m, CH_2 morpholine); 3.50–3.58 (5H, m, CH_2 morpholine, SiH); 4.67 (4H, s, OCH_2Ph); 7.24–7.36 (10H, m, H Ph). ^{13}C NMR spectrum, δ, ppm: 46.7 (NCH_2Si); 54.7 ($N\underline{C}H_2CH_2O$); 64.2 (OCH_2Ph); 66.0 ($NCH_2\underline{C}H_2O$); 126.8 (C-2,6 Ph); 127.3; 128.3 (C-3–5 Ph); 140.8 (C-1 Ph). Mass spectrum, *m*/*z* (I_{rel}, %): 343 $[M]^+$ (1), 237 (3), 207 (1), 193 (3), 173 (1), 149 (56), 143 (81), 133 (6), 121 (63), 115 (85), 105 (5), 99 (25), 91 (25), 75 (100), 59 (21). Found, *m*/*z*: 344.1686 $[M+H]^+$. $C_{19}H_{26}NO_3Si$. Calculated, *m*/*z*: 344.1682.

4-{[Tris(benzyloxy)silyl]methyl}morpholine (9b). Yields 1.06 g (62%) with 2 equiv of BnOH and 1.2 g (70%) with 3 equiv of BnOH, colorless liquid. ^{1}H NMR spectrum, δ, ppm: 2.05 (2H, s, NCH_2Si); 2.38–2.45 (4H, m, CH_2 morpholine); 3.56–3.64 (4H, m, CH_2 morpholine); 4.84 (6H, s, OCH_2Ph); 7.24–7.36 (15H, m, H Ph). ^{13}C NMR spectrum, δ, ppm: 49.4 (NCH_2Si); 56.7 ($N\underline{C}H_2CH_2O$); 64.7 (OCH_2Ph); 66.6 ($NCH_2\underline{C}H_2O$); 126.8 (C-2,6 Ph); 127.3; 128.3 (C-3–5 Ph); 140.8 (C-1 Ph). Mass spectrum, *m*/*z* (I_{rel}, %): 341 $[M–OCH_2Ph]^+$ (1), 234 (1), 219 (1), 205 (1), 189 (9), 179 (1), 161 (1), 149 (25), 143 (100), 133 (7), 121 (28), 115 (54), 103 (56), 91 (11), 75 (92), 59 (47). Found, *m*/*z*: 450.2108 $[M+H]^+$. $C_{26}H_{32}NO_4Si$. Calculated, *m*/*z*: 450.2100.

1-[(Di-*tert*-butoxysilyl)methyl]azepane (10a). Yields 0.254 g (23%) with 2 equiv of *t*-BuOH and 0.09 g (8%) with 3 equiv of *t*-BuOH, colorless liquid. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.28 (18H, s, CH_3); 1.51–1.70 (8H, m, CH_2 azepane); 2.03 (2H, d, *J* = 3.8, NCH_2Si); 2.50–2.61 (4H, m, CH_2 azepane); 3.42 (1H, t, *J* = 3.8, SiH). ^{13}C NMR spectrum, δ, ppm: 26.7 (CH_2); 27.8 (CH_2); 31.2 (CH_3); 47.3 (NCH_2Si); 58.7 ($\underline{C}H_2NCH_2Si$); 69.2 (C). Mass spectrum, *m*/*z* (I_{rel}, %): 287 $[M]^+$ (1), 272 (7), 260 (3), 248 (14), 204 (8), 175 (2), 112 (100), 93 (11), 58 (35). Found, *m*/*z*: 310.2175 $[M+Na]^+$. $C_{15}H_{33}NNaO_2Si$. Calculated, *m*/*z*: 310.2178.

1-[(Tri-*tert*-butoxysilyl)methyl]azepane (10b). Yields 0.83 g (60%) with 2 equiv of *t*-BuOH and 1.08 g (78%) with 3 equiv of *t*-BuOH, colorless liquid. ^{1}H NMR spectrum, δ, ppm: 1.32 (27H, s, CH_3); 1.51–1.70 (8H, m, CH_2 azepane); 1.96 (2H, s, NCH_2Si); 2.62–2.72 (4H, m, CH_2 azepane). ^{13}C NMR spectrum, δ, ppm: 26.9 (CH_2); 27.9 (CH_2); 31.6 (CH_3); 47.3 (NCH_2Si); 58.7 ($\underline{C}H_2NCH_2Si$); 69.2 (C). Mass spectrum, *m*/*z* (I_{rel}, %): 359 $[M]^+$ (4), 344 (8), 330 (1), 316 (5), 302 (3), 286 (17), 276 (1), 260 (2), 246 (2), 234 (3), 204 (2), 190 (6), 178 (2), 164 (2), 135 (10), 122 (3), 112 (100), 98 (4), 58 (20). Found, *m*/*z*: 360.2939 $[M+H]^+$. $C_{19}H_{42}NO_3Si$. Calculated, *m*/*z*: 360.2934.

1-{[Bis(benzyloxy)silyl]methyl}azepane (11a). Yields 1.02 g (75%) with 2 equiv of BnOH and 0.27 g (20%) with 3 equiv of BnOH, colorless liquid. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.46–1.70 (8H, m, CH_2 azepane); 2.31 (2H, d, *J* = 3.8, NCH_2Si); 2.51–2.56 (4H, m, CH_2 azepane); 3.41 (1H, t, *J* = 3.8, SiH); 4.70 (4H, s, OCH_2Ph); 7.26–7.41 (10H, m, H Ph). ^{13}C NMR spectrum, δ, ppm: 26.9 (CH_2); 27.1 (CH_2); 45.4 (NCH_2Si); 57.2 ($N\underline{C}H_2CH_2O$); 63.5 (OCH_2Ph); 126.5 (C-2,6 Ph); 127.1; 128.5 (C-3–5 Ph); 139.1 (C-1 Ph). Mass spectrum, *m*/*z* (I_{rel}, %): 355 $[M]^+$ (1), 339 (5), 324 (2), 310 (6), 296 (9), 282 (5), 270 (12), 252 (2), 238 (3), 227 (27), 213 (2), 197 (10), 165 (4), 151 (4), 137 (8), 121 (4), 112 (100), 107 (11), 91 (5), 77 (10). Found, *m*/*z*: 378.1868 $[M+Na]^+$. $C_{21}H_{29}NNaO_2Si$. Calculated, *m*/*z*: 378.1865.

1-{[Tris(benzyloxy)silyl]methyl}azepane (11b). Yields 0.18 g (10%) with 2 equiv of BnOH and 1.15 g (65%) with 3 equiv of BnOH, colorless liquid. ^{1}H NMR spectrum, δ, ppm: 1.83–2.04 (8H, m, CH_2 azepane); 2.17 (2H, s, NCH_2Si); 2.51–2.56 (4H, m, CH_2 azepane); 4.70 (6H, s, OCH_2Ph); 7.24–7.40 (15H, m, H Ph). ^{13}C NMR spectrum, δ, ppm: 26.8 (CH_2); 26.9 (CH_2); 47.3 (NCH_2Si); 58.5 ($N\underline{C}H_2CH_2O$); 65.7 (OCH_2Ph); 126.4 (C-2,6 Ph); 127.2; 128.4 (C-3–5 Ph); 138.6 (C-1 Ph). Mass spectrum, *m*/*z* (I_{rel}, %): 461 $[M]^+$ (2), 448 (5), 434 (3), 420 (12), 404 (2), 390 (3), 378 (2), 364 (8), 348 (3), 334 (2), 308 (4), 292 (3), 267 (4), 252 (15), 234 (5), 211 (20), 194 (11), 137 (3), 125 (3), 112 (100), 107 (2), 91 (10), 77 (2). Found, *m*/*z*: 462.2470 $[M+H]^+$. $C_{28}H_{36}NO_3Si$. Calculated, *m*/*z*: 462.2464.

References

1. (a) Lebedev, A. V.; Minas'yan, R. M.; Abramkin, A. M.; Sheludyakov, V. D.; Kuzmina, N. E.; Lebedeva, A. B.; Surikov, G. E.; Rybakov, V. B. *Russ. J. Gen. Chem.* **2016**, *86*, 1859. [*Zh. Obshch. Khim.* **2016**, *86*, 1321.] (b) Picard, J.-P. *Can. J. Chem.* **2000**, *78*, 1363. (c) Picard, J.-P. In *Advances in Organometallic Chemistry*; Academic Press, 2004, Vol. 52, p. 175. (d) Woski, M.; Berger, R. J. F.; Mitzel, N. W. *Dalton Trans.* **2008**, *41*, 5652. (e) Ohmura, T.; Nishiura, H.; Suginome, M. *Organometallics* **2017**, *36*, 4298.
2. (a) Feshin, V. P.; Romanenko, L. S.; Voronkov, M. G. *Russ. Chem. Rev.* **1981**, *50*, 248 [*Usp. Khim.* **1981**, *50*, 460.] (b) Waerder, B.; Steinhauer, S.; Reuter, C. G.; Bader, J.; Neumann, B.; Stammler, H. G.; Vishnevskiy, Y. V.; Hoge, B.; Mitzel, N. W. *Dalton Trans.* **2015**, *44*, 13347.

3. Mitzel, N. W.; Kiener, C.; Rankin, D. W. H. *Organometallics* **1999**, *18*, 3437.
4. Berkefeld, A.; Guerra, C. F.; Bertermann, R.; Troegel, D.; Daiß, J. O.; Stohrer, J.; Bickelhaupt, F. M.; Tacke, R. *Organometallics* **2014**, *33*, 2721.
5. Lukevits, E.; Sleiksha, I.; Liepin'sh, E.; Shat-ts, V. D.; Zitsmane, I.; Purvinya, A. *Chem. Heterocycl. Compd.* **1991**, *27*, 1319. [*Khim. Geterotsikl. Soedin.* **1991**, *27*, 1644.]
6. (a) Pfeiffer, J. *Alpha Silanes – New Building Blocks for High Performance Coatings*; Wacker Chemie: München, 2006. (b) Schindler, W. *Alpha-Silane-Terminated Polymers as Novel Binders for Fast Curing Elastic Adhesives*; Wacker Chemie: München, 2005. (c) Xu, H.; Gao, Y.; Liu, Z.; Bei, Y. *Materials* **2018**, *11*, 1526.
7. (a) Mitzel, N. W.; Vojinović, K.; Foerster, T.; Robertson, H. E.; Borisenko, K. B.; Rankin, D. W. H. *Chem.–Eur. J.* **2005**, *11*, 5114. (b) Whitmore, F. C.; Sommer, L. H. *J. Am. Chem. Soc.* **1946**, *68*, 481.
8. Yin, Y.; Zhang, Y.; Chi, Z.; Xu, J. *Eur. Polym. J.* **2008**, *44*, 2284.
9. Schulze zur Wiesche, E., US Patent 2014/0271750 A1.
10. (a) Brook, M. A. *Silicon in Organic*, *Organometallic*, *and Polymer Chemistry*; J. Wiley and Sons: New York, 2000, p. 680. (b) Fuchs, P. L. *Reagents for Silicon-Mediated Organic Synthesis*; Wiley-Blackwell, 2013, p. 816.
11. (a) Lukevits, E.; Luse, V.; Zitsmane, I.; Liepin'sh, E.; Trushule, M.; Germane, S.; Augustane, I.; Verovskii, V. N.; Prodanchuk, N. G.; Deineka, S. E.; Nivalov, V. N. *Chem. Heterocycl. Compd.* **1991**, *27*, 1328. [*Khim. Geterotsikl. Soedin.* **1991**, 1653.] (b) Lukevits, E.; Dremova, V. P.; Simchenko, L. I.; Voronkov, M. G. *Pharm. Chem. J.* **1974**, *8*, 611. [*Khim.-Farm. Zh.* **1974**, *8*(10), 29.]
12. (a) Voronkov, M. G.; D'yakov, V. M. *Silatrany* (*Silatranes*) [in Russian]; Nauka: Novosibirsk, 1978, p. 208. (b) Puri, J. K.; Singh, R.; Chahal, V. K. *Chem. Soc. Rev.* **2011**, *40*, 1791.
13. (a) Erchak, N.; Olszewska, E.; Kalvinsh, I.; Liepinsh, E.; Belyakov, S.; Sobolev, A.; Arsenyan, P. *Chem. Heterocycl. Compd.* **2015**, *50*, 1506. [*Khim. Geterotsikl. Soedin.* **2014**, 1634.] (b) Sperlich, J.; Becht, J.; Mühleisen, M.; Wagner, S. A.; Mattern, G.; Tacke, R. *Z. Naturforsch.*, *B*: *J. Chem. Sci.* **1993**, *48*, 1693. (c) Tacke, R.; Burschka, C.; Heermann, J.; Richter, I.; Wagner, B.; Willeke, R. *Eur. J. Inorg. Chem.* **2001**, 2211. (d) Bertermann, R.; Biller, A.; Kaupp, M.; Penka, M.; Seiler, O.; Tacke, R. *Organometallics* **2003**, *22*, 4104.
14. Eaborn, C. *Organosilicon Compounds*; Butterworths Scientific Publications, 1960, p. 200.
15. Lee, V. Y. *Organosilicon Compounds. Theory and Experiment (Synthesis)*; Academic Press, 2017.
16. Toutov, A. A.; Betz, K. N.; Haibach, M. C.; Romine, A. M.; Grubbs, R. H. *Org. Lett.* **2016**, *18*, 5776.
17. Lukevics, E.; Dzintara, M. *J. Organomet. Chem.* **1985**, *295*, 265.
18. Boyer, J.; Corriu, R. J. P.; Perz, R.; Reye, C. *J. Organomet. Chem.* **1978**, *157*, 153.
19. (a) Ventura-Espinosa, D.; Sabater, S.; Carretero-Cerdán, A.; Baya, M.; Mata, J. A. *ACS Catal.* **2018**, *8*, 2558. (b) Vijjamarri, S.; Chidara, V. K.; Rousova, J.; Du, G. *Catal. Sci. Technol.* **2016**, *6*, 3886.
20. (a) Harinath, A.; Bhattacharjee, J.; Anga, S.; Panda, T. K. *Aust. J. Chem.* **2017**, *70*, 724. (b) Lorenz, C.; Schubert, U. *Chem. Ber.* **1995**, *128*, 1267.
21. Skrodzki, M.; Zaranek, M.; Witomska, S.; Pawluc, P. *Catalysts* **2018**, *8*, 618.
22. Pypowski, K.; Koval', T. A.; Erchak, N. P. *Russ. J. Gen. Chem.* **2005**, *75*, 1674. [*Zh. Obshch. Khim.* **2005**, *75*, 1753.]
23. (a) Lukevits, E.; Moskovich, R. Ya.; Liepin'sh, E.; Yankovskaya, I. S. *Zh. Obshch. Khim.* **1976**, *46*, 604. (b) Lukevits, E.; Pestunovich, A. E.; Voronkov, M. G. *Chem. Heterocycl. Compd.* **1971**, *4*, 689. [*Khim. Geterotsikl. Soedin.* **1968**, 949.]
24. (a) Labrecque, D.; Nwe, K. T.; Chan, T. H. *Organometallics* **1994**, *13*, 332. (b) Adima, A.; Bied, C.; Moreau, J. J. E.; Wong Chi Man, M. *Eur. J. Org. Chem.* **2004**, 2582.
25. Yin, B.; Huang, Y.; Wang, G.; Wang, Y. *J. Mol. Model.* **2010**, *16*, 437.
26. Parnes, Z. N.; Bolestova, G. I. *Synthesis* **1984**, 991.
27. Stańczyk, W.; Chojnowski, J. *J. Organomet. Chem.* **1976**, *117*, 219.
28. Moser, W. H. *Tetrahedron* **2001**, *57*, 2065.
29. Lazareva, N. F.; Brodskaya, E. I. *Russ. J. Gen. Chem.* **2001**, *71*, 201. [*Zh. Obshch. Khim.* **2001**, *71*, 226.]
30. Spencer, J. N.; Wolbach, W. S.; Hovick, J. W.; Ansel, L.; Modarress, K. J. *J. Solution Chem.* **1985**, *14*, 805.
31. (a) Noll, J. E.; Daubert, B. F.; Speier, J. L. *J. Am. Chem. Soc.* **1951**, *73*, 3871. (b) Zingler, V. G.; Kelling, H.; Popowski, E. *Z. Anorg. Allg. Chem.* **1981**, *476*, 41.