Reaction of Allylamine with Hexylsilane

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Abstract—The reaction of hexylsilane with allylamine is accompanied by the liberation of hydrogen and formation of allylaminosilanes and compounds with the Si–Si bond. The hydrosilylation pathway virtually is not realized. The B3LYP/6-311G** calculations show that all the considered reactions are thermodynamically allowed.

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It is known that hydrosilylation of allylamine with dialkyl(aryl)silanes yields dialkyl(aryl)bisaminopropylsilanes [11]. Data on hydrosilylation of allylamine with trihydrosilanes are lacking. As investigation object we chose hexylsilane, which was prepared by hydrosilylation of hexene with trichlorosilane, followed by reduction of hexyltrichlorosilane.

It is most appropriate to perform the reaction in the presence of Speier's catalyst (solution of H_2PtCl_6 in isopropanol), because of its availability, simplicity of the reaction, and high yield of the target products; however, the use of this catalyst for hydrosilylation of hexene with trichlorosilane was not reported previously.

In this study, hexyltrichlorosilane was prepared by hydrosilylation of hexene with trichlorosilane in the presence of Speier's catalyst under mild conditions in 92% yield and was then reduced with lithium aluminum hydride. For more complete isolation of hexylsilane, we separated before the distillation the phases of hexylsilane in ether and AlCl₃ in ether, thus eliminating the negative effect of the salt on the reaction product. The highest yield of hexylsilane attained previously was 65% [2]; by our procedure, we prepared it in 74% yield.

Allylamine has two reactive centers: amino group and double bond. Depending on the catalyst, it can react with hydrosilanes at any of these centers.

CH_-CHCH_NH_+SiH

$$CH_2 = CHCH_2NH_2 + \geq SiH$$
$$\longrightarrow \geq SiCH_2CH_2CH_2NH_2, \qquad (1)$$

$$\longrightarrow CH_2=CHCH_2NHS_i \leq +H_2.$$
(2)

In the presence of octacarbonyldicobalt and dodecacarbonyltetrarhodium $Rh_4(CO)_{12}$ [3], the dehydrogenation occus first, and then excess silane adds to the remaining double bond. On platinum catalysts, the major process is usually hydrosilylation, with the dehydrocondensation also occurring to a certain extent. Therefore, in this study we chose platinum catalysts: Speier's catalyst and complexes of Pt(0) with divinyltetramethyldisiloxane (Karstedt's catalyst) (I) prepared according to [4] and with hexavinyldisiloxane (II) [5].



The reaction of allylamine with hexylsilane in the presence of Speier's catalyst was accompanied by hydrogen liberation, and three products were detected in 29 h. Their attempted isolation by distillation resulted in polymerization of the mixture. Presumably, the mixture contained mono-, bis-, and tris(allylamino)silanes. The complex catalysts proved to be more

active: On the catalyst with Pt(0), the synthesis was complete in 6–13 h. Also, we tested H_2PtCl_6 -based catalytic systems that appeared to be efficient in the synthesis of aminopropyltriethoxysilane: Speier's catalyst with additions of allyl glycidyl ether, vinyl-triethoxysilane, and tetramethyldivinyldisiloxane.

When performing the reaction, we varied the order of adding the reactants: addition of hexylsilane to allylamine or vice versa. Hydrogen liberation was observed in both cases; it was more active in the presence of traces of hexyltrichlorosilane, alkali, moisture, or grease. To eliminate these factors, the synthesis was performed under dry nitrogen. However, in the absence of oxygen the reactions were very slow, as it is known [6] that oxygen promotes platinum catalysts. Furthermore, the number of components in the reaction mixture increased.

A GC–MS analysis of the reaction mixture from the reaction of allylamine with hexylsilane revealed 46 substances; the major product (20%) was hexyltris-(allylamino)silane III. The mixture also contained 16 substances (0.8–14.8%) with molecular weights of 395, 398, 450, 452, 480, which can be tentatively identified as IVa–IVg, V, VI, VIIa–VIId, and VIIIa–VIIIc.

$$\begin{array}{c} R^{1}R^{2}C_{6}H_{13}SiSiC_{6}H_{13}R^{3}R^{4},\\ IVa-IVg \end{array}$$

$$\begin{array}{c} (CH=CHCH_2NH_2)_2C_6H_{13}SiNHCH_2C=CH_2\\ CH_2=CHCH_2NHSiHC_6H_{13}\\ \mathbf{V}\end{array}$$

 $(CH=CHCH_2NH_2)_2C_6H_{13}SiN^+H_2CH_2CH(CH_3)SiH_2C_6H_{13}$ VI



 $\begin{array}{c} R^1R^2C_6H_{13}SiSi(C_6H_{13})_2CH_2CH_2CH_2N^+H_3\\ \textbf{VIIIa-VIIIc} \end{array}$

Formation of these compounds can be accounted for by assuming that reactions (1) and (2) are accompanied, in any sequence, by dehydrogenative hydrosilylation (3), formation of disilane (4), and hydrosilylation of allylamine with the formation of β -isomer (5).

$$RR'R''SiH + CH_2 = CHCH_2NH_2$$

$$\longrightarrow RR'R''SiCH = CHCH_2NH_2, \qquad (3)$$

$$2RR'R''SiH \longrightarrow RR'R''SiSiRR'R'', \qquad (4)$$

$$RR'R''SiH + CH_2 = CHCH_2NH_2$$

$$\longrightarrow RR'R''SiCH(CH_3)CH_2NH_2.$$
(5)

The dehydrogenative hydrosilylation is known, but usually it is performed in the presence of rhodium catalysts [7]. On prolonged storage, a gas was released from the samples, and they became more viscous. The resulting polymers are soluble in toluene and insoluble in ethanol and acetone. Their UV spectrum contains a strong band at 320 nm characteristic of the Si–Si bond. It is known that the presence of the amino group in the zicronocene catalyst molecule positively affects the formation of polysilanes [8].

In the reaction mixture from the reaction of allylamine with hexylsilane in the absence of catalyst, after distilling low-boiling compounds off, a GC–MS analysis revealed 35 components in amounts of 0.2– 31.6%. The spectra of major products contained peaks differing by 84 amu, which corresponded to the loss of hexene. There were several groups of spectra differing in the mass by 1, 30, 56, and 60 units, which can be attributed to formation of polysilanes **IX** (6):



X, Y = H, NH₂, OC₂H₅, OH, and other groups in various combinations.

Calculation of the thermodynamics of model reaction (7) in *ab initio* approximations shows that polymer **IX** can form at continuous removal of hydrogen from the reaction zone.

It was concluded that, to exlude formation of polysilanes, it is necessary to perform the hydrosilylation

RUSSIAN JOURNAL OF GENERAL CHEMISTRY Vol. 76 No. 2 2006

Parameter	H ₂	AllNH ₂	SiH ₄	MeSiH ₃	MeOSiH ₃	ASiH ₃ ^a	BSiH ₃ ^b	MeSiA ^a	MeSiB ^b	MeOSiA ^a	MeOSiB ^b
-G, au $-\Delta G_r$, au $-\Delta G_r$, kcal mol ⁻¹	1.181 - -	173.230 - -	291.902 - -	331.220 - -	406.470 - -	465.150 0.01862 11.684	463.960 0.006357 3.989	504.470 0.01768 11.0955	503.280 0.00698 4.383	579.730 0.020723 13.00368	578.540 0.01513 9.492
-H, au $-\Delta H_r$, au $-\Delta H_r$, kcal mol ⁻¹	1.166 - -	173.201 _ _	291.880 - -	331.190 - -	406.440 _ _	465.110 0.03406 21.376	463.920 0.007622 4.7828	504.420 0.0344 21.589	503.232 0.009819 6.1614	579.680 0.038 23.98	578.490 0.019 12.056

Thermodynamic characteristics of amination and hydrosilylation pathways in reactions of allylamine with SiH_4 , CH_3SiH_3 , and CH_3OSiH_3 (B3LYP/6-311G*)

 $a = CH_2CH_2CH_2NH_2$. $bB = NHCH_2CH=CH_2$.

$$2CH_{3}SiH_{3} \longrightarrow HSi \longrightarrow SiH + H_{2} \qquad (7)$$

$$H H H$$

of allylamine with hexylsilane in a pressure vessel. This is confirmed by successful hydrosilylation of allylamine with dihydrosilane [1]. The reaction can yield polysilanes. However, even the synthesis at an N_2 or H_2 pressure of 20 atm yielded a mixture consisting mainly of mono-, bis-, and tris(allylamino)-silanes and polysilanes.

Thus, the reaction of allylamine with hexylsilane is very complex. The major processes are dehydrogenation and formation of polysilanes. The hydrosilylation occurs to only a minor extent.

According to published data [9], the synthesis of γ -aminopropyltriethoxysilane by hydrosilylation of allylamine with triethoxysilane is accompanied by formation of only a minor amount of the silylamino derivative. To account for an unusual behavior of hexylsilane in hydrosilylation of allylamine in the presence of platinum catalysts, we calculated the thermodynamic parameters of the possible reaction pathways in the *ab initio* approximation using the 6-311G** basis. The correlation corrections were taken into account in the B3LYP approximation of the density functional theory (DFT).

We considered model reactions (8) and (9):

$$RSiH_3 + NH_2CH_2CH=CH_2$$

$$\longrightarrow RSiH_2(CH_2CH_2CH_2NH_2), \quad (8)$$

$$\longrightarrow RSiH_2(NHCH_2CH=CH_2) + H_2, \quad (9)$$

 $R = H, CH_3, OCH_3.$

The calculation results are given in the table. They show that both hydrosilylation (8) and side amination reactions (9) are thermodynamically allowed.

EXPERIMENTAL

The mass spectra were taken on a Hewlett–Packard HP-5971A mass spectrometer at an ionizing voltage of 70 eV. The products were separated on a 25000×0.32 -mm quartz capillary column; the stationary phase was DV-5 methylphenylsiloxane elastomer (film thickness 25 µm). Analysis was performed at programmed column heating from 50 to 280°C at a rate of 7 deg min⁻¹; the carrier gas was He.

The UV spectra were taken on a Perkin–Elmer device in hexane and THF.

All the chemicals used were preliminarily purified. Their purity was checked by GLC. The compounds obtained were identified by GLC using authentic samples.

The composition of reaction mixtures and pure compounds was monitored by GLC on a Shimadzu G-8A device (15000×3 -mm packed stainless steel column, stationary phase SE-30, support Chromaton N-AW, carrier gas He). The carrier gas flow rate was 40 cm³ min⁻¹. The vaporizer temperature was 200, and the detector temperature, 180° C. The column was linearly heated from 50 to 150° C at a rate of 8 deg min⁻¹.

We also used a Tsvet-500 chromatograph ($1000 \times$ 3-mm glass column, stationary phase 5% SE-30 on Chromaton N-AW-DMCS, carrier gas helium). The carrier gas flow rate was 50 cm³ min⁻¹. The vaporizer and detector temperatures were 300°C. The column was linearly heated from 50 to 300°C at a rate of 15 deg min⁻¹. In determination of low-boiling compounds, the vaporizer and detector temperatures were

250°C, and the column was linearly heated from 50 to 250°C at a rate of 15 deg min⁻¹.

Hexyltrichlorosilane. Trichlorosilane (96.6 g) and hexene (50.2 g) were mixed, and seven drops of Speier's catalyst (one drop = 0.017-0.18 ml) were added to 1/3 of the mixture. The remaining mixture was added dropwise at 75°C over a period of 1 h. Within 3 h, the mixture warmed up from 85 to 110°C. The mixture was distilled at atmospheric pressure. A 10-g portion of low-boiling compounds was distilled off at 100°C/750 mm Hg. The vaccum distillation yielded two fractions (bp 92°C/38 mm Hg): first fraction, 3 g (98% hexyltrichlorosilane), and second fraction, 117 g (100% hexyltrichlorosilane). Yield of hexyltrichlorosilane 91%, n_D^{20} 1.4433 (published data [10]: bp 87–89°C/30 mm Hg, n_D^{20} 1.4435).

Hexylsilane. A 7.3-g portion of lithium aluminum hydride was dissolved in 200 ml of diethyl ether at 36°C over a period of 2 h. Then 50 g of hexyltrichlorosilane was added dropwise with stirring at 17-28.5°C over a period of 50 min. Within 5 min after starting the addition of hexyltrichlorosilane, the mixture began to warm up, and the addition was continued with cooling. The mixture was stirred for 35 min; in so doing, its temperature decreased to 18°C, and LiCl precipitated. The transparent solution was transferred into a separating funnel in which it was allowed to separate into two phases. The lower layer (150 ml), a solution of aluminum trichloride in diethyl ether, was discarded. The upper layer (62 ml) contained hexylsilane, diethyl ether, and a part of AlCl₃. The ether was distilled off, and the residue was distilled in a vacuum. The fraction obtained (21.87 g) consisted of 89.6% hexylsilane, 0.6% hexyltrichlorosilane, and 9.8% diethyl ether. Yield of hexylsilane 74%. The product was washed with water to remove traces of unchanged hexyltrichlorosilane, dried over zeolite A, and distilled; bp 116–118°C/750 mm Hg, $n_{\rm D}^{20}$ 1.4133 (published data [2]: bp 112–113°C/761 mm Hg, $n_{\rm D}^{20}$ 1.4131).

Reaction of allylamine with hexylsilane. *a*. A mixture of 2.3 g of allylamine, 1.4 g of hexylsilane, and three drops of Speier's catalyst was refluxed until a constant temperature (or 120°C) was attained.

b. Three drops of Speier's catalyst and three drops of an additive (vinyltriethoxysilane, allyl glycidyl ether) were heated for 20–30 min at 50–70°C. Then 2.3 g of allylamine and 1.4 g of hexylsilane were added. The mixture was refluxed until a constant temperature (or 120°C) was attained. The low-boiling components were distilled off, and the residue was analyzed by GC–MS. Mass spectra of the compounds obtained, m/z (I_{rel} , %): **III**, 281 [M]⁺⁻ (12), 266 [M –

 Me^{+}_{1} (5), 196 $[M - C_6H_{13}]^+$ (26), 141 $[Si(NHCH_2 \cdot$ $CH=CH_{2}_{3}^{+}$ (100); **IVa**, 395 $[M]^{+}$ (5), 366 [M - $(CH_3N)^{+}$ (5), 354 $[M - All]^{+}$ (10), 339 [M - $C_{3}H_{6}N^{+}$ (10), 310 $[M - C_{6}H_{13}]^{+}$ (100), 268 [310 - $C_{2}H_{4}N]^{+}$ (23); **IVb**, 395 $[M]^{+}$ (8), 366 $[M - CH_{3}]^{+}$ (6), 354 $[M - All]^+$ (16), 339 $[M - C_3H_6N]^+$ (14), 310 $[M - C_6 H_{13}]^+$ (100), 268 $[310 - C_2 H_4 N]^+$ (26); **IVc**, 395 $[M]^{+}$ (16), 366 $[M - CH_3N]^{+}$ (6), 354 $[M - CH_3N]^{+}$ All]⁺ (2), 339 $[M - C_3H_6N]^+$ (18), 310 $[M - C_6H_{13}]^+$ (100), 268 $[310 - C_2H_4N]^+$ (26); **IVd**, 395 $[M]^+$ (31), 366 $[M - CH_3N]^+$ (14), 354 $[M - All]^+$ (22), 339 $[M - C_3H_6N]^+$ (50), 310 $[M - C_6H_{13}]^+$ (100), 255 $[310 - \mathring{C}_{3}\mathring{H}_{5}N]^{+}$ (5); **IVe**, 395 $[M]^{+}$ (5), 339 $[M - \mathring{C}_{3}N]^{+}$ $C_{3}H_{6}N^{+}$ (100), 310 $[M - C_{6}H_{13}]^{+}$ (46), 297 [M - $98]^+$ (16); **IVf**, 452 $[M]^+$ (7), 394 $[M - 58]^+$ (60), 367 $[M - 85]^+$ (41), 337 $[M - 58 - 57]^+$ (72), 310 [M -56 - 57]⁺ (100), 297 (14), 268 (10), 255 (46); **IVg**, 450 $[M]^{+}$ (3), 394 $[M - C_3H_6N]^{+}$ (42), 364 $[M - C_3H_6N]^{+}$ $[86]^+$ (25), 337 $[M - 56 - 57]^+$ (100), 308 $[M - 142]^+$ (76), 268 $[M - 182]^+$ (12); **V**, 450 $[M]^{+}$ (4), 394 [M - $C_{3}H_{6}N]^{+}$ (55), 352 $[M - 57 - 41]^{+}$ (100), 323 [M - $C_{3}H_{6}N - 2Me]^{+}$ (97), 310 (25), 266 (50), 213 (18); **VI**, 398 $[M]^{+}$ (14), 369 $[M - \text{Et}]^{+}$ (100), 352 [M - $(57 - 41]^+$ (42), 339 (14), 300 $[M - 57 - All]^+$ (52), 268 $[M - C_3H_6N - 2Me]^+$ (50), 255 (56); VIIa, 395 $[M]^{+}$ (14), 366 $[M - CH_3N]^{+}$ (7), 354 $[M - All]^{+}$ (2), 339 $[M - C_3H_6N]^+$ (18), 310 $[M - C_6H_{13}]^+$ (68), 297 $[M - 98]^+$ (28), 268 $[310 - C_2H_4N]^+$ (100), 251 (22), 213 (42), 129 (30); VIIb, 395 $[M]^{+}$ (12), 366 $[M - CH_3N]^+$ (7), 354 $[M - All]^+$ (10), 339 [M - $C_{3}H_{6}N]^{+}$ (18), 310 $[M - C_{6}H_{13}]^{+}$ (70), 297 $[M - 98]^{+}$ (30), 268 $[310 - C_2H_4N]^+$ (100), 251 (20), 213 (28), 129 (25); **VIIc**, $395 [M]^+$ (10), 310 $[M - C_6H_{13}]^+$ (60), 297 $[M - 98]^+$ (18), 268 $[310 - C_2H_4N]^+$ (100), 251 (20), 213 (30), 129 (18); **VIId**, 395 $[M]^+$ (4), 339 $[M - C_3H_6N]^+$ (12), 310 $[M - C_6H_{13}]^+$ (25), 297 $[M - 98]^+$ (65), 268 $[310 - C_2H_4N]^+$ (100), 213 (26), 129 (26); VIIIa–VIIIc, 480 $[M]^+$ (1), 422 [M - C_2H_6N]⁺ (100).

c. Two drops of complex **II** were added to 2.3 g of allylamine, and, after a certain period, 1.4 g of hexylsilane was added. The mixture was refluxed for 5 h at 62°C and left to cool; in so doing, the mixture polymerized. Found, %: C 63.76, 63.38; H 11.42, 11.49; Si 13.66 13.42. $C_{12}H_{26}N_2Si$. Calculated, %: C 63.7; H 11.5; Si 12.4. In a similar experiment, excess allylamine was distilled off after heating. The residue also polymerized on standing. Found, %: C 63.40, 63.57; H 11.40, 11.50; Si 13.70, 13.50. $C_9H_{21}NSi$. Calculated, %: C 63.16; H 12.28; Si 16.37.

d. Two drops of catalyst **II** were mixed with 2.3 g of allylamine. The mixture was heated to reflux, and 1.4 g of hexylsilane was added over a period of 30 min. The mixture was refluxed for 18.5 h and then

RUSSIAN JOURNAL OF GENERAL CHEMISTRY Vol. 76 No. 2 2006

distilled. After distillation of 1.5 ml of allylamine, the mixture polymerized.

e. Two drops of catalyst **II** were mixed with 1.4 g of hexylsilane, and 2.3 g of allylamine was added dropwise. The mixture was refluxed for 15 h at $62-115^{\circ}$ C.

f. To two drops of catalyst **II**, 1.4 g of hexylsilane and 2.3 g of allylamine were added dropwise. The mixture was heated for 21 h at $56-100^{\circ}$ C, after which it was refluxed until a constant temperature (or 120° C) was attained.

g. To two drops of catalyst **II**, 1.4 g of hexylsilane and 2.3 g of allylamine were added at 70°C from two different funnels. Then the mixture was refluxed until a constant temperature (or 120° C) was attained.

h. A mixture of 1 ml of hexylsilane and 1.5 ml of allylamine was refluxed for 8 h. The temperature in the mixture rose to 120° C. A GC–MS analysis revealed 25 substances with a relative content ranging from 0.2 to 31.6%.

i. A glass beaker was charged with 6.2 ml of allylamine, three drops of a 0.2 M solution of Speier's catalyst, and 4.05 ml of hexylsilane. The beaker was placed in a 240-ml pressure vessel purged with dry nitrogen. Nitrogen or hydrogen was pumped in to a pressure of 13 atm. The vessel was shaken to pour out the mixture from the beaker. Then the vessel was heated on a boiling water bath for 12 h (in so doing, the pressure increased to 20 atm) and cooled; excess pressure (13 atm) was relieved, and the reaction mixture (5.5 g) was unloaded. The mixtures obtained in runs e-i are similar in composition to that from run b.

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