SYNTHESIS OF ORGANOCYCLOSILOXANES CONTAINING CYANOALKYL GROUPS ON THE SILICON ATOM

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The cohydrolysis of β-cyanoethyl- and γ-cyanopropylmethyldichlorosilanes with dimethyldichlorosilane has been studied and the optimum conditions ensuring the maximum yield of rings containing cyanoalkyl groups have been determined.

Bis(β-cyanoethyl)hexamethylcyclotetrasiloxane, γ-cyanopropylpentamethylcyclotetrasiloxane, and bis(γ-cyanopropyl)hexamethylcyclotetrasiloxane have been obtained for the first time and characterized.

Recently, great attention has been devoted to polydimethylisiloxane polymers containing cyanoalkyl groups attached to the silicon atoms [1–3]. The main advantage of these polymers, due to the presence of the strongly polar nitrile group, is their resistance to the action of solvents.

In the literature there is only one paper on the preparation of β-cyanoethylpentamethylcyclotetrasiloxane [4] by the cohydrolysis of β-cyanoethylmethyldichlorosilane with dimethyldichlorosilane in low yield (6.6%).

In the present work, an attempt has been made to synthesize cyclodimethylsiloxanes containing a nitrile group in the β- and γ-positions to the silicon atom, and the conditions affecting their yield have also been studied. The method of synthesis was based on the combined hydrolysis with water and sulfuric acid in the presence of a solvent of the bifunctional monomers.

$$m(CH_3)_2SiCl_2+nR(CH_3)SiCl_2+2(m+n)H_2O\rightarrow$$
$$[(CH_2)_2SiO]_m[(CH_3)RSiO]_n+2(m+n)HCl,$$
$$R=CH_2CH_2CN \text{ or } CH_2CH_2CH_2CN,$$
$$\text{and } m=1, 2, 3 \text{ or } 5, \; n=1.$$

The cohydrolysis of β-cyanoethylmethyldichlorosilane with dimethyldichlorosilane (I) gave a complex mixture of cyclic compounds (with approximately eight components) from which as yet only β-cyanoethylpentamethylcyclotetrasiloxane and bis(β-cyanoethyl) hexamethylcyclotetrasiloxane, identified for the first time, have been isolated. The cohydrolysis of γ-cyanopropylmethyldichlorosilane with I similarly gave a complex mixture of about eight cyclic compounds from which γ-cyanopropylpentamethylcyclotetrasiloxane and bis(γ-cyanopropyl)hexamethylcyclotetrasiloxane were isolated for the first time. The cyclic substances isolated are clear liquids that distill without decomposition and are readily soluble in ether, benzene, toluene, chloroform, and acetone; their properties are given in Table 1.

The structures of β-cyanoethylpentamethylcyclotetrasiloxane (II), bis(β-cyanoethyl)hexamethylcyclotetrasiloxane (III), γ-cyanopropylheptamethylcyclotetrasiloxane (IV), and bis(γ-cyanopropyl)hexamethylcyclotetrasiloxane (V) were established from the results of elementary analysis, molecular weight, molecular refraction, and IR spectra. The IR-spectroscopic data are given in Table 2.

It can be seen from Table 2 that in all the compounds there are characteristic frequencies corresponding to the vibration of the following bonds: Si—O in an eight-membered ring, Si—CH_3, and C≡N.

A study of the conditions affecting the yield of the cyclotetrasiloxanes containing nitrile groups in the γ position has shown that a change in the ratio in the cohydrolysis of I with γ-cyanopropylmethyldichlorosilane from 5 : 1 to 1 : 1, respectively, decreases the total yield of cyclosiloxanes containing γ-cyanopropyl groups, the equilibrium of the reaction shifting in the direction of the formation of bis(γ-cyanopropyl)hexamethylcyclotetrasiloxane. A fivefold increase in the concentration of the solvent, however, greatly increase the yields of cyclotetrasiloxanes. The replacement of ether by toluene lowers the yield of cyclosiloxanes somewhat. The temperature of cohydrolysis has a considerable influence on the yield of cyclotetrasiloxanes. Thus, when the temperature is raised from 0–2 to 36° C, the yield of cyclotetrasiloxanes containing γ-cyanopropyl groups rises from 60.9 to 79.1%. The results obtained show that the achieve the maximum yield of cyclotetrasiloxanes containing cyanoalkyl groups the cohydrolysis must be carried out in ether at ~36° C.

Table 2

Characteristic Bond Frequencies

Compound	Formula	Characteristic frequencies, cm^{-1}		
		Si—O in an eight-membered ring	Si—CH_3	C≡N
II	$[(CH_3)_2SiO]_3[NCCH_2CH_2(CH_3)SiO]$	1080	1278	2251
III	$[(CH_3)_2SiO]_2[NCCH_2CH_2(CH_3)SiO]_2$	1080	820, 1270	2242
IV	$[(CH_3)_2SiO]_3[NCCH_2CH_2CH_2(CH_3)SiO]$	1090	822	2255
V	$[(CH_3)_2SiO]_2[NCCH_2CH_2CH_2(CH_3)SiO]_2$	1085	822, 1268	2250

Table 1

Physical Properties of the Cyanoalkyltetrasiloxanes

Compound	Formula	Bp, °C (pressure, mm)	d_4^{20}	n_D^{20}	MR_D		M	
					found	calculated	found	calculated
β-Cyanoethylpentamethylcyclotetrasiloxane (II)	$[(CH_3)_2SiO]_3[NCCH_2CH_2(CH_3)SiO]$	93(2)	1.012	1.4190	83.56	83.40	340.1	335
Bis(β-cyanoethyl)hexamethylcyclotetrasiloxane (III)	$[(CH_3)_2SiO]_2[NCCH_2CH_2(CH_3)SiO]_2$	156(2)	1.055	1.4346	92.58	92.23	379.8	374
γ-Cyanopropylpentamethylcyclotetrasiloxane (IV)	$[(CH_3)_2SiO]_3[NCCH_2CH_2CH_2(CH_3SiO]$	120.5(4.5)	1.003	1.4201	88.09	88.20	353	349
Bis(γ-cyanopropyl)hexamethylcyclotetrasiloxane (V)	$[(CH_3)_2SiO]_2[NCCH_2CH_2CH_2(CH_3SiO]_2$	195(4.5)	1.034	1.4370	101.86	101.84	408	402

EXPERIMENTAL

Cohydrolysis of dimethyldichlorosilane with β-cyanoethylmethyldichlorosilane. A hydrolyzer fitted with a stirrer, dropping funnel, and thermometer was charged with 1 *l* of diethyl ether and 1 *l* of water. The mixture was cooled to 0° C and a mixture of 197.5 g (1.15 mole) of β-cyanoethylmethyldichlorosilane and 297.0 g (2.3 mole) of dimethyldichlorosilane was added to it in drops at a rate such that the temperature of the reaction mixture remained at about 0° C. After the completion of the addition, the reaction mixture was stirred for an additional 40 min at ~0° C. The acidic aqueous layer was separated from the ethereal layer and the latter was washed with cooled distilled water to neutrality. The ethereal solution of the cohydrolyzate was dried over calcined $CaCl_2$. The ether was distilled off and the residue was freed from volatile substances in a vacuum of 20 mm at 70° C. The cohydrolysis yield was 284.8 g (94%).

By repeated fractionation, the following fractions were isolated: octamethylcyclotetrasiloxane with bp 74–75° C (20 mm), yield 18%; β-cyanoethylpentamethylcyclotetrasiloxane with bp 93° C (2 mm), yield 31%. Found, %: Si 33.60, 33.60; N 4.80, 4.60. Calculated for $C_{10}H_{25}Si_4O_4N$, %: Si 33.43; N 4.18.

Bis(β-cyanoethyl)hexamethylcycloetetrasiloxane with bp 156° C (2 mm), yield 30%. Found, %: C 38.37, 38.72; Si 30.85, 30.63; H 7.1, 7.34; N 7.66, 7.71. Calculated for $C_{12}H_{26}Si_4O_4N_2$, %: C 38.50; Si 30.00; H 6.96; N 7.54.

Cohydrolysis of dimethyldichlorosilane with γ-cyanopropylmethyldichlorosilane at an elevated temperature. A hydrolyzer fitted with a stirrer, dropping funnel, and thermometer was charged with 1100 ml of ether and 440 ml of water. Over an hour a mixture of 91 g (0.05 mole) of γ-cyanopropylmethyldichlorosilane and 129 g (1 mole) of dimethyldichlorosilane was added dropwise to the reaction mixture heated to 36° C, the temperature in the hydrolyzer being kept at this figure. After the end of the addition, the reaction mixture was stirred additionally for 40 min at the same temperature and immediately afterwards the acidic aqueous layer was separated from the ethereal layer. The latter was washed to neutrality with distilled water. The ethereal solution of the cohydrolyzate was dried over calcined $CaCl_2$. The ether was driven off at 60° C and the volatile materials at 70° C (20 mm). The yield of cohydrolyzate was 117.6 g (85.5%).

Fractionation gave the following fractions:

Octamethyltetrasiloxane with bp 74.5–75° C (20 mm), yield 7.6%;

γ-Cyanopropylpentamethylcyclotetrasiloxane with bp 120.5° C (4.5) mm), yield 39.1%. Found, %: C 37.90, 37.62; H 7.83, 8.14; N 4.00, 4.11. Calculated for $C_{11}H_{27}Si_4O_4N$, %: C37.82; H 7.75; N 4.02.

Bis(γ-cyanopropyl)hexamethylcyclotetrasiloxane with bp 195° C (4.5 mm), yield 40.0%. Found %: Si 27.60; 27.90; N 6.95; 7.02. Calculated for $C_{14}H_{30}Si_4O_4N_2$, %: Si 27.86; N 6.96.

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