Chemistry

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1964

SovietRxiv

Abstract

Full Text

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On the Mechanism of Rearrangements of Dimethylcyclosilazanes

It was established by one of us, jointly with other authors, that dimethylcyclosilazanes rearrange with ring expansion under the action of hydrogen chloride ([1]) and sulfuric acid ([2]). Our experiments showed that, depending on the conditions, under the action of sulfuric acid on the rings the rearrangement also proceeds with ring contraction:

$$\text{cyclic dimethylsilazane trimer} \overset{\text{HX}^*}{\rightleftharpoons} \text{cyclic dimethylsilazane tetramer}$$

The reaction proceeds with opening of the rings:

1) $$\text{cyclic dimethylsilazane trimer} + \text{HX} \longrightarrow \text{ring-opened compound containing Si—X and Si—NH}_2 \text{ groups}$$

2) $$\text{ring-opened compound containing Si—X and Si—NH}_2 \text{ groups} + \text{HX} \longrightarrow \text{silazane fragments containing}$$

In the course of the rearrangement it is not possible to isolate intermediate products and, consequently, to confirm the reaction between the compounds formed, containing

$$\text{Si—X} \quad \text{and} \quad \text{Si—NH}_2$$

groups.

To elucidate the mechanism of the rearrangement reactions, experiments were carried out in which, using trimethylchlorosilane and triethylaminosilane as models of the intermediate products, the possibility of reactions of the indicated groups was shown. Trimethylchlorosilane reacts with triethylaminosilane according to the reaction:

$$(CH_3)_3SiCl+3(C_2H_5)_3SiNH_2 \rightarrow (CH_3)_3Si{-}NH{-}Si(C_2H_5)_3+(C_2H_5)_3SiNHSi(C_2H_5)_3+NH_4Cl \quad \text{(I)}$$

with the formation of 1-trimethyl-3-triethyldisilazane, hexaethyldisilazane, and NH_4Cl. The yield of 1-trimethyl-3-triethyldisilazane was 68%.

The formation of 1-trimethyl-3-triethyldisilazane serves as confirmation of the recombination of intermediate compounds in the indicated rearrangement reaction–

* X is the residue of hydrochloric or sulfuric acid.

group. Similar results were obtained also to confirm the mechanism of rearrangements of dimethylcyclosilazanes under the action of H_2SO_4. Bis(trimethylsilyl) sulfate reacts with triethylaminosilane according to the reaction:

$$[(CH_3)_3SiO]_2SO_2 + 6(C_2H_5)_3SiNH_2 \rightarrow 2(CH_3)_3SiNHSi(C_2H_5)_3+ \\ +2(C_2H_5)_3Si-NH-Si(C_2H_5)_3 + (NH_4)_2SO_4 \quad \text{(II)}$$

with formation of 28% 1-trimethyl-3-triethyldisilazane.

To confirm its structure, 1-trimethyl-3-triethyldisilazane was obtained by an independent synthesis from trimethyl- and triethylchlorosilane by joint ammonolysis.

Experimental Part

1) Coammonolysis of trimethylchlorosilane and triethylchlorosilane

a. In liquid ammonia. 10.86 g of trimethylchlorosilane and 15.06 g of triethylaminosilane, dissolved in ether, were added to liquid ammonia; the excess ammonia was evaporated. The precipitate of ammonium chloride was filtered off and washed with ether. Weight of precipitate 10.7 g (100%). Ether and a fraction with b.p. 125–170°, n_D^{20} 1.4275, amounting to 1.7 g, were distilled from the reaction product, after which distillation was carried out at atmospheric pressure and in vacuo, yielding 17.5 g of substance with b.p. 181–200° or 93°/30 mm Hg, n_D^{20} 1.4360.

Found, %: C 53.35, 53.26; H 12.26, 12.17; Si 26.96, 27.12;
N 6.79, 6.81

$(CH_3)_3SiNHSi(C_2H_5)_3$. Calculated, %: C 53.2; H 12.3; Si 27.6; N 6.9

Yield 86.1%.

b. In benzene. Gaseous ammonia was passed through a solution of 41.3 g (0.38 mole) of trimethylchlorosilane and 57.2 g (0.38 mole) of triethylchlorosilane in benzene. After completion of the reaction, the NH_4Cl precipitate was separated by filtration. After distilling off the solvent, intermediate reaction products were isolated—mainly hexamethyldisilazane and triethylaminosilane. The boiling point of this fraction was 100-160°, amount 22.4 g. The residue, 55.7 g, was distilled in vacuo.

Table 1

Fraction No.	B.p., °C	Weight, g	n_D^{20}
1	45-70°/15 mm Hg	4.3	1.4302
2	70-76.5/13 mm Hg	8.3	1.4339
3	76.5/13 mm Hg	16.6	1.4349
4	76.5-95/13 mm Hg	11.1	1.4354
5	95-135/11 mm Hg	13.1	1.4491
6	Still residue	2.3	

After repeated distillation of fractions Nos. 1, 2, and 4, an additional 15.9 g of substance with b.p. 72-75°/11-13 mm Hg, n_D^{20} 1.4346, d_4^{20} 0.8200, was isolated.

Found, %: C 53.97; H 13.1, 12.7; N 6.45, 6.7

$(CH_3)_3SiNHSi(C_2H_5)_3$. Calculated, %: C 53.2; H 12.3; N 6.9

Yield 41.7%. MR found 64.56, calculated 65.31.

2) Trimethylchlorosilane and triethylaminosilane

To 6.07 g (0.056 mole) of trimethylchlorosilane, with stirring, 22.0 g (0.168 mole) of triethylaminosilane was added. The reaction mixture was filtered from the ammonium chloride precipitate without washing. Weight of dry precipitate 1.7 g (56.8%). The filtrate, 19.7 g (79%), was distilled, giving 5.4 g of substance with b.p. 132-157°, n_D^{20} 1.4292—predominantly the starting triethylaminosilane; 7.07 g (68%) of substance with b.p. 185-199°, n_D^{20} 1.4355, which by boiling point and refractive index corresponds to the trimethyltriethyldisilazane isolated earlier; and 5.96 g (77%, based on the amount of NH_4Cl) of hexaethyldisilazane (n_D^{20} 1.4482).

3) Bis(trimethylsilyl) sulfate and triethylaminosilane

To 3.1 g (0.0128 mole) of bis(trimethylsilyl) sulfate was added

10 g (0.0765 mole) of triethylaminosilane. After stirring for one hour, the ammonium sulfate precipitate was filtered off without washing. 8.25 g (70.6%) of the filtrate was distilled, yielding 1.46 g (28%) of a liquid with b.p. 70-73°/10-12 mm Hg and n_D^{20} 1.4326, which, judging from its boiling point and refractive

index, consists predominantly of the previously isolated trimethyltriethyldisilazane, and 6.3 g (97%) of a liquid with b.p. 140-170°/7-10 mm Hg and n_D^{20} 1.4480—predominantly hexazethyldisilazane.

Institute of Organoelement Compounds
Academy of Sciences of the USSR

Received
18 II 1964

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