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Synthesis of (Methyl-β-cyanoethyl)cyclosiloxanes

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Abstract—Previously unknown (methyl-β-cyanoethyl)tri-, -tetra-, and -pentacyclosiloxanes were prepared by oxygen–halogen exchange between silicon and tin. The ^{29}Si NMR spectra of the products were measured and interpreted.

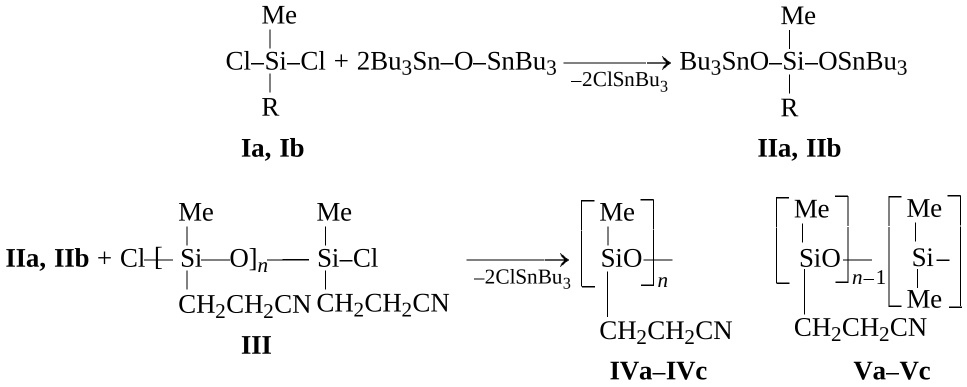
The polarity of organosilicon polymers can be substantially increased by introducing a nitrile group. The polarity of such polymers allows their use as polar dielectrics in variable-capacity condensers and in gas–liquid chromatography, and also as conducting contact lubricants. However, successful syntheses of methyl-β-cyanoethylsiloxane homopolymers have not been reported; only oligomers with the degree of polymerization of up to 20 have been prepared. This is due to sensitivity of the nitrile group to both base and acid agents [1], as the main route to polysiloxanes is acid- or base-catalyzed hydrolysis of diorganodichlorosilanes [2]. Polymerization of appropriate cyclosiloxanes could be an alternative route to such polymers [3], but the required cyclosiloxanes are unknown. Only cyclosiloxanes with one methyl-β-cyanoethylsilane unit in the ring have been prepared, with the other silicon atoms bearing two methyl groups. Isolation of pure products from the reaction mixture appears to be impossible because of close boiling points of the components and their large number [4]. The report [5] on the synthesis of (methyl-β-cyanoethyl)tetracyclosiloxanes seems to be erroneous, since formation of a precipitate in the liquid phase, identified in [5] as tetramethyltetrakis(β-cyanoethyl)cyclotetrasiloxane, suggests, according to our studies, transformations of the nitrile group rather than isolation of a particular isomer (e.g., *eeee*). The occurrence of such transformations is indicated by the appearance of the amide absorption band (ν 1640–1680 cm^{-1}) in the IR spectrum of the reaction mixture. Therefore, it is necessary to look for new routes to (methyl-β-cyanoethyl)cyclosiloxanes ensuring the stability of the methyl group and allowing preparation of a definite cyclosiloxane rather than an inseparable mixture of products.

In construction of the Si–O–Si fragments from appropriate dichlorosilanes, we suggest to use organodistannoxanes as the sources of oxygen. This route allows the reactions to be performed under homogeneous conditions at moderate temperatures. The method is based on relatively easy elimination of trialkylchlorostannane upon oxygen–halogen exchange between silicon, germanium, and tin; in this series, silicon exhibits the greatest affinity for oxygen [6]. Using this method, Winkelhofer *et al.* [7] prepared various heterosilsesquioxanes, and Veith *et al.* [8], amino- and chloro-substituted spirocyclosiloxanesilazanes.

Our synthesis scheme is shown below.

In both stages of cyclosiloxane synthesis, the yields are quite acceptable (70–80%). To exclude formation of oligomers, we performed the second stage in dilute solutions. The possibility of recovering tributylchlorostannane and reusing it for the synthesis of hexabutyldistannoxane [9] is also an advantage of the suggested procedure.

As a result, we prepared and characterized six new diorganocyclosiloxanes. Their structure was confirmed by ^{29}Si NMR spectroscopy (Fig. 1). Replacement of the CH_3 group by the CH_2CH_2CN group causes an upfield shift of the ^{29}Si signal. It is known that the decisive factor affecting the ^{29}Si resonance in siloxanes is the inductive effect of substituents at the Si atoms [10]. Owing to conjugation between the silicon and oxygen atoms, this influence is efficiently transferred to the α- and β-positions of the siloxane ring. The ^{29}Si NMR spectrum of (methyl-β-cyanoethyl)cyclotrisiloxane **IVa** consists of two signals (–10.56 and –10.64 ppm). Two signals (intensity ratio 1 : 2) are also observed in the spectrum of tetramethylbis-β-cyanoethyltrisiloxane **Va** (–11.36 and –11.48 ppm). The downfield signal apparently belongs to group D [D = $(CH_3)_2SiO$]. The ^{29}Si NMR spectra of the tetrasiloxanes (Fig. 1b) are more complex. Tetramethyltetrakis-β-cyanoethylcyclotetrasiloxane **IVb** is a mixture of four isomers (**A**, *eeee*; **B**, *aeee*, **C**, *aaee;* and **D**, *aeae*).



I, II, R = Me (**a**), CH_2CH_2CN (**b**); **III**, n = 1–3; **IV, V**, n = 3 (**a**), 4 (**b**), 5 (**c**).

According to the additive scheme suggested in [10], the spectrum should contain six lines belonging to the following isomers (counting upfield): **B**, **D**, **C**, **B**, **A**, **B**. Indeed, six signals are observed: –21.06, –21.11, –21.16, –21.25, –21.36, and –21.40 ppm.

The ^{29}Si NMR spectrum of the trisubstituted cyclotetrasiloxane N_3D **Vb** [N = $CH_3(CH_2CH_2CN)SiO$] is much more complicated. This compound exists as a mixture of three geometric isomers: **A**, *eee*; **B**, *eae*; and **C**, *aee*. Correspondingly, in the ^{29}Si NMR spectrum fragment D gives three signals of different intensities: –16.14 (**C**), –17.53 (**A**), and –17.62 ppm (**B**). The signals were assigned according to [10]. Fragment N gives four signals (–20.04, –20.59, –22.25, and –22.45 ppm) whose assignment is difficult.

The ^{29}Si NMR spectrum of cyclopentasiloxane N_5 is shown in Fig. 1c. The spectrum is very complex, and complete assignment of signals is impossible,

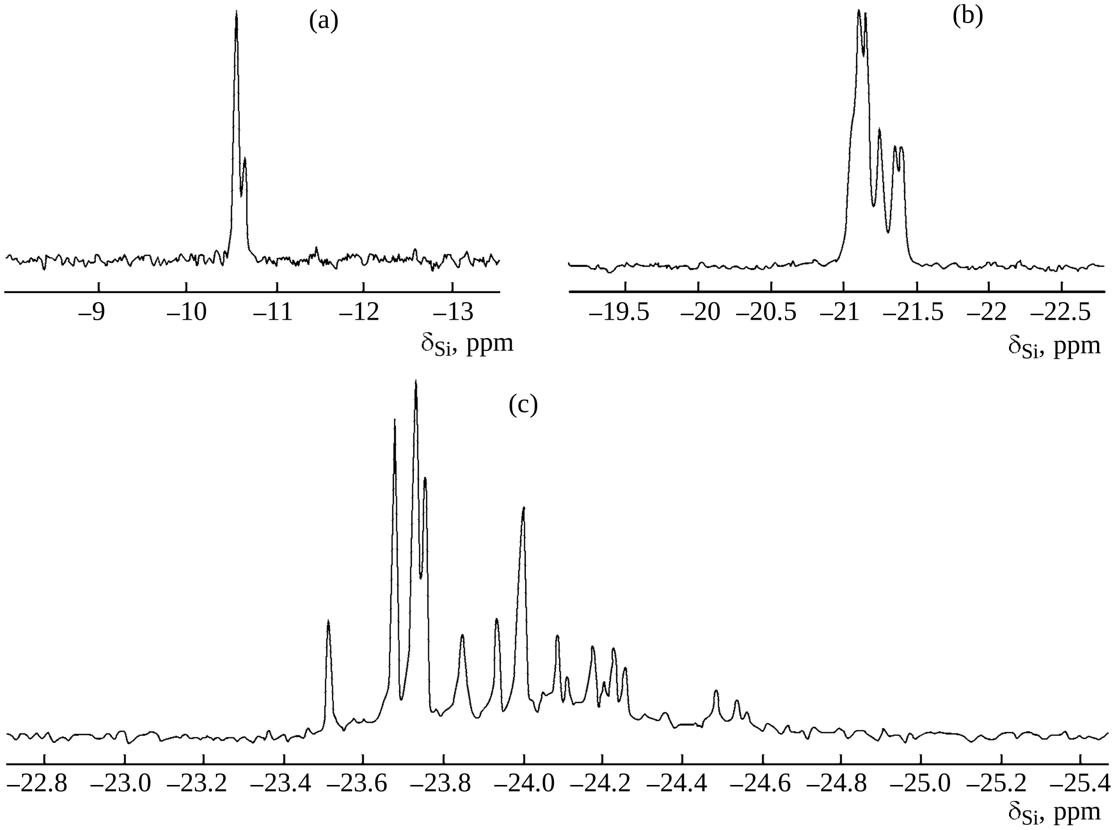


Fig. 1. ^{29}Si NMR spectra of cyclosiloxanes: (a) **IVa** (59.6 MHz), (b) **IVb** (59.6 MHz), and (c) **IVc** (99.4 MHz).

since the relative content of possible isomers (**A**, *eeeee*; **B**, *aeeee*; **C**, *aaeee*; **D**, *aeaee*) and the population of conformers of isomers **C** and **D** are unknown.

The ^{29}Si NMR spectrum of cyclopentasiloxane N_4D consists of three lines assignable to fragment D (–19.45, –20.06, –21.08 ppm) and three lines assignable to fragment N (–23.55, –24.22, –25.10 ppm).

Thus, we have prepared previously unknown (methyl-β-cyanoethyl)tri-, tetra-, and pentacyclosiloxanes by oxygen–halogen exchange between silicon and tin.

EXPERIMENTAL

The IR spectra were taken on a Bruker IFS-88 spectrophotometer (liquid samples on KBr lens). The NMR spectra were recorded on a Bruker DPX-300 or Bruker AM-500 (for Si) spectrometer (solvent $CDCl_3$, internal reference TMS; working frequencies, MHz: ^{1}H 300.13; ^{13}C, ^{13}C–{^{1}H} 75.468; ^{29}Si, ^{29}Si–{^{1}H} 59.627 or 99.378). The refractive index was determined with an IFS-22 Abbe refractometer.

Hexabutyldistannoxane was prepared according to [9]. α,ω-Dichloro(methyl-β-cyanoethyl)oligosiloxanes **II** were prepared according to [11].

Bis(tri-*n*-butylstannyloxy)dimethylsilane Ia. Hexabutyldistannoxane, 13.86 g, was slowly added dropwise with stirring to 3.0 g of dimethyldichlorosilane. The reaction mixture strongly warmed up. After adding the whole amount of hexabutyldistannoxane, the mixture was heated to 180°C for 4 h and then distilled in a vacuum. Tributylchlorostannane was distilled first. Yield of compound **Ia** 1.25 g (81%); transparent colorless liquid, bp 195°C (1 mm), n_D^{18} 1.4718, d_4^{20} 1.1806. IR spectrum, ν, cm^{-1}: 2960, 2932, 2870, 2855 (CH_3), 1460, 1245, 976, 513 (Sn–O). ^{1}H NMR spectrum, δ, ppm: –0.03 s (6H, CH_3–Si), 0.92 t (18H, CH_3), 1.04 t (12H, CH_2O), 1.32 m (12H, CH_3CH_2), 1.56 m (12H, OCH_2CH_2). ^{13}C NMR spectrum, δ_C, ppm: –0.58 (CH_3–Si), 13.13 (CH_3), 15.61 (OCH_2), 26.65 (CH_3CH_2), 27.46 (OCH_2CH_2). Found, %: C 46.11; H 8.97; Si 4.02. $C_{26}H_{60}O_2SiSn_2$. Calculated, %: C 46.59; H 9.02; Si 4.19.

Bis(tributylstannyloxy)methyl-β-cyanoethylsilane Ib was prepared similarly starting from methyl-β-cyanoethyldichlorosilane. Yield 75%; light yellow liquid, bp 232°C (2 mm), n_D^{18} 1.4847, d_4^{20} 1.1918. IR spectrum, ν, cm^{-1}: 2959, 2920, 2870, 2854 (CH_3), 1460, 1245, 990, 510 (Sn–O). ^{1}H NMR spectrum, δ, ppm: –0.09 s (3H, CH_3–Si), 0.70 t (2H, CH_2–Si), 0.92 t (18H, CH_3), 1.06 t (12H, CH_2O), 1.32 m (12H, CH_3CH_2), 1.58 m (12H, OCH_2CH_2), 2.20 t (2H, CH_2CN). ^{13}C NMR spectrum, δ_C, ppm: –0.03 (CH_3–Si), 13.81 (CH_3), 15.01 ($SiCH_2$), 15.97 (CH_2CN), 16.34 (OCH_2), 27.33 (CH_3CH_2), 28.14 (OCH_2CH_2), 121.96 (CN). Found, %: C 47.02; H 8.15; N 1.83; Si 4.15. $C_{28}H_{61}NO_2SiSn_2$. Calculated, %: C 47.41; H 8.67; N 1.97; Si 3.96.

Methyl(β-cyanoethyl)cyclosiloxanes IV and Va–Vc. Equimolar amounts of **I** or **II** and appropriate α,ω-dichlorosilane **III** in THF (20 ml of solvent per 2 g of reactants) were stirred at room temperature for 4 h. Then the solvent was distilled off, and tributylchlorostannane was distilled off in a vacuum. The residue was vacuum-distilled.

Trimethyltris(β-cyanoethyl)cyclotrisiloxane IVa. Yield 86%; colorless transparent liquid, bp 215°C (1 mm Hg), n_D^{18} 1.4682, d_4^{20} 1.2225. IR spectrum, ν, cm^{-1}: 2965, 2930, 2906 (CH_3), 2245 (CN), 1017 (Si–O–Si). ^{1}H NMR spectrum, δ, ppm: –0.21 s (3H, CH_3–Si), 0.81 t (2H, CH_2–Si), 2.21 t (2H, CH_2CN). ^{13}C NMR spectrum, δ_C, ppm: –0.50 (CH_3–Si), 10.67 ($SiCH_2$), 12.32 (CH_2CN), 120.89 (CN). Found, %: C 43.00; H 6.37; N 12.95; Si 24.57. $C_{12}H_{21}N_3O_3Si_3$. Calculated, %: C 42.45; H 6.29; N 12.48; Si 24.81.

Tetramethyltetrakis(β-cyanoethyl)cyclotetrasiloxane IVb. Yield 86%; colorless transparent liquid, bp 242°C (1 mm), n_D^{18} 1.4642, d_4^{20} 1.2219. IR spectrum, ν, cm^{-1}: 2970, 2936, 2906 (CH_3), 2251 (CN), 1430, 1083 (Si–O–Si). ^{1}H NMR spectrum, δ, ppm: 0.02–0.05 set of singlets (3H, CH_3–Si), 0.76 m (2H, CH_2–Si), 2.19 m (2H, CH_2CN). ^{13}C NMR spectrum, δ_C, ppm: –0.63 (CH_3–Si), 10.86 ($SiCH_2$), 12.42, 12.56, 12.74, 12.90 (CH_2CN), 120.89 (CN). Found, %: C 40.51; H 6.47; N 12.38; Si 26.01. $C_{15}H_{28}N_4O_4Si_4$. Calculated, %: C 40.88; H 6.31; N 12.71; Si 25.49.

Pentamethylpentakis(β-cyanoethyl)cyclopentasiloxane IVc. Yield 81%; transparent yellowish liquid, bp 280°C (1 mm), n_D^{18} 1.4637, d_4^{20} 1.2215. IR spectrum, ν, cm^{-1}: 2970, 2936, 2906 (CH_3), 2251 (CN), 1430, 1080 (Si–O–Si). ^{1}H NMR spectrum, δ, ppm: 0.02–0.05 set of singlets (3H, CH_3–Si), 0.75 m (2H, CH_2–Si), 2.20 m (2H, CH_2CN). ^{13}C NMR spectrum, δ_C, ppm: –0.62 (CH_3–Si), 10.84 ($SiCH_2$), 12.37, 12.58, 12.78, 12.90 (CH_2CN), 120.89 (CN). Found, %: C 40.11; H 6.60; N 13.02; Si 26.17. $C_{18}H_{35}N_5O_5Si_5$. Calculated, %: C 39.88; H 6.51; N 12.92; Si 25.91.

Tetramethylbis(β-cyanoethyl)cyclotrisiloxane Va. Yield 91%; transparent colorless liquid, bp 195°C (1 mm), n_D^{18} 1.4415, d_4^{20} 1.0561. IR spectrum, ν, cm^{-1}: 2964, 2930, 2907 (CH_3), 2249 (CN), 1263, 1020 (Si–O–Si). ^{1}H NMR spectrum, δ, ppm: 0.10 s

(6H, CH_3–Si–CH_2), 0.17 s [6H, $(CH_3)_2Si$)], 0.92 t (4H, CH_2–Si), 2.33 t (4H, CH_2CN). ^{13}C NMR spectrum, δ_C, ppm: –2.83 (CH_3–Si–CH_2), 0.71 [$(CH_3)_2$–Si)], 10.26 ($SiCH_2$), 11.81 (CH_2CN), 121.06 (CN). Found, %: C 34.28; H 7.01; N 9.75; Si 31.02. $C_8H_{20}N_2O_3Si_3$. Calculated, %: C 34.75; H 7.29; N 10.13; Si 30.47.

Pentamethyltris(β-cyanoethyl)cyclotetrasiloxane Vb. Yield 83%; transparent colorless liquid, bp 218°C (1 mm), n_D^{18} 1.4475, d_4^{20} 1.0671. IR spectrum, ν, cm^{-1}: 2965, 2930, 2907 (CH_3), 2250 (CN), 1264, 1083 (Si–O–Si), 808. ^1H NMR spectrum, δ, ppm: 0.28 m (9H, CH_3–Si–CH_2), 0.22 m [6H, $(CH_3)_2Si$], 0.97 m (6H, CH_2–Si), 2.40 m (6H, CH_2CN). ^{13}C NMR spectrum, δ_C, ppm: –0.09, 0.06, 0.20 (CH_3–Si–CH_2), 0.84 [$(CH_3)_2Si$], 10.26, 10.84, 11.06 ($SiCH_2$), 12.74, 12.86, 13.08, 13.64 (CH_2CN), 121.20 (CN). Found, %: C 38.45; H 7.01; N 11.50; Si 30.12. $C_{12}H_{27}N_3O_4Si_4$. Calculated, %: C 38.18; H 7.21; N 11.12; Si 29.74.

Hexamethyltetrakis(β-cyanoethyl)cyclopentasiloxane Vc. Yield 79%; transparent colorless liquid, bp 232°C (1 mm), n_D^{18} 1.4501, d_4^{20} 1.0615. IR spectrum, ν, cm^{-1}: 2965, 2930, 2907 (CH_3), 2250 (CN), 1263, 1084 (Si–O–Si), 808. ^1H NMR spectrum, δ, ppm: 0.23 m (12H, CH_3–Si–CH_2), 0.20 m [6H, $(CH_3)_2Si$], 0.98 m (8H, CH_2–Si), 2.40 m (8H, CH_2CN). ^{13}C NMR spectrum, δ_C, ppm: –0.07, 0.08, 0.18 (CH_3–Si–CH_2), 0.86 [$(CH_3)_2Si$], 10.25, 10.81, 11.02 ($SiCH_2$), 12.70, 12.85, 13.05, 13.60 (CH_2CN), 121.20 (CN). Found, %: C 35.01; H 6.60; N 10.10; Si 26.13. $C_{16}H_{34}N_4O_5Si_5$. Calculated, %: C 35.46; H 6.32; N 10.33; Si 25.91.

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