Chemistry

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Fig. 1

Figure 1: Fig. 1

Abstract

Full Text

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ON THE POSSIBILITY OF SYNTHESIZING N-ETHYLENIMINOSILANES BY THE DEHYDROCONDENSATION REACTION

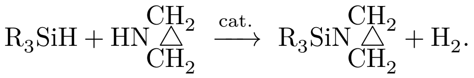
Organosilicon compounds containing a nitrogen—silicon bond, and especially N-ethyleniminosilanes, whose structure contains a strained three-membered heterocycle, are of undoubted theoretical and practical interest. N-ethyleniminosilanes with different structures and different kinds of organic radicals at the silicon atom have been obtained comparatively recently, and information about them is limited to two communications of a patent character ([1], [2]).

Fig. 1

In these patents methods are described for preparing N-ethyleniminosilanes from alkyl-, aryl-, and alkoxychlorosilanes and ethylenimine. The method proposed in the patents is inconvenient in that the hydrogen chloride liberated in the reaction leads to opening of the ethylenimine ring.

We have studied the possibility of using the dehydrocondensation reaction to obtain N-ethyleniminosilanes. This reaction has been investigated for a series of silanes and amines having different structures ([3]). In that work the authors showed that the dehydrocondensation reaction proceeds readily and in high yields for primary amines; secondary amines react with hydrosilanes with much greater difficulty at temperatures of about 200°, while secondary amines with radicals having a branched structure cannot be brought into the reaction at temperatures exceeding 250° and elevated pressure.

Taking into account the high reactivity of the hydrogen atom attached to nitrogen in the three-membered heterocycle of ethylenimine, we assumed that the dehydrocondensation reaction in this case would proceed under considerably milder conditions than in the case of aliphatic secondary amines. In carrying out the experiments, this assumption was fully confirmed. The dehydrocondensation reaction, if ethylenimine is used as the amine, proceeds practically quantitatively (according to the evolved hydrogen) under mild temperature conditions according to the following scheme:



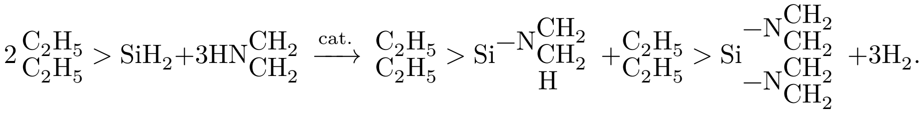
$$R_3SiH + HN\overset{CH_2}{\underset{CH_2}{\triangle}} \xrightarrow{cat.} R_3SiN\overset{CH_2}{\underset{CH_2}{\triangle}} + H_2.$$

Table 1

Physical constants and analytical data of the synthesized compounds

Formula	Boiling point, °C	Melting point, °C	d_4^{20}	n_D^{20}	MR_D, found	MR_D, calc.	Found, % C	Found, % H	Found, % Si	Found, % N	Found, % O	Calculated, % C	Calculated, % H	Calculated, % Si	Calculated, % N	Calculated, % O
$(C_2H_5)_3Si—N\langle CH_2CH_2\rangle$	81.5–83/59 mm		0.8160	1.4430	49.00	48.50	60.70	11.78	17.18	8.89	—	61.21	12.00	17.61	8.92	—
$(C_2H_5)_2CH_3Si—N\langle CH_2CH_2\rangle$	[illegible]/750 mm		[illegible]	[illegible]	[illegible]	44.82	53.73	11.86	19.69	9.19	—	58.70	11.70	19.50	9.70	—
$(C_2H_5)_2HSi—N\langle CH_2CH_2\rangle$ [[unclear: additional "Si" shown above formula]]	[illegible]30/731 mm		[illegible]	[illegible]	[illegible]	40.45	56.21	11.83	19.68	7.82	—	55.80	11.60	20.20	10.08	—
$(C_2H_5)_2Si(N\langle CH_2CH_2\rangle)_2$	67–68/10 mm		[illegible]	[illegible]	50.68	50.34	55.66	10.72	16.85	15.54	—	56.40	10.51	16.40	16.43	—
$CH_3(C_6H_5)_2Si—N\langle CH_2CH_2\rangle$	142–145/4 mm		[illegible]	[illegible]	[illegible]	75.44	75.30	17.15	11.78	5.42	—	75.30	7.40	11.75	5.85	—
$(C_6H_5)_3Si—N\langle CH_2CH_2\rangle$	186/2 mm	104	—	—	—	—	79.80	6.54	9.07	4.50	—	79.85	6.30	9.30	4.55	—
$(C_6H_5CH_2)_2CH_3Si—N\langle CH_2CH_2\rangle$	194–197/2 mm		[illegible]	[illegible]	[illegible]	[illegible]	76.32	7.84	10.36	5.25	—	76.40	7.86	10.48	5.20	—
$C_2H_5(C_2H_5O)_2Si—N\langle CH_2CH_2\rangle$	38/4 mm		[illegible]	[illegible]	[illegible]	[illegible]	50.78	10.31	14.89	7.1	16.92	50.80	10.05	15.80	7.40	16.95
$CH_3(C_2H_5O)_2Si—N\langle CH_2CH_2\rangle$	38/[illegible] mm		[illegible]	[illegible]	[illegible]	46.58	48.13	9.80	15.90	7.98	18.19	48.00	9.72	16.00	8.00	18.28

Alkali metals Li, Na, K were used as catalysts. In the temperature range 0–50°, the reaction took place for all the hydrosilanes taken. The physical constants and analysis of the compounds obtained are given in Table 1. Preservation of the ring in the reaction products is confirmed by the IR spectra of the compounds obtained (Fig. 1)*. Absorption bands were found at 3035, 1271, and 1136 cm^{-1}, characteristic of the ethylenimine ring. The spectra were recorded on an IR-10 spectrophotometer in a 0.005-mm layer. It is interesting that diethylsilane as a result of the reaction gives products of mono- and disubstitution:



$$2\begin{matrix}C_2H_5\\C_2H_5\end{matrix}>SiH_2+3HN\begin{matrix}CH_2\\CH_2\end{matrix}\xrightarrow{cat.}\begin{matrix}C_2H_5\\C_2H_5\end{matrix}>Si-N\begin{matrix}CH_2\\CH_2\\H\end{matrix}+\begin{matrix}C_2H_5\\C_2H_5\end{matrix}>Si\begin{matrix}-N\begin{matrix}CH_2\\CH_2\end{matrix}\\-N\begin{matrix}CH_2\\CH_2\end{matrix}\end{matrix}+3H_2.$$

In the case of phenylsilane, under the conditions we adopted, it was not possible to isolate derivatives containing the ethylenimine ring. This apparently cannot be explained by low stability of the compound obtained, since mention of the preparation of phenyltriethyleniminosilane is found in a patent ([2]).

The results of the experiments show that, in the dehydrocondensation reaction, ethylenimine occupies a special position in comparison with secondary aliphatic and cyclic amines. This is confirmed by experiments carried out with diethyl-, dipropylamine, and piperidine, which under analogous conditions do not enter into the dehydrocondensation reaction with silicon hydride hydrogen. Ethylenimine has reduced basicity, which is explained by participation in conjugation of the unshared electron pair of the nitrogen atom in the three-membered ethylenimine ring. An increase in ring size is accompanied by an increase in the electron density at the heteroatom, which corresponds to a change in the order of basicity ([4–6]).

Using aliphatic amines, piperidine, and ethylenimine as examples, it is clearly seen that a change in basicity corresponds to a change in the reactivity of the above compounds in the dehydrocondensation reaction.

The nature of the substituents at the silicon atom substantially affects the rate of the dehydrocondensation reaction of ethylenimine with hydrosilanes. The rate of the reaction was judged from the amount of hydrogen evolved per unit time at the moment of the maximum, since the reaction proceeds with different induction periods. It turned out that the reaction proceeds at the maximum rate when the substituents are phenyl and benzyl radicals, and at lower rates in the case of aliphatic radicals. The presence of an ethoxy group requires raising the temperature to 50° for the reaction to proceed at a noticeable rate.

Thus, the exceptionally high reactivity of ethylenimine in the dehydrocondensation reaction makes possible the synthesis of N-ethyleniminosilanes in high yields (40–80%). The reaction can be recommended as a preparative one.

Experimental part

All the N-ethyleniminosilanes described in this communication were obtained by the procedure given. Into a reactor equipped with a jacket and connected to a thermostat for removal of the heat formed as a result of the exothermic reaction, a dropping funnel, and a reflux condenser connected to

A hydridesilane (0.1 mole), finely cut lithium (0.2 g-at.), and ethylenimine (0.1 mole) were introduced into a three-necked flask provided with a thermometer, a stirrer, and a gas burette for measuring the hydrogen evolved. The reaction begins slowly, after which a period of rapid development ensues. The relative reaction rates of hydridesilanes of different structures were judged from the amount of hydrogen evolved per unit time at the maximum. After the reaction was complete, the catalyst was filtered off and the reaction mixture was fractionated. The absence of moisture in the starting products is a necessary condition, since moisture sharply reduces the yield of the reaction products.

Experiments with ethoxysilanes were carried out in ordinary flasks at a temperature of 40–50°. The yield of N-ethyleniminosilanes ranged from 40 to 80%.

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CITED LITERATURE

1. Patent GDR, 20 378, 1958.
2. Patent FRG, 834 990, 1952.
3. B. N. Dolgov, N. P. Kharitonov, M. G. Voronkov, ZhOKh, **24**, 678 (1954).
4. M. Tamres, S. Searles, E. M. Leighly, J. Am. Chem. Soc., **76**, 3983 (1954).
5. J. Popl, V. Schneider, G. Bernstein, *High-Resolution Nuclear Magnetic Resonance Spectra*, IL, 1962.
6. H. S. Gutowsky, R. L. Rutledge, M. Tamres, J. Am. Chem. Soc., **76**, 4242 (1954).

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

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* The IR spectra were recorded by V. D. Oppengeim in the laboratory of physical methods of investigation of the Institute of Petrochemical Synthesis, Academy of Sciences of the USSR, Prof. M. M. Kusakov.