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Abstract

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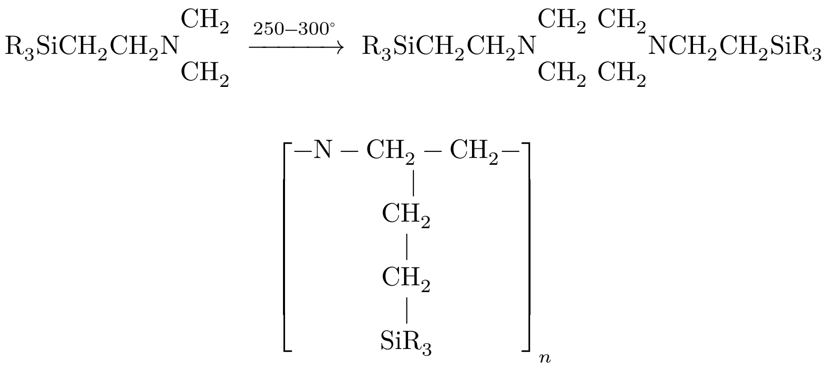
TRANSFORMATIONS OF β-(N-ETHYLENIMINO)ETHYLSILAN AT ELEVATED TEMPERATURES AND IN THE PRESENCE OF NUCLEOPHILIC AND ELECTROPHILIC REAGENTS

In paper (¹) the preparation of β-(N-ethylenimino)ethylsilanes by addition of ethylenimine to vinylsilanes in the presence of alkali metals was reported. It was shown that in such compounds the nitrogen atom is in the β-position with respect to the silicon atom. The facts concerning the exclusive influence of the position of substituents relative to the silicon atom on the stability of the Si—C bond are well known. Organosilicon compounds with radicals substituted in the β-position are especially sensitive to β-cleavage under the action of nucleophilic and electrophilic reagents (², ³). Organosilicon compounds containing a nitrogen atom in the hydrocarbon radical in the β-position to silicon are resistant to such cleavage (³) under the action of alkalis and sulfuric acid. The β-(N-ethylenimino)ethylsilanes obtained are of interest because they contain a three-membered ring capable of various transformations. In this connection we were interested in the strength of the Si—C bond in β-(N-ethylenimino)ethylsilanes at high temperatures and in the direction of transformations in the presence of nucleophilic and electrophilic reagents. It is known that N-phenylethylenimine and N-*p*-tolylethylenimine in aqueous methanol in the presence of NaJ give N,N′-diarylpiperazines (⁴). In the absence of NaJ, rapid polymerization of N-phenylethylenimine occurs (⁵). In the presence of aluminum chloride, N-acyl derivatives of ethylenimine give oxazolines (⁶), whereas ethylenimine polymerizes with ring opening. At elevated temperatures N-acyl derivatives give oxazolines (⁷); there is no information on other types of transformations under these conditions for N-substituted ethylenimines.

β-(N-Ethylenimino)ethylsilanes remain unchanged when heated at 200° for 5 hours. Raising the temperature to 250—300° leads to the formation of substantial amounts of products of thermal transformation; moreover, along with products of cyclodimerization to piperazine derivatives, products of higher molecular weight are also formed as a result of opening of the ethylenimine ring



$$R_3SiCH_2CH_2N\begin{matrix}CH_2\\ \\ CH_2\end{matrix}\xrightarrow{250\text{–}300^\circ}R_3SiCH_2CH_2N\begin{matrix}CH_2 & CH_2\\ & \\ CH_2 & CH_2\end{matrix}NCH_2CH_2SiR_3$$

$$\left[\begin{array}{c}-N-CH_2-CH_2-\\ | \\ CH_2\\ | \\ CH_2\\ | \\ SiR_3\end{array}\right]_n$$

where $R = C_2H_5,\ (CH_3)_2C_6H_5$.

It is interesting to note that, in the case where one of the substituents of the silicon atom is a phenyl radical, $n = 6$, whereas in the case of C_2H_5, $n = 3$.

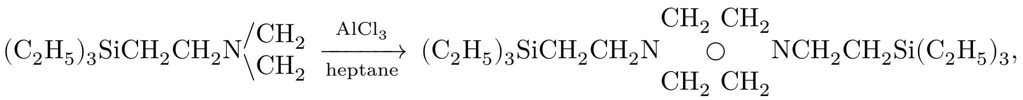
Increasing the temperature and increasing the contact time substantially affect the extent of conversion. This is well illustrated by the data in Table 1.

Table 1

Starting monomer	Temperature, °C	Duration, h	Yield of conversion products, %: dimer	Yield of conversion products, %: polymer
$(C_2H_5)_3SiCH_2CH_2N\begin{smallmatrix}/CH_2\\ \backslash CH_2\end{smallmatrix}$	200	5	–	–
$(C_2H_5)_3SiCH_2CH_2N\begin{smallmatrix}/CH_2\\ \backslash CH_2\end{smallmatrix}$	250	10	24	–
$(C_2H_5)_3SiCH_2CH_2N\begin{smallmatrix}/CH_2\\ \backslash CH_2\end{smallmatrix}$	300	3	35	–
$(C_2H_5)_3SiCH_2CH_2N\begin{smallmatrix}/CH_2\\ \backslash CH_2\end{smallmatrix}$	300	5	50	40
$(CH_3)_2C_6H_5SiCH_2CH_2N\begin{smallmatrix}/CH_2\\ \backslash CH_2\end{smallmatrix}$	250	5	24	66

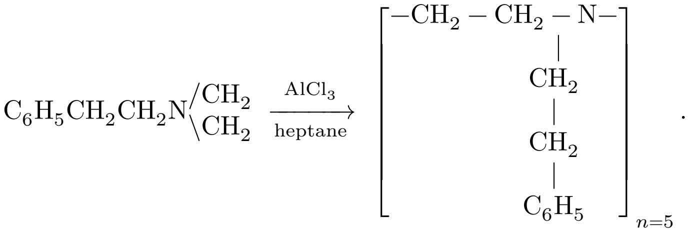
In the presence of nucleophilic reagents, β-(N-ethyleneimino)ethylsilanes give, as the sole conversion product, piperazine derivatives, regardless of the amount of NaJ taken. At the same time, the yield of the corresponding piperazine derivative increases from 22% at a molar ratio β-(N-ethyleneimino)ethylsilane : NaJ = 1 : 0.2 to 50% at a ratio equal to 1 : 1.

In the presence of aluminum chloride, β-(N-ethyleneimino)ethyltriethylsilane in boiling heptane gives the corresponding piperazine derivative in quantitative yield. At the same time, it is known that in the presence of electrophilic reagents, in particular aprotic acids, ethyleneimine polymerizes with opening of the three-membered ring. We believe that the cyclodimerization of β-(N-ethyleneimino)ethyltriethylsilane in the presence of $AlCl_3$ exclusively to piperazine derivatives is explained by a special interaction between the silicon atom and the unshared electron pair of nitrogen. Experiments carried out with β-(N-ethyleneimino)ethylbenzene confirm this point of view. If β-(N-ethyleneimino)ethyltriethylsilane dimerizes in quantitative yield in the presence of $AlCl_3$ to N,N′-bis-ethyl-(β-triethylsilyl)-piperazine,



$$(C_2H_5)_3SiCH_2CH_2N\begin{matrix}/CH_2\\ \backslash CH_2\end{matrix} \xrightarrow[\text{heptane}]{AlCl_3} (C_2H_5)_3SiCH_2CH_2N\begin{matrix}CH_2\ CH_2\\ \bigcirc\\ CH_2\ CH_2\end{matrix}NCH_2CH_2Si(C_2H_5)_3,$$

then β-(N-ethyleneimino)ethylbenzene, where interaction of the unshared pair of nitrogen with the aromatic ring is practically excluded or is manifested only very weakly, gives under identical conditions a polymeric product with ring opening



$$C_6H_5CH_2CH_2N\begin{matrix}/CH_2\\ \backslash CH_2\end{matrix} \xrightarrow[\text{heptane}]{AlCl_3} \left[\begin{matrix}-CH_2-CH_2-N-\\ |\\ CH_2\\ |\\ CH_2\\ |\\ C_6H_5\end{matrix}\right]_{n=5}.$$

Thus, we have shown that the synthesized β-(N-ethyleneimino)ethylsilanes are resistant to β-cleavage under fairly severe temperature conditions (200-300°), as well as under the action of nucleophilic and electrophilic reagents. Under the conditions employed, the principal direction of the transformations is their cyclodimerization into piperazine derivatives.

Experimental Part

Triethyl-, dimethylphenyl-β-(N-ethylenimino)ethylsilanes and β-(N-ethylenimino)ethylbenzene were taken as the objects of study.

Thermal transformations. Triethyl- and dimethylphenyl-β-(N-ethylenimino)ethylsilane were placed in ampoules and kept at the corresponding temperatures (200, 250, 300°) for 3-10 h.

The reaction products were subjected to fractionation and identification.

Transformation in the presence of NaJ. To 0.03 M triethyl-β-(N-ethylenimino)ethylsilane in 50 ml of acetone, 5 g of NaJ was added. The mixture was heated at the boiling temperature of acetone for 5 h. The solvent was distilled off; the residue was extracted with ether and washed with water. The ether layer was dried with K_2CO_3, and after removal of the solvent the product was fractionated in vacuo. The products obtained had the following constants.

1. N,N′-bis-ethyl-(β-triethylsilyl)-piperazine. B.p. 182–183°/1 mm, n_D^{20} 1.4805, d_4^{20} 0.8878. MR_D found 118.16, calculated 118.36. Molecular weight found 366, calculated 370.

Found, %: C 64.89; H 12.20; Si 14.90; N 7.48
$C_{20}H_{46}N_2Si_2$. Calculated, %: C 64.87; H 12.43; Si 15.13; N 7.55

2. N,N′-bis-ethyl-(β-dimethylphenylsilyl)-piperazine. M.p. 31–32°. Molecular weight found 143; calculated 410.

Found, %: C 66.22; H 8.68; Si 13.37; N 6.82
$C_{24}H_{38}N_2Si_2$. Calculated, %: C 66.30; H 9.01; Si 13.51; N 6.93

Transformation of triethyl-β-(N-ethylenimino)ethylsilane and β-(N-ethylenimino)ethylbenzene in the presence of $AlCl_3$.

To 0.03 M triethyl-β-(N-ethylenimino)ethylsilane in 10 ml of heptane, 0.003 M $AlCl_3$ was added. The temperature of the reaction mixture rapidly rose to 35–40°. The reaction mixture was kept at the boiling temperature of heptane for 1 h, filtered, and washed with slightly alkaline water until a neutral reaction for chloride ion was obtained. The solution of the product in heptane was dried with K_2CO_3 and fractionated in vacuo. A fraction with b.p. 194–195°/3.5 mm was obtained in 90% yield.

Molecular weight found 354; n_D^{20} 1.4812; d_4^{20} 0.8872.

Under analogous conditions, the transformation of β-(N-ethylenimino)ethylbenzene was carried out. A polymeric product with molecular weight 692 was obtained.

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Note: Figure translations are in progress. See original paper for figures.