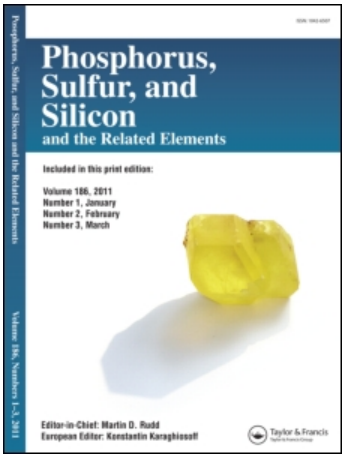

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THE SYNTHESIS OF METHYL-(β-CYANOETHYL)CYCLOSILOXANES

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A series of methyl-(β-cyanoethyl) cyclotri-, tetra-, and pentasiloxanes has been prepared using oxygen-halogen exchange between silicon and tin in the reaction of α,ω-dichloro(methyl-β-cyanoethyl)oligosiloxanes with bis-tri-n-butylstannyloxy-diorganosilanes.

Keywords: Hexabutyldistannoxanes; methyl-(β-cyanoethyl)cyclosiloxanes; NMR spectroscopy; synthesis

INTRODUCTION

The introduction of cyano groups into the organopolysiloxanes is an effective method for increasing of polarity. These polymers are polar dielectrics as compared with other polysiloxanes (unpolar dielectrics). Cyanopolysiloxanes may be potentially used as polar dielectrics in capacitors with variable capacity, as polar phases in chromatography, and as current conducting lubricants. To date, the synthesis of high polymers with methyl-β-cyanoethylsilanes fragment has not been reported, only that of oligomers with polymerization degree up to 20.[1] This is due to the sensitivity of nitrile group to basic and acidic reagents[2] because basic or acidic hydrolysis of organosilanes is the most frequently used way of synthesizing these polymers.[1] Another way of obtaining polysiloxanes is the polymerization of cyclosiloxanes. However (methyl-β-cyanoethyl)cyclosiloxanes have not yet been synthesized for the same reason: Their synthesis take place with basic or acidic catalysts.[3] In these conditions, the cyano groups are transformed into amide or carbonyl groups and undergo further reactions.[2] Therefore,

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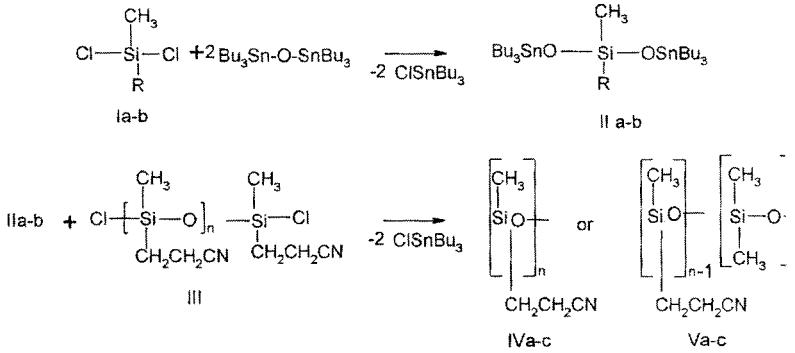
the cyclosiloxanes with only one methyl-β-cyanoethyl silane fragment in the cycle (other dimethylsilane) have been synthesized.[1] The main problem in their synthesis is the preparative isolation of pure cyclosiloxanes from the reaction mixture because this mixture contains many products with similar boiling points and structures.[4] A report about the synthesis of (methyl-β-cyanoethyl)cyclotetrasiloxane[5] was wrong. The liquid assumed as this cyclosiloxane contain a residue. This does not indicate the separation one isomer (for example, "eeee") but shows the partial transformation of the nitrile groups in amide.[5] We recorded the IR spectrum of a similar mixture with precipitate. The spectrum contains amide groups bands (1640–1680 cm^{-1}). The aim of this article is the search for the synthesis of (methyl-β-cyanoethyl)cyclosiloxanes, which ensures the stability of cyano groups and allows the preparation of only one cyclosiloxane in a single stage.

Our strategy for the construction of (methyl-β-cyanoethyl)cyclosiloxanes requires the use of hexaorganostannoxanes as oxygen source for obtaining the Si—O—Si fragment. These reactions are carried out at miderate temperatures and in the homogeneous phase. This method is based on the easy elimination of chlorotributylstannane during oxygen-halogen exchange between silicon and tin because silicon has the greatest affinity for oxygen in this group of the Periodical Table.[6] Roesky et al. synthesized heterosilasesquioxane[7] and Veith et al. a spirocyclosilaxanesilazane[8] in a similar way.

RESULTS AND DISCUSSION

Our strategy for the construction of the (methyl-β-cyanoethyl)cyclosiloxanes is illustrated in Scheme 1.



I, II: a-CH_3, b-CH_2CH_2CN, III: n = 1-3

IV, V: a-n = 3; b-n = 4; c-n = 5

The yield is good in the both stages of this synthesis. In the second step of this synthesis, we used a dilution conditions to lessen any possibility of polymer products formation. This reaction allows the formation of cyclosiloxanes **IV–V** under conditions that are sufficiently mild to tolerate sensitive functionality of these cycles (nitrile groups). As a result, we synthesized six new (methyl-β-cyanoethyl)cyclosiloxanes **IV–V**.

^{29}Si NMR Spectral Data

^{29}Si NMR spectroscopy is very important for the characterization of cyclosiloxanes.We recorded ^{29}Si NMR spectra of cyclosiloxanes **IV–V** (Figure 1). The replacement of CH_3 group by CH_2CH_2CN in these cycles leads to upfield shift of ^{29}Si resonance. It is well known that the inductive effect of the substituents at Si-atom determines the NMR resonance of neighbored Si-atoms in siloxanes.[9] This effect is increased by the Si—O conjugation in cyclosiloxanes. As a result, the influence of substituents is effectively transferred to α and β positions in cyclosiloxane. In ^{29}Si NMR spectrum of (methyl-β-cyanoethyl)cyclotrisiloxane **IVa** occur two lines −10.56 and −10.64 ppm (Figure 1a). Two lines

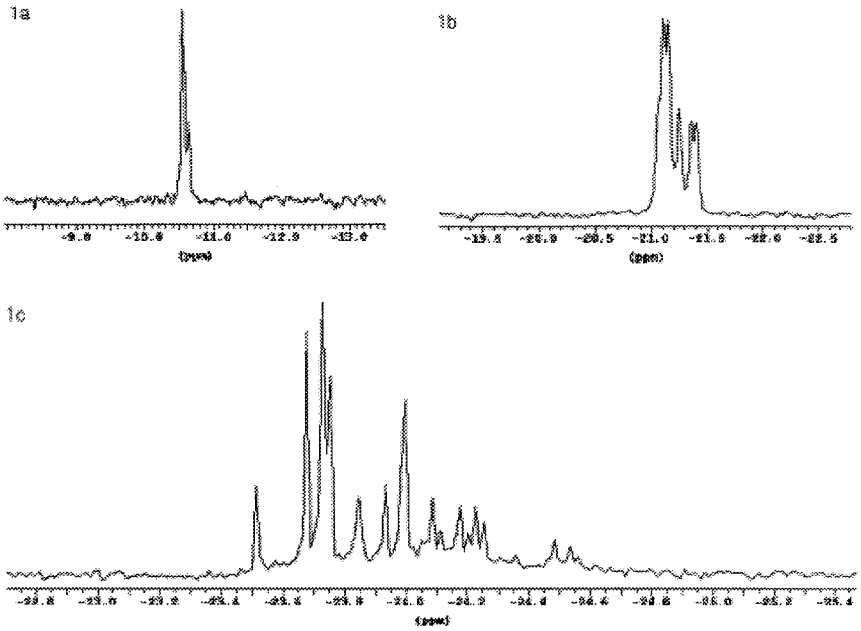


FIGURE 1 ^{29}Si NMR spectra of cyclosiloxanes **IV**. (a) **IVa** (59.6 MHz); (b) **IVb** (59.6 MHz); (c) **IVc** (99.4 MHz).

with relative intensities 1:2 present in the spectrum of tetramethyl-bis-β-cyanoethylcyclotrisiloxane **Va** (−11.36 and −11.48 ppm). It is clear that downfield signal corresponds to D ($(CH_3)_2SiO$) fragment. The ^{29}Si NMR spectra of tetracyclosiloxanes **IVb–Vb** are more complex (Figure 1b). Tetramethyl-tetrakis-β-cyanoethyltetracyclosiloxane **IVb** is a mixture of four isomers (A-"eeee", B- "aeee", C-"aaee", and D-"aeae"). The additive scheme of Pestunovich et al.[9] can be used to simulate the number of lines in the spectrum. This number is six and is attributed (in the upfield order) to isomers B, D, C, B, A, and B. The chemical shifts are −21.06, −21.11, −21.16, −21.25, −21.36, and −21.40 ppm. ^{29}Si NMR spectrum of tetracyclosiloxane N_3D (where $N{=}CH_3(CH_2CH_2CN)SiO$) is more complex. This compound may exist as a mixture of three isomers (A-"eee", B-"eae", and C-"aee"). In agreement with this, the D-part of ^{29}Si NMR spectrum contains three lines with different intensity (−16.14 (C), −17.53 (A), and −17.62 (B) ppm). The lines are attributed according to Pestunovich et al.[9] N part of this spectrum contains four lines (−20.04, −20.59, −22.25, and −22.45 ppm). Their attribution is nontrivial.

The ^{29}Si NMR spectrum of N_5 is given on Figure 1c. This spectrum is complex and contains much lines.

The ^{29}Si NMR spectrum of N_4D contains three lines in D part (−19.45, −20.06, and −12.08 ppm) and three lines in N part (−23.55, −24.22, and −25.10 ppm).

CONCLUSIONS

In conclusion, the procedure reported here represents a new synthetic approach to the (methyl-(β-cyanoethyl)cyclosiloxanes, which ensures the stability of cyano groups and allows the preparation of only one cyclosiloxanes in a single stage in good yields. The easy availability of the starting materials, the simplicity of this short and clean procedure and the good yields of products render this process particularly attractive.

EXPERIMENTAL

IR spectra were obtained using potassium bromide cell on Bruker IFS-88 instrument. NMR spectra were recorded o Bruker DPX 300 or AM 500 (for 29-silicon) spectrometers for $CDCl_3$ solutions with TMS as internal standard. The diffraction index were obtained on Abbe type IFS-22 (USSR) refractometer.

Hexabutyldistannoxanes was synthesized as described,[10] and α,ω-dichlorooligosilaxanes **III** was prepared by the method.[11]

Bis-(tri-n-butylstannyloxa)-dimethylsilane IIa

To stirred 3.0 g (2.3 mmol) of dimethyldichlorosilane was slowly added 13.86 g (4.6 mmol) of hexabutyldistannoxane. During this addition, temperature of mixture was rising. After this the mixture was heated at 180°C for 4 h. Than the mixture was distillated at vacuum. Yield 1.25 g (81%) as colorless liquid (195°C, 1 mm Hg). $n_D^{18} = 1.4718$, $d_4^{20} = 1.1806$. IR: 2960, 2932, 2870, 2855 (CH_3), 1460, 1245, 976, 513 (Sn—O).

^{1}H NMR (300 MHz, $CDCl_3$), δ, −0.03 s (CH_3—Si, 6H); 0.92 t (CH_3, 18H); 1.04 t (CH_2O, 12H); 1.32 m ($CH_3C\underline{H}_2$, 12H) 1.56 m ($OCH_2C\underline{H}_2$, 12H). ^{13}C NMR (75.5 MHz, $CDCl_3$), δ, −0.58 (CH_3—Si); 13.13 (CH_3); 15.61 (OCH_2); 26.65 ($CH_3\underline{C}H_2$); 27.46 ($OCH_2\underline{C}H_2$). Found,%: C 46.11; H 8.97; Si 4.02. Calcd. for $C_{26}H_{60}O_2Si\ Sn_2$,%: C 46.59; H 9.02; Si 4.19.

The same procedure was used for synthesis of *bis-(tri-n-butylstannyloxa)-methyl-β-cyanoethylsilane IIb.* Yield 75% as hell yellow oil (232°C, 2 mm Hg). $n^{18}{}_D = 1.4847$, $d^{20}{}_4 = 1.1918$. IR: 2959, 2920, 2870, 2854 (CH_3), 1460, 1245, 990, 510 (Sn—O). ^{1}H NMR (300 MHz, $CDCl_3$), δ, −0.09 s (CH_3—Si, 3H); 0.70 t (CH_2—Si, 2H); 0.92 t (CH_3, 18H); 1.06 t (CH_2O, 12H); 1.32 m ($CH_3C\underline{H}_2$, 12H) 1.58 m ($OCH_2C\underline{H}_2$, 12H); 2.20 t (CH_2CN, 2H). ^{13}C NMR (75.5 MHz, $CDCl_3$), δ, −0.03 (CH_3—Si); 13.81 (CH_3); 15.01 ($SiCH_2$); 15.97 (CH_2CN); 16.34 (OCH_2); 27.33 ($CH_3\underline{C}H_2$); 28.14 ($OCH_2\underline{C}H_2$); 121.96 (CN). Found,%: C 47.02; H 8.15; N 1.83; Si 4.15. Calcd. for $C_{28}H_{61}O_2\ N\ Si\ Sn_2$,%: C 47.41; H 8.67; N 1.97; Si 3.96.

The Synthesis of Cyclosiloxanes IV–V

The eqvimolar quantity of II and III was stirred in THF solution (10 ml for 1 g of reagents) at rt for 4 h. The solvent was evaporated and residue was distilated in vacuum.

Trimethyl-tri-β-cyanoethyl-cyclotrisiloxane IVa. Yield 86% as colorless liquid 215°C, 1 mm Hg) $n^{18}{}_D = 1.4682$, $d^{20}{}_4 = 1.2225$. IR: 2965, 2930, 2906 (CH_3), 2245 (CN), 1017 (Si—O—Si). ^{1}H NMR (300 MHz, $CDCl_3$), δ, −0.21 s (CH_3—Si, 3H); 0.81 t (CH_2—Si, 2H); 2.21 t (CH_2CN, 2H). ^{13}C NMR (75.5 MHz, $CDCl_3$), δ, −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.Calcd. for $C_{12}H_{21}O_3\ N_3Si_3$,%: C 42.45; H 6.29; N 12.48; Si 24.81.

Tetramethyl-tetrakis-β-cyanoethyl-cyclotetrasiloxane IVb. Yield 86% as colorless liquid (242°C, 1 mm Hg) $n^{18}{}_D = 1.4642$, $d^{20}{}_4 = 1.2219$. IR: 2970, 2936, 2906 (CH_3), 2251(CN),1430, 1083(Si—O—Si). ^{1}H NMR (300 MHz, $CDCl_3$), δ, 0.02–0.05 number of singlets (CH_3—Si, 3H); 0.76 m (CH_2—Si, 2H); 2.19 $_M$ (CH_2CN, 2H). ^{13}C NMR (75.5 MHz, $CDCl_3$), δ, −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. Calcd. for $C_{15}H_{28}O_4\ N_4Si_4$,%: C 40.88; H 6.31; N 12.71; Si 25.49.

Pentamethyl-pentakis-β-cyanoethyl-cyclopentasiloxane IVa. Yield 81% as colorless liquid (280°C 1 mm Hg) $n_D^{18} = 1.4637$, $d_4^{20} = 1.2215$. IR: 2970, 2936, 2906 (CH_3), 2251 (CN), 1430, 1080 (Si—O—Si). ^{1}H NMR (300 MHz, $CDCl_3$), δ, 0.02–0.05 number of singlets (CH_3—Si, 3H); 0.75 m (CH_2—Si, 2H); 2.20 m (CH_2CN, 2H). ^{13}C NMR (75.5 MHz, $CDCl_3$), δ, −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. Calcd. for $C_{18}H_{35}O_5\ N_5Si_5$,%: C 39.88; H 6.51; N 12.92; Si 25.91.

Tetramethyl-bis-β-cyanoethyl-cyclotrisiloxane Va. Yield 91% as colorless liquid (195°C, 1 mm Hg) $n_D^{18} = 1.4415$, $d_4^{20} = 1.0561$.IR: 2964, 2930, 2907 (CH_3), 2249 (CN), 1263, 1020 (Si—O—Si). ^{1}H NMR (300 MHz, $CDCl_3$), δ, 0.10 s (CH_3—Si—CH_2, 6H); 0.17 s ((CH_3)$_2$Si, 6H); 0.92 t (CH_2—Si, 4H); 2.33 t (CH_2CN, 4H). ^{13}C NMR (75.5 MHz, $CDCl_3$), δ, −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. Calcd. for $C_8H_{20}O_3\ N_2Si_3$,%: C 34.75; H 7.29; N 10.13; Si 30.47.

Pentamethyl-tri-β-cyanoethyl-cyclotetrasiloxane Vb. Yield 83% as colorless liquid (218°C, 1 mm Hg) $n_D^{18} = 1.4475$, $d_4^{20} = 1.0671$. IR: 2965, 2930, 2907 (CH_3), 2250(CN), 1264, 1083 (Si—O—Si), 808. ^{1}H NMR (300 MHz, $CDCl_3$), δ, 0.28 m (CH_3—Si—CH_2, 9H); 0.22 m ((CH_3)$_2$Si, 6H); 0.97 m (CH_2—Si, 6H); 2.40 m (CH_2CN, 6H). ^{13}C NMR (75.5 MHz, $CDCl_3$), δ, −0.09, 0.06, 0.20 (CH_3—Si—CH_2); 0.84 ((CH_3)$_2$—Si); 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.Calcd. for $C_{12}H_{27}O_4\ N_3Si_4$,%: C 38.18; H 7.21; N 11.12; Si 29.74.

Hexamethyl-tetrakis-β-cyanoethyl-cyclotpentasiloxane Vc. Yield 79% as colorless liquid (232°C, 1 mm Hg) $n_D^{18} = 1.4501$, $d_4^{20} = 1.0615$. IR: 2965, 2930, 2907 (CH_3), 2250 (CN), 1263, !084 (Si—O—Si), 808. ^{1}H NMR (300 MHz, $CDCl_3$), δ, 0.23 m (CH_3—Si—CH_2, 12H); 0.20 m ((CH_3)$_2$Si, 6H); 0.98 m (CH_2—Si, 8H); 2.40 m (CH_2CN, 8H). ^{13}C NMR (75.5 MHz, $CDCl_3$), δ, −0.07, 0.08, 0.18 (CH_3—Si—CH_2); 0.86 ((CH_3)$_2$—Si); 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. Calcd. for $C_{16}H_{34}O_5N_4Si_5$,%: C 35.46; H 6.32; N 10.33; Si 25.91.

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