TABLE II

Preparations of Compounds

Starting Materials				Reaction Products			
Compound	Wt., g.	Compound	Wt., g.	Chief product	Wt., g.	Yield, %	Other products
$C_6H_5CH_2SiH_3$	6.3	$HgCl_2$[a]	11.3	$C_6H_5CH_2SiH_2Cl$	5.4	67	Hg, HCl
$C_6H_5CH_2SiH_3$	6.3	$HgBr_2$[a]	13.5	$C_6H_5CH_2SiH_2Br$	9.5	92	Hg, HBr
$C_6H_5CH_2SiH_3$	8.9	$Hg(NCS)_2$[b]	23	$C_6H_5CH_2SiH_2NCS$	6.0	46	Hg, $H_3N_3C_3S_3$, $C_6H_5CH_2Si(NCS)_3$[c]
$C_6H_5CH_2SiH_3$	4.2	Br_2[d]	16.7	$C_6H_5CH_2SiHBr_2$	7.2	75	HBr
$C_6H_5CH_2SiH_3$	4.5	Br_2[e]	25	$C_6H_5CHBrSiBr_3$	14.3	89	HBr
$C_6H_5CHBrSiBr_3$	17.4	Br_2[f]	10	$C_6H_5CBr_2SiBr_3$	10.6	52	HBr
$C_6H_5CHBrSiBr_3$	40	$LiAlH_4$	8	$C_6H_5CHBrSiH_3$	5.5	30	LiBr, $AlBr_3$, $C_6H_5CH_2SiH_3$[h]
$C_6H_5CH_2SiH_2Cl$	5.6	H_2O[i]	3	$(C_6H_5CH_2SiH_2)_2O$	4.2	92	HCl
$C_6H_5CH_2SiI_3$	14.3	40% HF[j]	25	$C_6H_5CH_2SiF_3$	2.6	51	HCl, residues[j]

[a] Addition in five equal lots over 2 hr. with gentle warming. [b] Use of 16 g. of carbon tetrachloride as solvent; addition of 2 g. of mercuric thiocyanate every 5 min., with 30 min. reflux at end of additions. [c] Probable formula of untested residue weighing 5 g. [d] Addition over 2 hr. in dark with constant very slow flow of bromine. [e] Very slow constant addition of bromine over 3 hr. at 0° in weak daylight. [f] Gentle heating for 6 hr. in sunlight; then addition of 5 g. of bromine with 2 more hr. heating. [g] One hour of reflux in 300 ml. of ether, then gradual addition to 500 ml. of stirred 4M hydrochloric acid–ice mixture, next distillation of ether, then drying with anhydrous sodium sulfate and finally fractional distillation. [h] Weight 5.4 g. (48% yield). [i] Use of 3 g. of ethyl bromide as solvent; strong agitation with 3 g. of water twice. [j] One-half hour of vigorous shaking at 75°; next cooling and then extraction with 5 g. of ethyl bromide; next distillation; residues included 0.8 g. of unidentified liquid of b.p. approximately 125° under 1 mm. pressure.

tain halides. Because of the complications involved, it is necessary to present the preparations of benzylsilane and the benzyliodosilanes in detail.

Benzylsilane. Gradual addition of 2.2 l. of 0.7 M benzylmagnesium chloride to 1400 g. of silicon tetrachloride in 600 ml. of ether over a period of 3 hr., then storage overnight, next filtration and washing, and then fractional distillation produced 410 g. of crude benzyltrichlorosilane, b.p. 215°. Thereupon, the preparation included gradual addition of 390 g. of benzyltrichlorosilane over 1 hr. to 65 g. of lithium aluminum hydride dissolved in 700 ml. of ether, next 3 hr. reflux, then a very slow pouring of the ether solution with constant stirring into 1200 ml. of 4M hydrochloric acid–ice mixture (enough to maintain acidity), next separation of the ether layer and finally fractional distillation. Fractional distillation in a 50-cm. column 10 mm. in i.d. filled with cut-up steel gauze furnished 185 g. (87% yield) of crude benzylsilane, 140 g. of which had the b.p. 91–92° under 116 mm. pressure. Table I lists the properties of a 45 g. center cut, which had a weak aromatic odor. Storage of benzylsilane was in sealed glass tubes with little air present. The end fraction of the benzylsilane contained 10 g. of *sym*-diphenylethane, later purified by fractional freezing to a m.p. of 47° and a b.p of 281°, and to a very low Si-H content.

Benzyliodosilane and benzyltriiodosilane. Gradual addition of 35 g. of iodine, added in 5-g. portions one every 25 min., to 18 g. of benzylsilane over 3 hr. with gentle warming and then fractional distillation gave 5 g. of unchanged benzylsilane, 9 g. (25% yield) of crude benzyliodosilane, b.p. 100–116° under 15 mm., and approximately 20 g. of higher boiling material evidently largely a mixture of benzyldiiodosilane and benzyltriiodosilane. Two fractional distillations of the benzyliodosilane under first 15 mm. and then 1 mm. pressure furnished a 3.6 g. center cut for the study of properties. Reflux of the 20 g. of mixed benzyldiiodosilane and benzyltriiodosilane with more iodine, until a slight excess of iodine remained, produced a liquid containing some dark solid not decolorized by reflux with 2 g. of fine copper wire. Total distillation and then fractional distillation furnished approximately 3.5 g. of tetraiodosilane, a white solid of m.p. above 100° and of b.p. below 155° at 1 mm. pressure, and then 30.6 g. (43% yield) of benzyltriiodosilane, the center-boiling 11 g. of which served for study of the properties. An altered method of addition of benzyliodosilane was necessary in the analysis for silane hydrogen.

Philadelphia 4, Pa.

[Contribution from the Silicone Products Department, General Electric Co.]

Silanols and Cyclosiloxanes from Difunctional Cyanoalkylchlorosilanes

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The preparation of methyl(β-cyanoethyl)silanediol, methyl(γ-cyanopropyl)silanediol, and phenyl(β-cyanoethyl)silanediol is reported. These were condensed to polymers, and crystalline methylcyanoethyl and phenylcyanoethyl cyclic tetramers were isolated. Some new thoughts are presented on the probability of formation of the various stereoisomeric forms of cyclic oligomers of the $(RR'SiO)_n$ type.

Cyanoalkylsilicon compounds have been of considerable interest in recent years, as potential raw materials for making silicone elastomers with improved resistance to swelling and disintegration by certain fuels and solvents.[2,3] The cyanoethylsilanes are of particularly practical interest since

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they are based on acrylonitrile. It has however been difficult to make suitable difunctional monomers. Whereas acrylonitrile readily reacts with trichlorosilane to give β-cyanoethyltrichlorosilane,[4-8] methyldichlorisilane adds to acrylonitrile with much more difficulty, and shows a much greater tendency to give mixtures of the α-cyanoethyl and β-cyanoethyl adducts.[9-13] Other methods are therefore commonly employed to make methyl (β-cyanoethyl)dichlorosilane[7,14-17]

Methyl(γ-cyanopropyl)dichlorosilane on the other hand is readily prepared by the addition of methyldichlorosilane to allyl cyanide, generally using platinum-type catalysts.[18,19] but also under other conditions.[13]

It has been claimed that phenyl(β-cyanoethyl)-dichlorosilane can be made by addition of phenyldichlorosilane to acrylonitrile.[13] We report here its preparation by action of phenylmagnesium chloride on β-cyanoethyltrichlorosilane.

Hydrolysis of these chlorosilanes yields silanols and linear and cyclic polysiloxanes. Some of these have been described, while others are reported here for the first time.

Silanediols are, generally speaking, labile compounds. An earlier attempt in these laboratories to make methyl(β-cyanoethyl)silanediol was for this reason not successful.[17] We have found that the method devised by Takiguchi,[20] for making dimethylsilanediol, etc., permits preparation not only of methyl(β-cyanoethyl)silanediol but also of methyl(γ-cyanopropyl)silanediol and phenyl(β-cyanoethyl)silanediol.

These three diols are solids, melting respectively at 75-76°, 70-75°, and 79-82°. The infrared spectrum of each was consistent with the assigned structure. The diols are soluble in water and in polar organic solvents, and may be recrystallized from diethyl ether. The two methyl compounds may be stored as solids in Pyrex containers in a refrigerator, or under hexane at room temperature. They condense readily at room temperature yielding colorless fluids. The phenyl compound is more stable to storage in Pyrex glass. However, unexpectedly, it seemed to condense more readily in the presence of dry sodium carbonate than either of the methyl compounds.

Condensation of each of these silanediols can be accomplished by heating with benzene and sodium carbonate, and removing the water from the benzene-water azeotrope by means of a Dean-Stark trap. This procedure yields mixtures of cyclic polysiloxanes and silanol chain-stopped linear polysiloxanes. The same types of polysiloxanes are obtained by simple hydrolysis of the chlorosilanes.

The cyclic tetramer, 1,3,5,7-tetramethyl-1,3,5,7-tetrakis(β-cyanoethyl)cyclotetrasiloxane, has been described as a viscous liquid boiling at 277-280° at 0.2 mm., n^{25}_d 1.4580 [12g]. We have observed that most samples of this fluid on standing at room temperature deposit small amounts of solid. Storage in a refrigerator resulted in an increase in the amount of precipitation. The solid, which proved to be a tetramer, was freed of residual oil by recrystallization from benzene, methanol, or a mixture of pentane and chloroform. The yield of solid tetramer varied but was of the order of 15-20% (that of recrystallized compound about 5-10%) of the weight of the polysiloxane condensate. It is apparent that the crystalline tetramer we have observed represents only a portion of the total tetramer formed, as molecular distillation of the mixed polysiloxane hydrolyzates yielded fractions (which, according to molecular weight determinations, were largely tetramer, and which showed no trimer band in the infrared spectrum) from which only the usual small proportion of solid tetramer precipitated.

In the case of the poly[phenyl(β-cyanoethyl)-siloxanes], two crystalline tetramers were observed, one melting at 128-129°, the other at 117°. The infrared spectra of these two solids differed, but in solution the spectra were identical. For this reason we believe these to be polymorphs rather than stereoisomers. No crystalline compounds were obtained from the methyl(γ-cyanopropyl)siloxane

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(2) *Rubber World*, Sept. 1958, p. 904.

(3) T. C. Williams, R. A. Pike, and F. Fekete, Abstracts of the 134th Meeting of the American Chemical Society, Chicago, Ill., Sept. 1958; *Chem. Eng. News*, **36**, No. 38, p. 73, Sept. 22, 1958.

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(6) V. B. Jex and J. E. McMahon, Belgian Patent **553,603** (1956).

(7) J. C. Saam and J. L. Speier, *J. Org. Chem.*, **24**, 427 (1959).

(8) R. A. Pike, J. E. McMahon, V. B. Jex, W. T. Black, and D. L. Bailey, *J. Org. Chem.*, **24**, 1939 (1959).

(9) S. Nozakura, *Bull. Chem. Soc. Japan*, **29**, 660 (1956).

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(12) V. B. Jex and J. E. McMahon, U.S. Patents: (a) **2,906,764**, (b) **2,906,765**, (c) **2,907,784**, (d) **2,908,699**, (e) **2,908,700**, (f) **2,908,701**, (g) **2,911,426**, (all 1959).

(13) A. D. Petrov and V. M. Vdovin, *Izvest. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk*, 1490 (1957).

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(16) M. Prober, U.S. Patent **2,913,472** (1959).

(17) G. D. Cooper and M. Prober, *J. Org. Chem.*, **25**, 240 (1960).

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preparations, though the presence of cyclic polymers was evident from infrared spectra, and cyclic trimers, tetramers, etc., can be distilled out of the product.[21]

Any unsymmetrically substituted cyclopolysiloxane of the type $(RR'SiO)_n$ should theoretically exist in several stereoisomeric forms. Lewis[22] isolated two crystalline forms of 1,3,5-trimethyl-1,3,5-triphenylcyclotrisiloxane and surmised that the higher melting of these was the more symmetrical stereoisomer, with the phenyl groups all on the same side of the trisiloxane ring. Young and co-workers[23] also obtained these two crystalline trimers, and furthermore observed that a portion of their methylphenyl tetramer (1,3,5,7-tetramethyl-1,3,5,7-tetraphenylcyclotetrasiloxane) distillate crystallized on standing. They also obtained both liquid and crystalline forms of ethylphenyl tetramer. They pointed out that there should be four stereoisomers of such tetramers, because of the *cis-trans* arrangements of the R and R′ groups about the siloxane ring.

In view of the deposition of crystalline isomers, and the very broad melting ranges of the methyl-(β-cyanoethyl),- the methylphenyl,- the ethylphenyl,- and phenyl-(β-cyanoethyl)cyclotetrasiloxanes, literature reports of the melting points of other $(RR'SiO)_4$ systems are rather surprising. For example, $(CH_3SiHO)_4$ melts at −69 ± 3°[24]; $([CH_3][C_2H_5]SiO)_4$ at −37 to −43°, and the trimer at −2.7°[25]; $(CH_3SiClO)_4$ at 76°[26], $(C_2H_5SiClO)_4$ at −62°,[27] and $(CH_3[CH_2{=}CH]SiO)_4$ at −43.5 ± 0.1°.[28] While it is true that lack of knowledge of the phase diagrams of such isomer mixtures detracts from the significance of such data, and while we realize that it is difficult to make accurate observations of freezing points at low temperatures, the frequency with which narrow melting ranges have been reported is unexpected. We are nevertheless inclined to accept the hypotheses of Lewis and Young as valid. Certainly, regardless of whether or not it is directly connected to observations on the formation of different crystalline forms, stereoisomerism of the type they described must occur.

Relative to the probability of formation of the various stereoisomers, we have a few thoughts which were not brought out in Young's treatment of the subject. When two molecules of methyl(β-cyanoethyl)silanediol combine, they may theoretically do so to give either a *dl* (racemic) form, or a *meso* form, of the disiloxane diol. If the unsymmetrical siloxane units combine randomly in this sense to build polysiloxane chains, and if all varieties of a four unit chain (a tetramer) cyclize with equal ease, the four theoretically possible steric isomers of the cyclic tetramer will form in unequal amounts. If we assume the Walden inversion[29] does not occur during cyclization, the isomer with all the cyanoethyl groups on the same side of the ring results from cyclization of either the *dddd* or the *llll* form. It should constitute only 12.5% of the tetramer mixture if our assumptions are correct. The isomer with three cyanoethyls on one side and one on the other side can result from cyclization of *dddl ddld, dldd, lddd, llld, lldl, ldll,* or *dlll* and should comprise 50% of the tetramer. The symmetrical isomer with two cyanoethyl groups on each side, diagonal to each other, can come only from *dldl* or *ldld,* and should make up only 12.5% of the tetramer. Finally, the isomer with two vicinally located cyanoethyl groups on each side of the ring can come from *ddll, dlld, lldd,* or *lddl,* and should comprise 25% of the tetramer. If we assume the Walden inversion does occur on ring closure, the *dddd* arrangement yields the 3-1 isomer, and *dddl* yields either the all *cis* (4-0) or the vicinal (2-2), depending on which terminal silicon inverts on closure. It can be shown that the same isomer distribution should result regardless of whether inversion occurs or not. The same reasoning leads us to expect 75% of the *trans* isomer and 25% of the *cis* isomer in the case of trimers.

We would expect, intuitively, that completely random coupling and cyclizing would never occur in practice. Actual yield data, which cannot be interpreted literally since solubility relationships are not known, were surprisingly uniform in that Young obtained about 10 or 20% of his methylphenyl and ethylphenyl tetramers in crystalline form, and we observed similar yields of crystalline methylcyanoethyl tetramer. In the case of the methylphenyl trimers Lewis got 69% of the lower melting (*trans*) form, and 31% of the higher melting (*cis*) form. Young, on the other hand, reported the isolation of equal amounts of the two forms.

The assignment of configuration should be possible through x-ray diffraction studies, but we have not attempted these. We have obtained results of proton magnetic resonance studies on the crystalline isomer of methylcyanethyl tetramer and on the largely tetrameric mother liquor from which it had precipitated, and also on the two crystalline forms of phenyl-β-cyanoethyl tetramer. The spectra of each pair of samples proved to be identical. Thus, PMR provided no evidence of structural isomerism. Dipole moment studies are being made, and will be reported separately when complete.

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EXPERIMENTAL

Methyl(β-cyanoethyl)dichlorosilane, b.p. 127° (50 mm.), was made by reaction of methylmagnesium bromide with β-cyanoethyltrichlorosilane in the presence of pyridine.[14]

The principal infrared absorption bands occur at 3.44, 4.45 (C≡N), 6.99, 7.08, 7.13, 7.54, 7.91 (Si—CH_3), 8.36, 8.47, 8.68, 9.91, 11.02, 11.28, 12.36, 12.64, 12.92, 13.26, 14.10, 14.66, and 15.36 μ.

Methyl(γ-cyanopropyl)dichlorosilane, b.p. 152° (50 mm.), was made by addition of methyldichlorosilane to allyl cyanide using platinum on carbon catalyst.[18]

The principal infrared absorption bands occur at 3.42, 4.45 (C≡N), 6.86, 7.00, 7.09, 7.40, 7.92 (Si—CH_3), 8.46, 8.77, 9.85, 10.03, 10.30, 10.44, 10.77, 11.57, 12.04, 12.29, 12.69, 13.34, 14.35 μ.

Phenyl(β-cyanoethyl)dichlorosilane was made by treating β-cyanoethyltrichlorosilane with phenylmagnesium chloride. Phenylmagnesium chloride was prepared by the method of Ramsden, *et al.*,[30] using 57 g. chlorobenzene (0.5 mole) in 120 ml. of tetrahydrofuran, and 15 g. of magnesium (0.62 mole), initiating the reaction with ethyl bromide (0.5 ml.). The Grignard preparation was filtered through glass wool and the glass wool was washed with a little dry benzene. The filtered Grignard preparation was added to a stirred solution of β-cyanoethyltrichlorosilane (240 g., 1.27 moles) in benzene (300 ml.) while controlling the reaction temperature at 10–18° by external cooling. All manipulations were accomplished under dry nitrogen.

The reaction mixture was filtered and a crude product was obtained by simple distillation of this filtrate. Careful fractionation of this crude material through a 1.8 × 20 cm. column packed with protruded nickel gave 30.0 g. of product, b.p. 152° at 6 mm., d_4^{25} 1.2275.

Anal. Calcd. for $C_9H_9Cl_2SiN$: C, 46.96; H, 3.94; N, 6.09; Si, 12.20; Cl, 30.81. Found: C, 46.77; H, 4.02; N, 6.34; Si, 12.20; Cl, 30.72.

The principal infrared absorption bands are at 3.31, 3.48, 4.46 (C≡N), 6.30, 6.73, 7.00, 7.49, 7.56, 7.66, 8.42, 8.71, 8.96 (Si—C_6H_5), 9.93, 10.03, 11.14, 11.35, 13.12, 13.53, 14.08, 14.40 μ.

Methyl(β-cyanoethyl)silanediol. A 5-l., three-necked Morton flask equipped with stirrer, dropping funnel, thermometer, ice water cooling bath, and an exit system protected by a Drierite tube was charged with 2500 ml. of ethyl ether, 140 g. (1.5 moles) of freshly distilled aniline, 27 g. (1.5 moles) of distilled water, and 125 ml. of acetone. A solution of 126 g. (0.75 mole) of methyl(β-cyanoethyl)-dichlorosilane in 1 l. of ethyl ether was added slowly to the stirred contents of the flask over a 4-hr. period at about 0–2°. The reaction mixture was filtered and the aniline hydrochloride was washed with 100 ml. of ether. The filtrate was evaporated *in vacuo.* By the time about 2 l. of ether had been removed, most of the diol had crystallized. The white crystalline material was filtered off and washed with pentane. The mother liquor was evaporated to about 200 ml. An equal volume of pentane was added and the precipitated solids were filtered off. The two fractions were then combined and dried *in vacuo.* The yield was 92 g. (96%). The melting point, taken on a hot-stage melting point apparatus (Fisher-Johns) preheated to 65°, was 75–76°.

Anal. Calcd. for $C_4H_9O_2NSi$: C, 36.7; H, 6.9; N, 10.7; Si, 21.4. Found: C, 36.5; H, 6.7; N, 11.0; Si, 21.3.

The principal infrared absorption bands (mineral oil mull) occur at 3.22 (O—H), 4.45 (C≡N), 7.02, 7.56, 7.89 (Si—CH_3), 8.30, 8.42, 8.65, 9.90, 10.85, 11.26, 11.41, 11.62, 12.40, 12.64, 13.25, 14.56, 15.28 μ.

Condensation of methyl(β-cyanoethyl)silanediol. A 90-g. (0.69 mole) sample of vacuum dried diol was slurried with 1 l. of anhydrous benzene and 26 g. (0.25 mole) of sodium carbonate. The mixture was heated and stirred. The benzene-water azeotrope was condensed and separated in a Dean-Stark trap. After 4 hr. of refluxing, a total of 11.5 ml. (0.65 mole) of water had been collected. Further refluxing yielded no more water. The sodium carbonate was filtered off, and the benzene filtrate was washed with distilled water until neutral to Brom Thymol Blue. Evaporation of the benzene left an oil. This was filtered through a fritted glass filter using Celite 545. The filtrate weighed 54 g. (0.48 mole of C_4H_7ONSi).

Crystalline 1,3,5,7-tetramethyl-1,3,5,7-tetrakis(β-cyanoethyl)-cyclotetrasiloxane. Fifty grams of the above condensed fluid was diluted with ether (it is only partly miscible) and stored in a refrigerator for 2 days. A crystalline solid precipitated. This was filtered off, washed with cold ether, and dried *in vacuo.* The yield was 5.2 g. of solid melting at 94–98°. The solid was recrystallized in benzene, after which it melted at 112–114° (Fisher-Johns apparatus). Repeated recrystallizations indicate that the melting point is 112–113° in a capillary tube.

Anal. Calcd. for C_4H_7ONSi: C, 42.44; H, 6.23; N, 12.38; Si, 24.81. Found for the recrystallized solid: C, 42.45; H, 6.35; N, 12.28; Si, 24.75. Found for the liquid: C, 42.63; H, 6.61; N, 12.21; Si, 24.64.

The cryoscopic molecular weight of the solid as determined in ethylene bromide was 434 and 439, using a freezing point depression constant of 12.5. Calculated molecular weight for $(C_4H_7ONSi)_4$ is 452.

The principal infrared absorption bands (mineral oil mull) are at 4.45 (C≡N), 6.99, 7.59, 7.90 (Si—CH_3), 8.40, 9.27 (Si—O—Si), 9.92, 11.06, 12.35, 13.36, 14.53 μ. In chloroform solution the principal infrared bands occur at 3.38, 3.42, 4.45 (C≡N), 6.99, 7.58, 7.89 (Si—CH_3), 9.22 (Si—O—Si), 9.89, 11.06, and 11.31 μ.

Evidence for liquid tetramer. Methyl(β-cyanoethyl)dichlorosilane (1000 g., 5.95 moles) was added over a period of 55 min. to a stirred mixture of water (1170 ml.) and toluene (910 ml.) and the reaction mixture was maintained at 40–50°. Agitation was continued for an additional 15 min., the layers were allowed to separate and the aqueous portion was discarded. The toluene solution was washed three times with an aqueous sodium chloride solution. The toluene was distilled from the mixture by heating to a maximum pot temperature of 100° at 10 mm. pressure and the residual fluid was filtered through a bed of Celite 545. The yield of siloxane was 652 g. or 97%. This was cooled to 10° for 72 hr. to precipitate the solid isomer of 1,3,5,7-tetramethyl-1,3,5,7-tetra(β-cyanoethyl)cyclotetrasiloxane. Diethyl ether (37 ml.) was added to the cooled siloxane mixture to reduce the viscosity and the crystalline precipitate was removed by filtration. The yield of crude crystals was 101 g. or 15.5% of the total siloxane mixture. The diethyl ether was removed from the filtrate by distillation at reduced pressure.

A 904-g. charge of methyl(β-cyanoethyl)siloxanes freed of the crystalline tetramer isomer by the above procedure was molecularly distilled in a Consolidated Vacuum Corporation Model CMS-5 Centrifugal Still. The following fractions were taken at 4–6 microns pressure:

Fraction	Rotor Temp.	Yield, G.	Mol. Wt.[a]	Viscosity, Cstks. at 25°[b]
1	100–103	32	462	292
2	120–122	80	440	319
3	138–146	344	452	312
4	158	203	515	447
5	178	98	590	679
6	200	97	554	843
Total		854		

[a] Obtained cryoscopically in ethylene dibromide (K_f, 12.5). [b] Determined with an Ostwald viscosimeter.

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A similar fractionation yielded a liquid tetramer fraction for which the experimentally determined molecular weight was 491. For this fraction the principal infrared absorption bands occurred at 3.38, 3.41, 3.43, 4.44 (C≡N), 6.98, 7.56, 7.90 (Si—CH_3), 8.37, 9.24 (Si—O—Si), 9.91, 11.03, 11.29, 12.55, and 13.15 μ. The spectrum in chloroform solution was similar to, but not identical to, that of the chloroform solution of the crystalline tetramer.

Methyl(γ-cyanopropyl)silanediol. This preparation was analogous to that of the cyanoethyl diol. From 91 g. (0.5 mole) of methyl(γ-cyanopropyl)dichlorosilane and 93 g. (1.0 mole) of aniline, there was obtained 38 g. (0.26 mole) of crystals melting at 70–75° (Fisher-Johns).

Anal. Calcd. for $C_5H_{11}O_2NSi$: C, 41.4; H, 7.6; N, 9.76; Si, 19.3. Found: C, 41.3; H, 7.8; N, 10.1; Si, 20.0.

The principal infrared absorption bands (mineral oil mull) occur at 3.18 (O—H), 4.46 (C≡N), 7.06, 7.41, 7.49, 7.81, 7.91 (Si—CH_3), 8.02, 8.45, 8.55, 8.75, 9.57 (probably Si—O—Si formed by condensation of silanol groups during mulling), 10.03, 10.41, 11.26, 11.41, 11.58, 11.81, 12.18, 12.73, 13.15, 15.0 μ. The strong Si—O—Si band indicates condensation of part of this diol.

Condensation of methyl(γ-cyanopropyl)silanediol. The diol was condensed using sodium carbonate and benzene as has been described for the cyanoethyl homolog. From 44 g. (0.30 mole) of methyl(γ-cyanopropyl)silanediol there was obtained 5.1 ml. (0.28 mole) of water. The sodium carbonate was filtered off, leaving a two-phase filtrate. The silicone (lower) layer was separated, washed with water, and vacuum dried, giving 23 g. (0.18 mole of C_5H_9ONSi) of a viscous oil.

Anal. Calcd. for C_5H_9ONSi: C, 47.21; H, 7.10; N, 11.01; Si, 22.08. Found: C, 47.44; H, 7.25; N, 10.92; Si, 21.97.

Phenyl(β-cyanoethyl)silanediol. From 57 g. (0.25 mole) of phenyl(β-cyanoethyl)dichlorosilane, 47 g. (0.5 mole) of aniline, and 9 g. water, in ether and acetone as described for the other preparations, 35 g. (0.18 mole) of crystals melting at 79–82° were obtained. In this preparation, after the aniline hydrochloride had been filtered off, and the solvent removed by vacuum evaporation, the residue was a colorless oil. This crystallized at once when 50 ml. of ether was added.

Anal. Calcd. for $C_9H_{11}O_2NSi$: C, 55.9; H, 5.7; N, 7.26; Si, 14.5. Found: C, 56.2; H, 6.0; N, 7.6; Si, 15.0.

The principal infrared absorption bands (mineral oil mull) are at 2.99 (O—H), 4.45 (C≡N), 6.29, 7.00, 7.62, 7.78, 8.40, 8.66, 8.86 (Si—C_6H_5), 10.04, 10.77, 11.03, 11.31, 11.92, 13.34, 13.54, 14.33, 14.93 μ.

Condensation of phenyl(β-cyanoethyl)silanediol. From 141 g. (0.73 mole) of phenyl(β-cyanoethyl)silanediol, 500 ml. of dry benzene, and 16 g. of sodium carbonate there was obtained 12.5 ml. of water (0.69 mol, 95%). In this case condensation occurred without external heating; the temperature rose 10° and the sodium carbonate became fluffy, presumably due to hydration. The water was azeotroped off with benzene in the usual way, with the results cited above.

The sodium carbonate was filtered off and the benzene solution was washed with water until neutral to Bromthymol Blue. After removal of the solvent there remained 115 g. (0.66 mole of C_9H_9ONSi) of fluid.

1,3,5,7-Tetraphenyl-1,3,5,7-tetrakis(β-cyanoethyl)cyclotetrasiloxanes. The 115 g. of fluid was diluted with 50 ml. of ether and refrigerated. A white crystalline solid deposited. It was filtered off, washed with ether, and dried *in vacuo*. It melted at 110–119°. This solid (32 g.) was dissolved in chloroform-methanol and fractionally crystallized. Three crops of crystals were obtained, one melting at 128–129°, another at 123–126°, and a third at 117°.

Anal. Calcd. for $(C_9H_9ONSi)_4$: C, 61.66; H, 5.15; N, 7.99; Si, 16.02; Mol. wt., 701. Found for the solid melting at 117°: N, 8.05; Si, 16.21; Mol. wt., 723 (cryoscopic, in ethylene bromide). Found for the solid melting at 128–129°: C, 61.86; H, 5.61; N, 7.83; Si, 16.33; Mol. wt., 714.

The 117° and 128° tetramers appear to be polymorphs rather than stereoisomers. The 117° material was dissolved in chloroform and the solvent was evaporated. The residue melted at 123°. Its spectrum had changed to become nearly identical with that of the 128° material.

For the 117° tetramer the principal infrared absorption bands (mineral oil mull) occur at 4.45 (C≡N), 6.26, 7.00, 7.07, 7.57, 7.77, 8.28, 8.38, 8.48, 8.88 (Si—C_6H_5), 9.05, 9.26 (Si—O—Si), 9.73, 10.02, 11.13, 11.38, 13.36, 13.52, 13.76, 13.95, 14.20, 14.28, 14.93 μ.

For the 128° tetramer the principal infrared absorption bands (mineral oil mull) occur at 4.46 (C≡N), 6.29, 7.00, 7.56, 8.36, 8.65, 8.90 (Si—C_6H_5), 9.32 (Si—O—Si), 9.73, 9.93, 10.02, 10.96, 11.23, 12.77, 13.08, 13.36, 13.67, 13.80, 14.33, 14.91 μ.

In chloroform solution the two tetramers had identical infrared spectra. The principle absorption bands occurred at 3.42, 4.45(C≡N), 6.27, 7.00, 7.57, 7.79, 8.88 (Si—C_6H_5), 9.27(Si—O—Si), 9.71, 10.01, 11.03, 11.18, and 11.34 μ.

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