## Reaction of Hexylsilane with N-Substituted Allylamine and Allyl Chloride

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**Abstract**—Reactions of allyldiethylamine and allylbis(trimethylsilyl)amine with hexylsilane are studied. The former reaction involves hydrogen evolution and Si–Si bond formation. The contribution of hydrosilylation is insignificant. Substituent exchange between the nitrogen and silicon atoms in the silane is found. In the reaction with allylbis(trimethylsilyl)amine, no evolution of hydrogen is observed, and hydrosilylation takes place. With allyl chloride, hydrosylilation, reduction, and Si–Si bond formation are observed. Quantum-chemical calculations for the reactions with diethylallylamine and allylbis(trimethylsilyl)amine were carried out at the PM3, B3LYP/6-31G\*\*, and B3LYP/LanL2DZ levels to show that these reactions all are thermo-dynamically allowed, and the difference in the behavior of the amines is explained by kinetic and conformational factors.

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We previously showed that the reaction of allylamine with hexylsilane involves dehydrocondensation to form a Si–Si bond as the major pathway [1]. To exclude dehydrocondensation and assess the effect of substituents on the relative contributions of hydrosilylation and Si–Si bond formation, we took compounds  $CH_2=CHCH_2X$  [X = NEt<sub>2</sub>, NAll<sub>2</sub>, N(SiMe<sub>3</sub>)<sub>2</sub>] as objects for study. The reaction of hexylsilane with triallylamine gave polymer that was not investigated in the present work.

In the course of hydrosilylation of allylbis(trimethylsilyl)amine with hexylsilane, no hydrogen evolution was observed. The reaction mixture contained 36% of monoadduct and, probably, di- and triadducts [Eq. (1)].

$$(Me_{3}Si)_{2}NCH_{2}CH=CH_{2} + C_{6}H_{13}SiH_{3}$$

$$\longrightarrow (Me_{3}Si)_{2}NCH_{2}CH_{2}CH_{2}SiH_{2}C_{6}H_{13}$$

$$+ [(Me_{3}Si)_{2}NCH_{2}CH_{2}CH_{2}]_{2}SiHC_{6}H_{13}$$

$$+ [(Me_{2}Si)_{3}NCH_{2}CH_{2}CH_{3}]_{2}SiC_{4}H_{12}, \qquad (1)$$

The mass spectrum of hexyl[ $\gamma$ -bis(trimethylsilyl)aminopropyl]silane contains an [M - 1] peak and also a peak at m/z 174 corresponding to the CH<sub>2</sub>=N<sup>+</sup>.  $(\text{SiMe}_3)_2$  ion formed from  $\text{C}_6\text{H}_{13}\text{SiH}_2\text{CH}(\text{CH}_3)\text{CH}_2\text{N} \cdot (\text{SiMe}_3)_2$  by cleavage of the  $\beta$  bond with respect to nitrogen [2]. The mass spectrum of possible di- and triadducts contains no molecular ion peaks, but contain a peak at m/z 174. In the UV spectrum, the Si–Si absorption band at 320–330 nm is absent.

By contrast, the reaction of diethylallylamine with hexylsilane involved vigorous hydrogen evolution to form compounds I [Eq. (2)].

$$nC_{6}H_{13}SiH_{3} \longrightarrow H[C_{6}H_{13}SiH]_{n}H + (n - 1)H_{2}, \quad (2)$$
**Ia**, **Ib**

$$n = 3 \quad (a), 4 \quad (b).$$

About 28% of such compounds were found in the reaction mixture. In their mass spectrum, successive evolution of hexane  $(m/z \ 84)$  was observed.

The UV spectrum in THF shows a band at 320–330 nm, implying presence of a Si–Si bond [3].

The reaction mixture also contains about 1% of  $[\gamma$ -(diethylamino)propyl]hexylsilane. Its mass spectrum contains a molecular ion peak and the base peak at m/z 86 ([CH<sub>2</sub>NEt<sub>2</sub>]<sup>+</sup>) formed by cleavage of the  $\beta$  bond with respect to nitrogen.

$$Et_2NCH_2CH=CH_2 + C_6H_{13}SiH_3$$
$$\longrightarrow Et_2N(CH_2)_3SiH_2C_6H_{13}.$$
 (3)

Among the products of the reaction of hexylsilane with diethylallylamine, allyl(ethyl)(hexyl)amine (13%), diethyl(hexenyl)amine (11%) and allyl(ethyl)-(hexenyl)amine (10%) were found, as well as a complex of hexylsilane with diethylallylamine evidently containing a Si-N bond. Its molecular mass is equal to that of the hydrosilylation product, but their fragmentation patterns are different. The mass spectrum of the complex contains a molecular ion peak (m/z)229), the base peak at m/z 102 ([H<sub>2</sub>SiNEt<sub>2</sub>]<sup>+</sup>), and a peak at m/z 113 (allyldiethylamine). One of the specific features of its fragmentation is the presence of an [M - Et] peak which is incharacteristic of amines and points to mobility of the ethyl substituent. Evidence for the mobility of the allyl fragment is provided by its absence in the ion that forms the base peak (m/z 102). Evidently, substituent exchange takes place in the complex. The formation of hexenyl substituents can be explained by hydrogenation-dehydrogenation of the allyl and hexyl substituents. Polysilanes contain the ethyl substituent along with hexyl. Analogous complexes in the reactions with allylamine and allylbis(trimethylsilyl)amine were not found.

$$\begin{array}{rcl} & \operatorname{Et_2NAll} + \operatorname{C_6H_{13}SiH_3} \longrightarrow \operatorname{C_6H_{13}SiH_3} \cdot \operatorname{EtNAll} \\ & \longrightarrow \operatorname{C_6H_{13}NEt_2} + \operatorname{C_6H_{11}NEt_2} + \operatorname{C_6H_{11}NEtAll.} \end{array}$$
(4)

The reaction of hexylsilane with allyl chloride took usual addition and reduction pathways to form 7% of ( $\gamma$ -chloropropyl)hexylsilane (**V**, 22% of chloro( $\gamma$ chloropropyl)(hexyl)silane (**VII**), 14.2% of dichloro( $\gamma$ chloropropyl)hexylsilane (**IX**), 8.4% of chloro( $\gamma$ chloropropyl)(hexyl)(propyl)silane (**X**), as well as a small amount of compounds with a Si–Si bond.

Calculated electronic parameters of compounds  $CH_2$ = CH-CH<sub>2</sub>NR<sub>2</sub> (PM3 method)

R = H	R = Et	$R = SiMe_3$
1	Charge	
-	-	0.462
-0.153	-0.136	-0.161
-0.140	-0.173	-0.172
-0.310	-0.081	-0.281
Energies of frontier MOs, eV		
-9.33004	-9.06124	-8.32826
-10.42615	-10.18916	-9.74425
1.09583	1.10778	0.42632
3.0185	2.46832	1.16475
	R = H -0.153 -0.140 -0.310 of frontier -9.33004 -10.42615 1.09583 3.0185	$\begin{array}{c c c c c c c c c c c c c c c c c c c $



 $R = C_6H_{13}$ ,  $R' = CH_2CH_2CH_2CI$ , A is addition and R is reduction

The structure of the compounds was confirmed by the mass spectra which contain molecular and  $[M-1]^+$ ion peaks, and the fragmentation patterns do not contradict the proposed structures. Moreover, the mixture contains 17 compounds (1-4% each, 25% total). In their mass spectra we observe consecutive loss of either propylene or hexene with preservation of ions containing 1-4 chlorine atoms. Evidently, they can be assigned formula  $X[C_6H_{13}SiH]_1[C_6H_{13}SiCI]_n$ .  $[C_6H_{13}SiPr]_mY.$ Analysis of the electronic structures of the allylamines under study carried out on the basis of quantum-chemical calculations (PM3, B3LYP/ 6-31G\*\*, and B3LYP/LanL2DZ) shows that the preferred pathways of their reactions with hexylamine are those involving the reaction center on the nitrogen atom: dehydrocondensation in the case of allylamine and polysilane formation in the case of diethylallylamine. The observation of dehydrosilylation in the case of bis(trimethylsilyl)amine can be explained by steric hindrances for reaction by nitrogen because of the considerable volume of the SiMe<sub>3</sub> group, that is by steric and conformational reasons. In the case of allylamine and diethylallylamine, the nucleophilic center on nitrogen is conformationally accessible, whereas in allylbis(trimethylsilyl)amine it is conformationally shielded. All the considered patways of the reactions of allylamine with hexylsilane are thermodynamically allowed ( $\Delta G < 0$ ).

Note that the divergence of calculated interatomic distances from known experimental data are within the experimental error and do not exceed 2-3% for the N–Si bond and 0.5-1% for the C–C and C–N bonds. The atomic charge distributions are poorly informative and contradictory (see table). At the same time, analysis of the parameters of the frontier orbitals

points to prevailing contribution of nitrogen in the HOMO (74–79%). This orbital is a  $\sigma$  orbital, which suggests localization of the most active nucleophilic center in the allylamines on the nitrogen atom. Note that the HOMO energy increases in the series allylamine < diethylallylamine < allylbis(trimethylsilyl)amine, implying increasing nucleophilicity (electrondonor ability) of the corresponding reaction centers. The second, less active nucleophilic center in the molecules in hand is localized on the carbon atoms of the double bond (HOMO-1). The activity of these reaction centers increases along the same series. It is characteristic that the HOMO-1 energy in allylbis(trimethylsilyl)amine is close to that in allylamine (see table). Evidently, in allylbis(trimethylsilyl)amine with its conformational hindrances at the nitrogen atom, this circumstance opens the way for hydrosilylation. The LUMO in allylamine and allyldiethylamine relates to the  $\pi^*$ -MO of the double bond, and in allylbis(trimethylsilyl)amine it is a  $\sigma$ -MO mostly contributed by Si and N (the total contribution is 54%).

## EXPERIMENTAL

The mass spectra were obtained on a Hewlett-Packard HP-5971A GC–MS system at the ionizing voltage 70 V. Chromatography was performed on a DB-5 quartz capillary column  $(25000 \times 0.32 \text{ mm})$  programmed from 50 to  $280^{\circ}$ C at a rate 7 deg min<sup>-1</sup>, carrier gas helium. The UV spectra were measured on a Perkin–Elmer instrument in hexane and THF.

Allylbis(trimethylsilyl)amine. To a mixture of 53 g of allylamine and 150.1 g of hexamethyldisilazane, 2 g of ammonium sulfate was added, and the reaction mixture was refluxed for 14.5 h at 60–68°C and then distilled to obtain 101 g of low-boiling fractions and 51.8 g (34%) of allylbis(trimethylsilyl)amine [bp 42–45°C (6 mm Hg),  $n_D^{20}$  1.4400, purity 95.1%]. Published data [3]: bp 179°C (741 mm Hg,  $n_D^{20}$  1.4363.

**Reaction of hexylsilane with allyldiethylamine**. Spaier's catalyst, 3 drops, was added to a mixture of 0.8 ml of hexylsilane and 2.8 ml of allyldiethylamine, and the resulting mixture was refluxed for 9 h, during which it warmed up from 88 to 96°C. Gas evolution was observed, and two almost equal layers formed. Both layers were analyzed by GC–MS. The upper layer contained 1% of ( $\gamma$ -diethylaminopropyl)hexylsilane {mass spectrum, m/z ( $I_{rel}$ , %): 229 [M]<sup>+</sup> (0.5), 114 [(CH<sub>2</sub>)<sub>3</sub>NSiEt<sub>2</sub>]<sup>+</sup> (28), 86 [CH<sub>2</sub>=NEt<sub>2</sub>] (100)}; 16.5% of a complex of hexylsilane with allyldiethylamine {mass spectrum, m/z ( $I_{rel}$ , %): 229 [M]<sup>+</sup> (5), 200 [M – Et}<sup>+</sup> (10), 113 [AllNEt<sub>2</sub>]<sup>+</sup> (10), 102 [H<sub>1</sub>Si= NEt<sub>2</sub>]<sup>+</sup> (100), 86 [CH<sub>2</sub>=NEt<sub>2</sub>]<sup>+</sup> (5)}; 13% of allyl(ethyl)(hexyl)amine {mass spectrum, m/z ( $I_{rel}$ , %): 169  $[M]^+$  (10), 154  $[M - Me]^+$  (8), 140  $[M - Et]^+$  (4), 126  $[M - Pr]^+$ , 97  $[EtN(CH_2CH)_2]^+$  (100), 72 (14)}; 14% of compound **Ia**, n = 3 {mass spectrum, m/z ( $I_{rel}$ , %): 345  $[M+1]^+$  (0.2), 86  $[C_6H_{14}]^+$ (100)}; and 31.1% of compound **Ib**, n = 4 {mass spectrum, m/z ( $I_{rel}$ , %): 458  $[M]^+$  (0.1), 86  $[C_6H_{14}]^+$ (100)}.

The lower layer contained 14% of allyl(ethyl)-(hexyl)amine {mass spectrum, m/z ( $I_{rel}$ , %): 169 [M]<sup>+</sup> (10), 154 [M – Me]<sup>+</sup> (8), 140 [M – Et]<sup>+</sup> (4), 97 [EtN(CH<sub>2</sub>CH)<sub>2</sub>]<sup>+</sup> (100), 72 (14)}; 22% of diethyl-(hexyl)amine {mass spectrum, m/z ( $I_{rel}$ , %): 155 [M]<sup>+</sup> (14), 140 [M – Me]<sup>+</sup> (100), 111 [M – Me – Et]<sup>+</sup> (70), 94 [M – 2Me – Et]<sup>+</sup> (50)}; and 20% of allyl(ethyl)-(hexenyl)silane {mass spectrum, m/z ( $I_{rel}$ , %): 167 [M]<sup>+</sup> (36), 152 [M – Me]<sup>+</sup> (100), 138 [M – Et]<sup>+</sup> (30), 124}.

Reaction of hexylsilane with allylbis(trimethylsilyl)amine. Spaier's catalyst, 3 drops, was added to a mixture of 1 ml of hexylsilane and 4.9 ml of allylbis(trimethylsilyl)amine. The reaction mixture was heated for 9 h, during which it warmed up from 65 to 100°C. No visible changes were noted over the course of the process. The reaction mixture was analyzed by GC-MS to find 15.4% of the starting allylbis(trimethylsilyl)amine {mass spectrum, m/z ( $I_{rel}$ , %): 201  $[M]^+$  (22), 186  $[M - Me]^+$  (100), 174  $[CH_2=N(Si - Me)^+$  $Me_{3}_{2}^{+}$  (20), 73  $[SiMe_{3}]^{+}$  (60), 59  $[SiHMe_{2}]^{+}$  (8)}; 35.9% of hexyl[ $\gamma$ -bis(trimethylsilyl)aminopropyl]silane, M/z ( $I_{rel}$ , %): 316  $[M - 1]^+$  (0.5), 302  $[M - Me]^+$  (2), 228  $[M - Me - SiMe_3]^+$  (2), 174  $[CH_2=$  $N(SiMe_3)_2]^+$  (100), 86  $[C_6H_{14}]^+$  (14), 73  $[SiMe_3]^+$ (18), 59  $[SiHMe_2]^+$  (7); 5.4% of the product of double addition, mass spectrum, m/z ( $I_{rel}$ , %): 174 [CH<sub>2</sub>=N·  $(SiMe_3)_2$ ]<sup>+</sup> (100); 3.1% of the product of triple addition, mass spectrum, m/z: 174 [CH<sub>2</sub>=N(SiMe<sub>3</sub>)<sub>2</sub>]<sup>+</sup> (100).

Reaction of hexylsilane with allyl chloride. A mixture of 1.6 ml of hexylsilane and 2.0 ml of allyl chloride was treated with 3 drops of Spaier catalyst. Gas evolution was observed. The reaction mixture was boiled for 24 h, and its temperature rose from 60 to 79°C. The reaction mixture contained 7% of compound **V**, mass spectrum, m/z ( $I_{rel}$ , %): 191 [M - 1]<sup>+</sup> (8), 149  $[C_6H_{13}SiCl]^+$  (75), 107 (CH<sub>2</sub>)<sub>3</sub>SiCl<sup>+</sup> (10), 79 [107 - $(CH_2)_2$ ]<sup>+</sup> (80); 22% of compound VII, mass spectrum,  $m/z \ (I_{\rm rel}, \%): 225 \ [M-1]^+ \ (15), \ 183 \ [M-Pr]^+ \ (50),$ 141  $[PrSiCl_2]^+$  (100), 113  $[MeSiCl_2]^+$  (36), 99  $[HSiCl_2]^+$  (14)}; 14.2% of compound IX {mass spectrum, *m/z* (*I*<sub>rel</sub>, %): 217 [*M*]<sup>+</sup> (8), 175 [Cl(CH<sub>2</sub>)<sub>3</sub>SiCl<sub>2</sub>]<sup>+</sup> (100), 133  $[SiCl_3]^+$  (60)}; 8.4% of compound **X** {mass spectrum, m/z ( $I_{rel}$ , %): 267  $[M - 1]^+$  (1), 183  $[C_6H_{13}SiCl_2]^+$  (10), 149  $[C_6H_{13}Cl_2]$  (10), 149

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## REFERENCES

- Storozhenko, P.A., Belyakova, Z.V., Knyazev, S.P., Shutova, O.G., Khromykh, N.N., Starikova, O.A., and Chernyshev, E.A., *Russ. J. Gen. Chem.*, 2006, vol. 76, no. 2, p. 220.
- Polyakova, A.A. and Khmelnitskii, R.A., *Mass-spektry* v organicheskoi khimii (Mass Spectra in Organic Chemistry), Moscow: Khimiya, 1972, p. 303.
- West, R., J. Organomet. Chem., 1986, vol. 300, no. 2, p. 327.
- 4. Spaier, J.L., Zimmerman, R., and Webster, J., J. Am. Chem. Soc., 1956, vol. 78, p. 2278.