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Abstract

Full Text

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On Rearrangements of Hexamethyl- and Octamethylcyclosilazanes

There are no data in the literature on rearrangements of organocyclosilazanes. We found that in the series of dimethylcyclosilazanes a rearrangement is observed with a change in the silicon-nitrogen framework of the molecules. Thus, for example, when hexamethylcyclotrisilazane is acted upon by trimethylchlorosilane and ammonia, ring expansion already occurs at 20–40°. Along with the normal reaction products, namely octamethyltrisilazane and a polymer (with a molecular weight of about 2000), which is formed in an amount of 12.3 and 18.9% of the high-boiling reaction products, 36.5% of octamethylcyclotetrasilazane is formed:

$$\text{[Hexamethylcyclotrisilazane structure]}$$
$$+(CH_3)_3SiCl + NH_3 \longrightarrow$$

$$\longrightarrow (CH_3)_3SiNHSi(CH_3)_2NHSi(CH_3)_3 + \text{[Octamethylcyclotetrasilazane structure]} + \text{polymers}$$

When hexamethylcyclotrisilazane is heated for 48 hr at 250° in the presence of ammonium chloride, about 3% octamethylcyclotetrasilazane is formed.

The rearrangement reaction in the presence of trimethylchlorosilane and ammonia, or of ammonium chloride, may be represented as follows: under the conditions of our experiments, hydrogen chloride is formed upon the action of ammonia on trimethylchlorosilane, or as a result of the thermal dissociation of ammonium chloride. Hydrogen chloride, acting on the silicon-nitrogen bond, opens the ring:

$$\text{[Hexamethylcyclotrisilazane structure]} + HCl \rightleftharpoons$$
$$\text{[Chlorinated linear intermediate structure]}$$

Ammonia reacts with chlorine bound to silicon

$$\text{chlorinated hexamethylcyclotrisilazane derivative} + NH_3 \rightleftarrows$$
$$\text{amino hexamethylcyclotrisilazane derivative} + HCl.$$

Thus hydrogen chloride is regenerated, which cleaves the silicon–nitrogen bond according to the scheme:

$$\text{amino hexamethylcyclotrisilazane derivative} + \text{HCl} \rightleftarrows$$
$$\text{chlorosilyl- and aminosilyl-containing linear intermediates}$$
$$\text{or}$$
$$\text{chlorosilyl- and aminosilyl-containing cyclic intermediates.}$$

The intermediate compounds formed as a result of recombination give both hexamethylcyclotrisilazane and octamethylcyclotetrasilazane. The same result was obtained when hexamethylcyclotrisilazane was treated with triethylmethylammonium iodide at 300°.

An analogous rearrangement reaction with ring expansion was also observed by us when hexamethylcyclotrisilazane was treated with catalytic amounts of caustic potash at 160°. A small amount of octamethylcyclotetrasilazane was isolated. It is of special interest to note that, on heating octamethylcyclotetrasilazane with catalytic amounts of ammonium chloride at 280°, rearrangement with ring contraction occurs, and hexamethylcyclotrisilazane is formed in low yield:

$$3\,\text{octamethylcyclotetrasilazane} \xrightarrow{\text{NH}_4\text{Cl}} 4\,\text{hexamethylcyclotrisilazane.}$$

Rearrangement with ring contraction also occurs when octamethylcyclotetrasilazane is treated with aniline at 250–300°. Here, along with the transamination reaction, rearrangement also takes place, and about 20% of tri-*N*-phenylhexamethylcyclotrisilazane is formed:

$$3\,\text{octamethylcyclotetrasilazane} + 12\,\text{C}_6\text{H}_5\text{NH}_2 \rightarrow 4\,\text{tri-}N\text{-phenylhexamethylcyclotrisilazane} + 12\,\text{NH}_3.$$

The experimental conditions are given in Table 1.

Experimental Part

1. Aminolysis of trimethylchlorosilane in a solution of hexamethylcyclotrisilazane. In 65.4 g (0.3 g-mol) of hexamethylcyclotrisilazane, 7 ml (0.06 g-mol) of trimethylchlorosilane was dissolved.

With vigorous stirring, dry ammonia was introduced. During the reaction a white precipitate separated. The reaction mixture was filtered. On washing with petroleum ether, part of the precipitate dissolved. After evaporation of the resulting solution, 5.8 g (8.3%) of a crystalline substance with m.p. 96° was obtained. The filtrate was distilled, collecting fractions: 165–180°, 1.50 g, 28%,

n_D^{20} 1.4300, corresponding to octamethyltrisilazane; 180–188°, 17.73 g, 33.6%, n_D^{20} 1.4443. From the residue 14.9 g (28.3%) of a crystalline substance with m.p. 96° was isolated. After removal of volatiles up to 250°, 6.5 g (12.3%) of a light-yellow, vaseline-like product with an average molecular weight of 2000 remained.

2. **Heating hexamethylcyclotrisilazane with ammonium chloride.** 21.9 g (0.1 g-mol) of hexamethylcyclotrisilazane and 0.1 g of ammonium chloride were heated for 48 h at 220–250°. After heating, 0.65 g of crystals with m.p. 96° was isolated.

3. **Heating hexamethylcyclotrisilazane with triethylmethylammonium iodide.** 21.9 g (0.1 g-mol) of hexamethylcyclotrisilazane and 0.1 g of triethylmethylammonium iodide were heated for 17 h at 300°. After heating, 0.8 g of crystals with m.p. 96° was isolated.

Table 1

Starting substance	Reagents	Reaction duration, h	Reaction temp., °C	Rearrangement product	M.p., °C	n_D^{20}	Literature data
$[(CH_3)_2SiNH]_3$	$(CH_3)_3SiCl+NH_3$		20–40	$[(CH_3)_2SiNH]_4$	96		97° (1)
$[(CH_3)_2SiNH]_3$	NH_4Cl	48	220–250	$[(CH_3)_2SiNH]_4$	96		97°
$[(CH_3)_2SiNH]_3$	$[(C_2H_5)_3N]I\cdot CH_3$	17	300	$[(CH_3)_2SiNH]_4$	96		97°
$[(CH_3)_2SiNH]_3$	KOH	216	160	$[(CH_3)_2SiNH]_4$	96		97°
$[(CH_3)_2SiNH]_4$	$C_6H_5NH_2$	24	300	$[(CH_3)_2SiNC_6H_5]_3$	248–249		249–250° (2)
$[(CH_3)_2SiNH]_4$	NH_4Cl	72	300	$[(CH_3)_2SiNH]_3$	b.p. 186–188	1.4436	188°, (1) 1.4448

4. **Heating hexamethylcyclotrisilazane with caustic potash.** 10.0 g of hexamethylcyclotrisilazane and 0.1 g of caustic potash were heated for 216 h at 160°. The reaction mixture was dissolved in petroleum ether, filtered, and evaporated. 4.9 g of tricyclotridecamethylheptasilazane and 0.1 g of crystals with m.p. 96° were isolated.

5. **Heating octamethylcyclotetrasilazane with aniline.** 29.2 g (0.1 g-mol) of octamethylcyclotetrasilazane and 18.6 g (0.2 g-mol) of aniline were heated for 24 h at 300°. The reaction mixture was distilled; from the distillate, 5.8 g of crystals with m.p. 248–249° was isolated.

Found, %: C 64.47, 64.37; H 7.87, 7.92; Si 18.65, 19.02; N 10.78, 10.75. $C_{24}H_{33}Si_3N_3$. Calculated, %: C 64.38; H 7.43; Si 18.80; N 9.38.

For tri-*N*-phenylhexamethylcyclotrisilazane, $C_{24}H_{33}Si_3N_3$, calculated, %: C 64.38; H 7.43; Si 18.80; N 9.38.

6. **Heating octamethylcyclotetrasilazane with ammonium chloride.** 5 g of octamethylcyclotetrasilazane and 0.1 g of ammonium chloride were heated for 72 h at 300°. After cooling, a drop of liquid with n_D^{20} 1.4436 was pressed out.

29.2 g (0.1 g-mol) of octamethylcyclotetrasilazane, 1.6 g (0.01 g-mol) of hexamethylcyclotrisilazane, and 0.5 g of ammonium chloride were heated for 48 h at 245°. From the reaction mixture 2.52 g of liquid with b.p. 186–188° and n_D^{20} 1.4436 was distilled off.

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