# Chemistry

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## Abstract

## Full Text

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# SYNTHESIS AND TRANSFORMATIONS OF $\alpha,\omega$-DICYANOALKYLTETRAMETHYLDISILOXANES

Cyanoalkylsiloxane polymers have recently found practical application as special silicone rubbers, pastes, resins, and other materials ($^1$). It is also known that cyanoalkyl silicon compounds are starting substances for the synthesis of a whole series of carbofunctional organosilicon monomers, in particular $\gamma$-aminopropyltriethoxysilane ($^2$), $\alpha,\omega$-di-(aminoalkyl)-tetraalkyldisiloxanes ($^3$), and diacids ($^{4,5}$).

In the present work we studied the possibility of obtaining $\alpha,\omega$-di-(cyanoalkyl)-tetramethyldisiloxanes by the method of ($^4$). Under the conditions described in the experimental part, the following reactions were carried out:

$$XCH_2CH_2CH_2Si(CH_3)Cl_2 \xrightarrow[\text{ether}]{CH_3MgHal} \xrightarrow{H_2O} [XCH_2CH_2CH_2Si(CH_3)_2]_2O + XCH_2CH_2CH_2Si(CH_3)_3,$$

$$X = CN,\ OCH_2CH_2CN \qquad Hal = Cl,\ Br; \qquad (1)$$

$$NCCH_2CH_2SiCl_3 \xrightarrow[\text{ether}]{n\,CH_3MgHal} \xrightarrow{H_2O} [NCCH_2CH_2Si(CH_3)_2]_2O + NCCH_2CH_2Si(CH_3)_3,$$

$$n = 2;\ 2.3;\ 2.5 \qquad Hal = Cl,\ Br,\ I. \qquad (2)$$

It turned out that in reaction (2), in ether at a temperature from −3 to 36°, the best yields of the $\alpha,\omega$-dinitrile are achieved with Hal = Cl and $n = 2.5$, whereas with Hal = I the $\alpha,\omega$-dinitrile could not be isolated. At $n = 2$, owing to the high rate of substitution at room temperature of all three chlorines on silicon, it is not possible to obtain any appreciable amounts of $\alpha,\omega$-di-($\beta$-cyanoethyl)-tetramethyldisiloxane from the compound $NCCH_2CH_2SiCl_3$. Apparently this is explained by the fact that, owing to formation of $NCCH_2CH_2Si(CH_3)_3$, a considerable amount of the difunctional nitrile $NCCH_2CH_2Si(CH_3)Cl_2$ remains in

the mixture; at the hydrolysis stage this enters into reaction with the monofunctional $NCCH_2CH_2Si(CH_3)_2Cl$, with formation of linear polysiloxanes of probable structure
$NCCH_2CH_2Si(CH_3)_2O[NCCH_2CH_2(CH_3)SiO]_{kSi}(CH_3)_2CH_2CH_2CN$. The first member of this series with $k = 1$ was isolated by us in all experiments, and in the case $n = 2$ in the greatest amount.

The prepared $\alpha, \omega$-dicyanoalkyltetramethyldisiloxanes were copolymerized with dimethylsilicocyclopolysiloxanes according to the reaction:

$$[NCCH_2CH_2Si(CH_3)_2]_2O + n[(CH_3)_2SiO]_4 \rightarrow$$

$$\rightarrow NCCH_2CH_2Si(CH_3)_2O[Si(CH_3)_2O]_{4n}Si(CH_2)_2CH_2CH_2CN. \qquad (3)$$

The copolymerization was carried out with the aid of 2-6 wt. % conc. $H_2SO_4$ at $20 \pm 2°$; under these conditions no cleavage of the cyanoalkyl radical was observed.

At the same time, according to Prober' s data (6), cyclic polysiloxanes with $\alpha$-cyanoalkyl radicals under the conditions we used cleave off the cyanoalkyl radical and form cross-linked polymers.

The cyano group is one of the most polar functional groups (7) and causes the appearance of strong forces of intermolecular inter-

interactions, in particular, also in molecules of cyanoalkylpolysiloxanes(6). Therefore, the linear $\alpha$,$\omega$-dicyanoalkyldimethylpolysiloxanes obtained by us, in contrast to nonpolar dimethylpolysiloxanes, proved to be highly viscous liquids. At the same time, their viscosity index remained close to that of dimethylpolysiloxanes(8).

Under reaction conditions analogous to those described above, we obtained disiloxanes in which the terminal groups were reactive CN-alkyl and Cl-alkyl groups

$$[NC(CH_2)_{kSi}(CH_3)_2]_2O + n[ClCH_2Si(CH_3)_2]_2O \xrightarrow{H_2SO_4}$$

$$\rightarrow 2NC(CH_2)_{kSi}(CH_3)_2OSi(CH_3)_2CH_2Cl + (n-1)[ClCH_2Si(CH_3)_2]_2O. \qquad (4)$$

When $n$ was taken equal to 7, chloronitriles were obtained in 70–90% yield.

It is known that organosilicon chloromethyl compounds are very active in substitution reactions(9). The siloxane $\alpha$,$\omega$-chloronitriles obtained by us can be used for preparing various other $\alpha$,$\omega$-dicarbofunctional disiloxanes with different functional groups. We established, in particular, that reaction (5)

$$NCCH_2CH_2Si(CH_3)_2OSi(CH_3)_2CH_2Cl \xrightarrow[\text{acetone}]{\text{KJ}} NCCH_2CH_2Si(CH_3)_2OSi(CH_3)_2CH_2J \quad (5)$$

is not complicated by side reactions at the $\equiv Si-O-Si\equiv$ bonds, and the iodide is obtained in 83% yield.

## Experimental Part

The conditions for the synthesis of $\alpha$,$\omega$-dicyanoalkyltetramethyldisiloxanes are given in Table 1. Below we describe one standard experiment.

**Synthesis of $\alpha$,$\omega$-di-($\beta$-cyanoethyl)-tetramethyldisiloxane.** In a round-bottom flask fitted with a reflux condenser, stirrer, and inlet tube for introducing $CH_3Cl$, 62 g (2.6 mol) of Mg and 1.2 l of absolute ether were placed. The resulting organomagnesium compound was poured into 188.6 g (1 mol) of $Cl_3SiCH_2CH_2CN$ in 0.5 ml of absolute ether at a temperature of $\sim 20°$ over 4 h. The next day the mixture was decomposed with water, the aqueous layer was separated from the organic layer, the latter was washed with water, and the aqueous layer was extracted twice with ether. The organic layer and the ethereal extracts were combined and dried over $CaCl_2$ for 24 h. Distillation gave a fraction of the dinitrile $NCCH_2CH_2Si(CH_3)_2OSi(CH_3)_2CH_2CH_2CN$ with b.p. 150-155°/3 mm and of the trinitrile $[NCCH_2CH_2(CH_3)_2SiO]_2Si(CH_3)CH_2CH_2CN$ with b.p. 230-238° (2-3 mm).

The properties of the dinitrile and trinitrile obtained, as well as of the other compounds synthesized for the first time, are presented in Table 2.

**Reaction of $\alpha$,$\omega$-di-($\beta$-cyanoethyl)-tetramethyldisiloxane with octamethyltetracyclosiloxane.** In a flask equipped with a stirrer were placed 22.2 g (0.075 g-mol) of $[(CH_3)_2SiO]_4$ and 18 g (0.075 g-mol) of $[NCCH_2CH_2Si(CH_3)_2]_2O$; then 1.3 ml (5.6 wt.%) of conc. $H_2SO_4$ was added as catalyst. The contents of the flask were stirred at room temperature for 24 h, after which they were treated with water. The organic layer was separated from the aqueous layer, and the latter was extracted twice with ether. The organic layer and the ethereal extracts were combined and dried over $CaCl_2$ for 6 h. After removal of the ether, the residue was subjected to vacuum distillation in a stream of nitrogen; 6 g of low-boiling compounds with b.p. up to 180°/2 mm (pot temperature 200°/2 mm) were thereby isolated. The residue was a transparent, light-yellow, oil-like polymer, weight 29 g; yield 72% based on the starting reagents.

Found, %: N 5.34; 5.43

$C_{18}H_{44}Si_6N_2O_5$. Calculated, %: N 5.21

**Table 1**

| No. | Starting nitrile, g-mol | Mg, g-atom | Mononitrile obtained, g-mol | Dinitrile* obtained, g-mol | Halides in $CH_3X$ | Reaction duration, h | Reaction temp., °C |
|---|---|---|---|---|---|---|---|
| 1 | $Cl_3SiCH_2CH_2CN$; 1 | 2.6 | $(CH_3)_3SiCH_2CH_2CN$; 0.16 | $[NCCH_2CH_2Si(CH_3)_2]_2O$; 0.14 | Cl | 4 | 20 |
| 2 | $Cl_3SiCH_2CH_2CN$; 1 | 2.6 | $(CH_3)_3SiCH_2CH_2CN$; 0.27 | $[NCCH_2CH_2Si(CH_3)_2]_2O$; 0.1 | Br | 4 | 36 |
| 3 | $Cl_3SiCH_2CH_2CN$; 1 | 2.3 | $(CH_3)_3SiCH_2CH_2CN$; 0.25 | $[NCCH_2CH_2Si(CH_3)_2]_2O$; 0.09 | Br | 1.5 | −3 |
| 4 | $Cl_3SiCH_2CH_2CN$; 1 | 2.3 | $(CH_3)_3SiCH_2CH_2CN$; 0.17 | $[NCCH_2CH_2Si(CH_3)_2]_2O$; 0.1 | Br | 1.5 | 20 |
| 5 | $CH_3Cl_2SiCH_2CH_2CH_2CN$; 0.8 | 1.2 | $(CH_3)_3SiCH_2CH_2CH_2CN$; 0.21 | $[NCCH_2CH_2CH_2Si(CH_3)_2]_2O$; 0.13 | Br | 3.5 | 30 |
| 6 | $CH_3Cl_2SiCH_2CH_2CH_2CN$; 1.09 | 2 | $(CH_3)_3SiCH_2CH_2CH_2CN$; 0.71 | $[NCCH_2CH_2CH_2Si(CH_3)_2]_2O$; 0.07 | Br | 3.5 | 0 |
| 7 | $CH_3Cl_2SiCH_2CH_2CH_2CN$; 0.45 | 0.6 | $(CH_3)_3SiCH_2CH_2CH_2CN$; 0.13 | $[NCCH_2CH_2CH_2Si(CH_3)_2]_2O$; 0.05 | Cl | 1.5 | 0 |
| 8 | $CH_3Cl_2Si(CH_2)_3O(CH_2)_2CN$; 0.44 | 0.66 | $(CH_3)_3Si(CH_2)_3O(CH_2)_2CN$; 0.05 | $[NC(CH_2)_2O(CH_2)_3Si(CH_3)_2]_2O$; 0.075 | Cl | 4 | 15 |
| 9 | $CH_3Cl_2Si(CH_2)_3O(CH_2)_2CN$; 0.64 | 0.94 | $(CH_3)_3Si(CH_2)_3O(CH_2)_2CN$; 0.2 | $[NC(CH_2)_2O(CH_2)_3Si(CH_3)_2]_2O$; 0.03 | Br | 3.5 | 36 |
| 10 | $CH_3Cl_2Si(CH_2)_3O(CH_2)_2CN$; 1 | 2 | $(CH_3)_3Si(CH_2)_3O(CH_2)_2CN$; 0.55 | $[NC(CH_2)_2O(CH_2)_3Si(CH_3)_2]_2O$; 0.067 | Br | 3.5 | 0 |

* The reaction temperature fluctuated within the range 3–5°.

**Table 2**

| No. | Substance | B.p., °C/mm Hg | $n_D^{20}$ | $d_4^{20}$ | $MR_D$, found | $MR_D$, calc. | Found Si, % | Found C, % | Found H, % | Found Cl, % | Calculated Si, % | Calculated C, % | Calculated H, % | Calculated Cl, % |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | $[NCCH_2CH_2Si(CH_3)_2]_2O$ | 153–155/3 | 1.4520 | [illegible] | 67.06 | 67.08 | 23.18 | [illegible] | [illegible] | — | 23.36 | 49.94 | 8.38 | — |
| 2 | $[NCCH_2CH_2Si(CH_3)_2O]_2Si(CH_3)(CH_2CH_2CN)$ | 234–238/3 | [illegible] | [illegible] | [illegible] | [illegible] | [illegible] | [illegible] | [illegible] | — | 23.82 | 47.55 | 7.69 | — |
| 3 | $[NCCH_2CH_2Si(CH_3)_2]_2$ | 161/1.5 | [illegible] | [illegible] | [illegible] | [illegible] | 29.90 | [illegible] | [illegible] | — | 29.9 | 53.7 | 9.0 | — |
| 4 | $[NCCH_2CH_2OCH_2CH_2CH_2Si(CH_3)_2]_2O$ | 212–214/3 | [illegible] | [illegible] | [illegible] | [illegible] | [illegible] | [illegible] | [illegible] | — | 15.75 | 53.88 | 9.04 | — |
| 5 | $NCCH_2CH_2Si(CH_3)_2OSi(CH_3)_2CH_2Cl$ | 120–123/5 | [illegible] | [illegible] | [illegible] | [illegible] | [illegible] | [illegible] | [illegible] | [illegible] | [illegible] | 40.72 | 7.69 | 15.03 |
| 6 | $NCCH_2CH_2Si(CH_3)_2OSi(CH_3)_2CH_2CH_2Cl$ | 140–142/7 | [illegible] | [illegible] | [illegible] | [illegible] | [illegible] | [illegible] | [illegible] | [illegible] | [illegible] | 43.24 | 8.06 | 14.18 |

| No. | Substance | B.p., °C/mm Hg | $n_D^{20}$ | $d_4^{20}$ | $MR_D$, found | $MR_D$, calc. | Found Si, % | Found C, % | Found H, % | Found Cl, % | Calculated Si, % | Calculated C, % | Calculated H, % | Calculated Cl, % |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 7 | $NCCH_2CH_2Si(CH_3)_2OSi(CH_3)_2CH_2$[illegible] | [illegible]<br>119/2 | [illegible] | [illegible] | [illegible] | [illegible] | [illegible] | [illegible] | 5.60 | — | 17.16 | 29.35 | 5.54 | — |

Average molecular weight 525.2 (cryoscopic method in benzene). Viscosity $v_{20^\circ} = 17.68$ cSt, $v_{50^\circ} = 8.04$ cSt, $v_{100^\circ} = 3.97$ cSt. In the IR spectrum (on an IKS-12 instrument with a LiF prism, layer 0.05 mm) a band at 2248 cm$^{-1}$ was found, characteristic of the –C N bond.

The reaction was carried out in an analogous manner with 16.4 g (0.055 g-mol) $[(CH_3)_2SiO]_4$, 3.12 g (0.013 g-mol) $[NCCH_2CH_2Si(CH_3)_2]_2O$, and 0.7 ml (2 wt. %) conc. $H_2SO_4$. The contents of the flask were stirred at room temperature for 24 hr, after which they were treated analogously. The residue was subjected to vacuum distillation in a stream of nitrogen; 1.32 g of low-boiling products was isolated, with a maximum pot temperature of 249°/2 mm. The polymer is a light-yellow transparent viscous oil, weight 15.6 g. Yield 90% based on the dinitrile taken.

$$C_{42}H_{116}Si_{18}O_{17}N_2. \quad \begin{array}{ll} \text{Found \%:} & N\ 2.01;\ 2.34 \\ \text{Calculated \%:} & N\ 1.97 \end{array}$$

Average molecular weight 1356 (cryoscopic method in benzene). Viscosity $v_{-20^\circ} = 164.3$ cSt, $v_{0^\circ} = 80$ cSt, $v_{20^\circ} = 48.3$ cSt, $v_{50^\circ} = 25.9$ cSt, $v_{100^\circ} = 12.73$ cSt.

**Synthesis of $\gamma$-cyanopropylchloromethyltetramethyldisiloxane.** In the experiment, 10.5 g (0.04 mole) $[NCCH_2CH_2CH_2Si(CH_3)_2]_2O$, 61.88 g (0.28 mole) $[ClCH_2Si(CH_3)_2]_2O$, and 0.4 g (4 wt. % of the dinitrile) conc. $H_2SO_4$ were used. The contents of the flask were stirred at room temperature for 24 hr, after which they were treated with water. After the usual work-up, the excess $[ClCH_2Si(CH_3)_2]_2O$ was distilled off and the residue was subjected to vacuum distillation. Sixteen grams of product with b.p. 140—142°/7 mm was isolated, consisting of $NCCH_2CH_2CH_2Si(CH_3)_2OSi(CH_3)_2CH_2Cl$. Yield 80% based on the dinitrile taken. The excess dichloride $[ClCH_2Si(CH_3)_2]_2O$ isolated from the reaction can be used repeatedly without preliminary purification.

**Synthesis of $\beta$-cyanoethylchloromethyltetramethyldisiloxane.** Analogously to the preceding experiment, from 29 g (0.12 g-mol) $[NCCH_2CH_2Si(CH_3)_2]_2O$, 139.2 g (0.48 g-mol) $[ClCH_2Si(CH_3)_2]_2O$, and 1.74 g (6 wt. % of the dinitrile) conc. $H_2SO_4$, the disiloxane $ClCH_2Si(CH_3)_2OSi(CH_3)_2CH_2CH_2CN$ was obtained in an amount of 44 g, with b.p. 120—123°/5 mm. Yield 77% based on the dinitrile taken.

**Synthesis of $\beta$-cyanoethyliodomethyltetramethyldisiloxane.** Into a flask fitted with a reflux condenser were placed 17 g (0.072 g-mol) $ClCH_2Si(CH_3)_2OSi(CH_3)_2CH_2CH_2CN$, 300 ml of absolute acetone, and 23.9 g (0.144 g-mol) of dry KJ. The mixture was boiled for 50 hr. It was then filtered from the precipitate and, after the acetone had been distilled off, vacuum distillation gave 19 g (0.06 g-mol) $JCH_2Si(CH_3)_2OSi(CH_3)_2CH_2CH_2CN$, with b.p. 116—119°/2 mm. Yield 83% based on the chloride taken.

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

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