Chemistry

Corresponding Member of the Academy of Sciences of the USSR N. S. NAMETKIN,

1965

SovietRxiv

Abstract

Full Text

Chemistry

Corresponding Member of the Academy of Sciences of the USSR N. S. NAMETKIN,
V. N. PERCHENKO, L. G. BATALOVA

THE CYCLODIMERIZATION REACTION OF N-ETHYLENIMINOSILANES

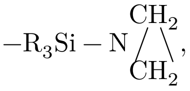
The presence in N-ethyleniminosilanes of a reactive three-membered ring directly bonded to a silicon atom made it possible to expect a number of interesting transformations associated with ring opening. Since the Si—N bond is hydrolytically unstable and is destroyed by the action of acids, alcohols, and certain other compounds possessing various functional groups, we studied the thermal transformations of N-ethyleniminosilanes of different structures.

There are a number of works on the thermal transformations of various ethylenimine derivatives; among these we note the conversion of 1-acetyl-2,2-dimethylethylenimine at a temperature of about 160° into N-(β-metallyl)acetamide (⁀1). It is interesting to note that, under the same conditions, 2,2-dimethylethylenimine remained unchanged upon prolonged heating. At a temperature of 240°, 1-benzoylethylenimine is converted mainly into 2-phenyl-2-oxazoline (⁀2). Also of interest is the conversion of 1-(p-bromobenzenesulfonyl)-2,2-dimethylaziridine into p-bromobenzenesulfonamide (⁀3). From the known works on the thermal transformations of ethylenimine derivatives it is difficult to establish regularities in the direction of the transformations occurring; however, there is no doubt that these transformations proceed with cleavage of the C—N bond in the three-membered ring.

We have shown that ethylenimine itself at a temperature of 250° also undergoes transformations with the formation of small amounts of piperazine and polymeric products.

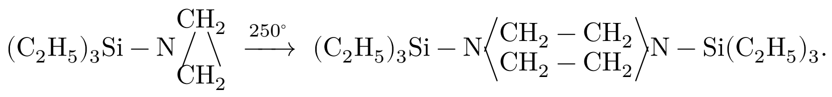
In this connection it seemed of interest to study analogous transformations of the N-ethyleniminosilanes described by us previously (⁀4).

The present communication is devoted to the thermal transformations of N-ethyleniminosilanes,



$$-R_3Si-N\begin{matrix}CH_2\\ / \quad \backslash\\ CH_2\end{matrix},$$

where R denotes various radicals: aliphatic, aromatic, alkoxyl, and mixed. The experiments were carried out at temperatures of 200, 250, and 300° in sealed ampoules. Triethylethyleniminosilane at a temperature of 250° undergoes transformations that lead to the formation of N,N′-bis-(triethylsilyl)piperazine



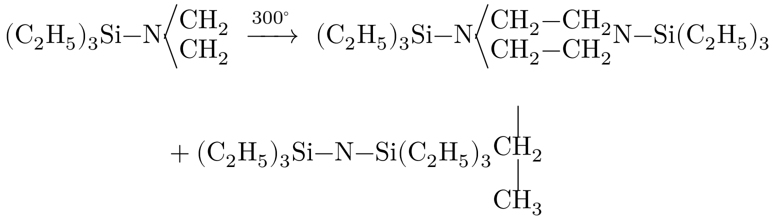
To prove the structure of the compound obtained, N,N′-bis-(triethylsilyl)piperazine was prepared by a counter synthesis (dehydrocondensation reaction) from triethylsilane and piperazine in the presence of metallic potassium; its physicochemical properties coincide with those of the product isolated from the reaction mixture after five hours of heating of triethylethyleniminosilane.

Under analogous conditions, dimethylphenyl-, methyl-

diphenyl-, methyldibenzyl-, diethylphenyl- and ethyldiethoxy-ethyleniminosilanes. Introduction of platinized charcoal into the reaction mixture does not lead to substantial changes in the yields of N,N′-bis-silyl-substituted piperazines, whereas with addition of azodiisobutyric acid dinitrile it proved possible, already at 200°, to obtain the cyclodimerization product in 30% yield based on the starting material.

The nature of the radicals at the silicon atom has a substantial effect on the yields of the cyclodimerization products. Triethylethyleniminosilane, heated at 250° for 5 h, is converted into N,N′-bis-(triethylsilyl)piperazine in 25% yield; diethylphenylethyleniminosilane gives a yield of 40%, whereas ethyldiethoxyethyleniminosilane under these conditions undergoes no change.

Triethylethyleniminosilane at 300°, in addition to N,N′-bis-(triethylsilyl)piperazine, forms N,N-bis-(triethylsilyl)ethylamine and products of more profound transformation



The presence of condensation products and of N,N-bis-(triethylsilyl)ethylamine gives grounds to assume that saturation proceeds at the expense of hydrogen disproportionation reactions. It is interesting to note that triethylethyleniminosilane, in the presence of triethylsilane, which is a reducing agent, gives N,N-bis-(triethylsilyl)ethylamine only at the expense of triethylsilyl–

Table 1

NN′-bis-(silyl)piperazines

Compounds	B.p., °C/mm	M.p., °C	d_4^{20}	n_D^{20}	MR_D, found	MR_D, calc.	Yield, %	Si, %, found	Si, %, calc.
$(C_2H_5)_3Si—N(CH_2CH_2)_2N—Si(C_2H_5)_3$	146–148/4		0.8905	1.4740	98.51	98.66	25	17.31	17.83
$(C_6H_5)(C_2H_5)(CH_3)Si—N(CH_2CH_2)_2N—Si(CH_3)(C_2H_5)(C_6H_5)$	220/5	121					60	11.90	11.70
$(C_6H_5)(CH_3)_2Si—N(CH_2CH_2)_2N—Si(CH_3)_2(C_6H_5)$	133–136/3.5		1.0045	1.5480	110.57	110.24	50	15.42	15.80
$(C_6H_5)(C_2H_5)_2Si—N(CH_2CH_2)_2N—Si(C_2H_5)_2(C_6H_5)$	193–200/5		1.9990	1.5413	128.91	129.28	40	–	13.66
$(C_6H_5CH_2)(CH_3)(C_6H_5)Si—N(CH_2CH_2)_2N—Si(CH_2C_6H_5)(CH_3)(CH_2C_6H_5)$	215–220/1.5		1.0383	1.5670	168.24	168.59	30	10.40	10.53
$[(C_2H_5)_3Si]_2N—CH_2—CH_3$	135–137/5		0.8620	1.4625	87.42	87.72	25	20.12	20.51

···of ethyleniminosilane. Triethylsilane is quantitatively distilled off from the reaction mixture, and the reaction products are N,N′-bis-(triethylsilyl)-piperazine and NN-bis-(triethylsilyl)-ethylamine.

Thus, we have shown that the cyclodimerization reaction of N-substituted ethylenimines can proceed not only in the presence of acid catalysts and nucleophilic agents, but also under thermal action.

The transformations of the named N-ethyleniminosilanes were carried out under analogous conditions. The N-ethyleniminosilanes were heated in sealed ampoules for 5 h at a temperature of 250-300°. The NN′-bis-(silyl)-piperazines were isolated from the reaction mixture by fractionation in vacuo. The characteristics of the products obtained are given in Table 1.

Institute of Petrochemical Synthesis
named after A. V. Topchiev
Academy of Sciences of the USSR

Received
25 IX 1964

REFERENCES

1. P. E. Fanta, A. S. Deutsch, *J. Org. Chem.*, **23**, 72 (1958).
2. H. W. Heine, *Angew. Chem.*, **74**, 772 (1962).
3. D. V. Kashelikar, P. E. Fanta, *J. Org. Chem.*, **26**, 1841 (1961).

4. N. S. Nametkin, V. N. Perchenko, L. G. Batalova, *DAN*, **158**, No. 3 (1964).

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

Source: Math-Net.Ru and CyberLeninka. Machine translation. Verify with the original.