

are 2.77 and 3.15, respectively.<sup>19</sup> In each of these cases the larger value is associated with a decrease in this distance.<sup>8c</sup> On such a basis, the data would seem to present additional cogent evidence for the imidic type of dissociation in uracil (where the acidic group is now a part of the ring (A  $\leftrightarrow$  B)) rather than the enolic type of dissociation (where the acidic group is exocyclic C.)<sup>9</sup> The additional possibility that although the original comparison was made with *p*-substituted benzene derivatives, we actually are dealing (in the case of the 6-uracil derivatives) with dissociation from the nitrogen proximal to the substituent group and that the increased effect of the substituent is related in part to added short-range or inductive effects still leads to the same conclusion favoring imidic dissociation. (The acidifying power of these substituents is lowered by placing them in an intermediate, *i.e.*, *meta* position in the benzene series.<sup>2-4</sup>)

The curves in Figs. 2 and 3 indicate that in certain cases a relatively simple dependence of  $\sigma$  on  $\rho$  can be demonstrated and that the dependence appears to be of a limiting type involving a term such as  $A/\rho$ .<sup>20</sup> The ubiquitous similarity of the  $\sigma$  values for phenol and aniline may stem, therefore, from the fact that the  $\rho$ -values for these two systems lie close together and are of a relatively high order of magnitude.

**Acknowledgment.**—The author wishes to express his appreciation to Professor Arnold D. Welch for his continued interest in the investigation of these derivatives of uracil and to Professor Fritz Arndt for several conversations concerning the structure of uracil and related compounds.

(19) The "acidic group" refers to the actual proton releasing group, *i.e.*, the -OH group of the carboxylic acid. The values are from ref. 13 except for the estimation of pyridine which was calculated from the values of  $pK_a$  for pyridine (5.23) (A. Gero and J. J. Markham, *J. Org. Chem.*, **16**, 1835 (1951)) and 4-pyridine methyl sulfone (1.74) (S. Greenbaum, to be published).

(20) Any relationship between  $\sigma$  and  $\rho$  obviously must require reference to a common solvent system.

## Experimental

(a) The 6-uracilsulfonic acid, sulfonamide and methyl sulfone were analytical samples prepared as previously described.<sup>5,6</sup> Five-ml. aliquots of 0.005 *M* solutions were titrated with 0.1 *N* carbonate-free sodium hydroxide by means of a 500- $\mu$ l. "Micrometric" buret assembly and a Beckman *pH* meter. The temperature was maintained at  $25 \pm 1^\circ$ . Readings were taken after the addition of every 10  $\mu$ l. of titrant except at the critical regions where the readings were taken after the addition of every 5  $\mu$ l. The  $pK_a$  was determined from three points on the curve for which approximate thermodynamic corrections were calculated by means of the Debye-Hückel equation. The final values are given in Table I.

(b) The basic dissociation of sulfanilamide was determined by ultraviolet absorption spectroscopy. A stock solution was prepared by dissolving 39.79 mg. of triply recrystallized sulfanilamide (Merck and Co., Inc.) in 500 ml. of water. Ten ml. of the stock solution and the appropriate quantity of carefully prepared 0.1 *N* hydrochloric acid were used to prepare 100-ml. portions which were 0, 0.005, 0.01 and 0.02 *N* with respect to the acid. A solution which was 2 *N* with respect to acid also was prepared. Blanks were prepared for each type of solution by the omission of the sulfanilamide. The *pH* of the dilute acid solutions were determined at  $25^\circ$  with the *pH* meter and these values were checked against values calculated from the "International Critical Tables." The solutions (still maintained at  $25^\circ$ ) were transferred quickly to a Beckman model DU spectrophotometer equipped with a water-cooled cell compartment and the absorption at 275  $m\mu$  was then determined. (The measured temperature variations were less than  $1^\circ$  by this procedure.) A Beer's law check was made at the given wave length and from the intercept the cell correction of +0.004 was obtained. The data are given in Table IV.

TABLE IV  
DETERMINATION OF  $pK_a$  OF 4-AMINO GROUP OF SULFANILAMIDE, concentration, 7.96 mg./l.

Buffer, <i>N</i> HCl	<i>pH</i> <sup>a</sup>	$\frac{D}{(275\ m\mu)}$	$\log \frac{BH^+}{B}$	$\log \frac{fBH^+}{fB}$	$pK_a$
0.005	2.34	0.250	-0.26	-0.04	2.04
.010	2.03	.185	+ .07	- .05	2.05
.020	1.74	.125	+ .38	- .07	2.05

*D* (275  $m\mu$ ) 0.377 in  $H_2O$ , 0.020 in 2 *N* HCl,  $pK_a$  (av.) 2.05,  $K_b$   $1.12 \times 10^{-12}$ . <sup>a</sup> *pH* of 0.005, 0.010, 0.020 *N* HCl solutions calcd., 2.33, 2.04, 1.75, respectively. ("International Critical Tables," McGraw-Hill Book Co., Inc., New York, N. Y., 1930, Vol. VII, p. 233.)

NEW HAVEN, CONN.

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF THE GENERAL ELECTRIC CO.]

## Cyanomethyl Silicon Compounds

BY MAURICE PROBER

RECEIVED NOVEMBER 17, 1954

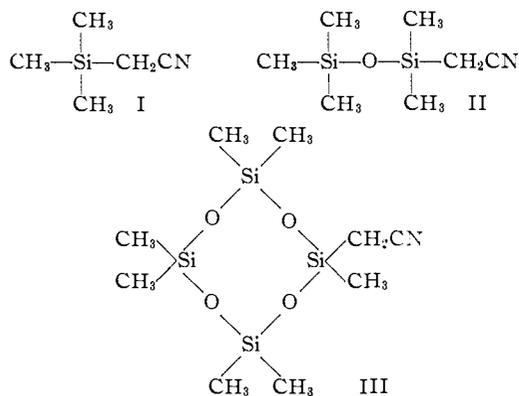
Cyanomethyltrimethylsilane, cyanomethylpentamethyldisiloxane and cyanomethylheptamethylcyclotetrasiloxane were prepared by treating the chloromethyl Grignard reagents with cyanogen. Iodomethyltrimethylsilane was cleaved by silver cyanide. The hydrolytic behavior and equilibration of these nitriles is discussed. The physical properties of the compounds indicate increased intermolecular forces.

It has long been felt that the properties of siloxanes would be altered significantly by introducing polar groups into the hydrocarbon portion of the siloxane chain. The nitrile group is one of the very polar functional groups, and the preparation of cyanomethyl silicon compounds was one of the objectives of a program on carbon-functional silicon compounds undertaken in this Laboratory. Cyanomethyl silicon compounds hitherto have not been prepared, and very few nitrile containing

carbon-functional silicon compounds have been reported.<sup>1</sup>

The compounds selected for study were cyanomethyltrimethylsilane (I), cyanomethylpentamethyldisiloxane (II) and cyanomethylheptamethylcyclotetrasiloxane (III).

(1) L. H. Sommer and J. Rockett, *THIS JOURNAL*, **73**, 5310 (1951); D. W. Lewis and G. C. Gainer, *ibid.*, **74**, 2931 (1952); D. Speck, *J. Org. Chem.*, **18**, 1689 (1953); L. H. Sommer, G. M. Goldberg, G. H. Barnes and L. S. Stone, Jr., *THIS JOURNAL*, **76**, 1609 (1954).



The preparation of the nitriles was first attempted *via* displacement reactions of the chloromethyl compounds. Chloromethyltrimethylsilane and chloromethylpentamethyldisiloxane were refluxed with alcoholic sodium cyanide, but cleavage of the silicon-carbon bond (bearing the substituent) was the main reaction, and none of the desired nitrile was obtained. The products formed in the chloromethyltrimethylsilane reaction were similar to those reported by Hauser and Hance<sup>2</sup> for the reaction of the bromomethyl compound with potassium cyanide in ethanol. Krieble and Elliott<sup>3</sup> reported silicon-carbon bond cleavage when chloromethylheptamethylcyclotetrasiloxane was refluxed with alcoholic sodium cyanide. The failure to obtain the nitrile is not due to the low reactivity of the chloro compounds toward cyanide ion, but rather to the rapid cleavage of the Si-CH<sub>2</sub>CN bond in the basic medium. Semi-quantitative experiments indicated that the nitrile was formed very rapidly. In addition recent work by Cooper and the author<sup>4</sup> demonstrated that the chloromethyl silicon compounds are very reactive in S<sub>N</sub>2 reactions.

A low yield of I can be obtained by heating chloromethyltrimethylsilane with sodium cyanide at 200° in the absence of solvent. Chloromethylpentamethyldisiloxane and the corresponding iodo compound were less reactive under similar conditions.

Copper and silver cyanides did not react with the chloromethyl compounds. Chloromethyltrimethylsilane was unreacted after 16 hours in a sealed tube at 200°, and chloromethylpentamethyldisiloxane was recovered unchanged after refluxing (152°) overnight with both metal cyanides. Hauser and Hance<sup>2</sup> have noted the non-reactivity of bromomethyltrimethylsilane toward silver cyanide in refluxing ether. Small scale experiments demonstrated that the iodides were reactive. When iodomethyltrimethylsilane and silver cyanide were heated the reaction took an unexpected course. Instead of forming the anticipated isocyanide or nitrile, the following reaction took place



Silver iodide was formed but the fate of the methylene group is not known. The actual reaction path may be formation of isocyanomethyl or cyanomethyltrimethylsilane followed by the cleavage reactions.

(2) C. R. Hauser and C. R. Hance, *THIS JOURNAL*, **74**, 5091 (1952).

(3) R. H. Krieble and J. R. Elliott, *ibid.*, **68**, 2291 (1946).

(4) G. D. Cooper and M. Prober, *ibid.*, **76**, 3943 (1954).

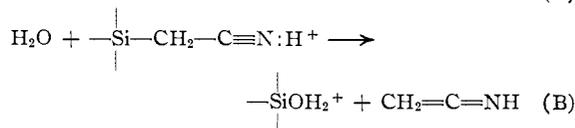
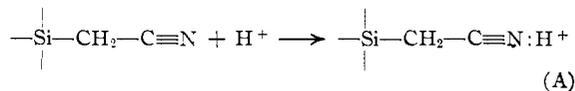
The most satisfactory method for preparing the desired nitriles was reaction of the chloromethyl Grignard reagents with cyanogen.<sup>5</sup> The reactions were initially carried out at -40 to -50°, and the over-all yields were: I, 54%; II, 38%; III, 52%. The lower boiling nitriles have very strong sweetish odors. In this work the Grignard reagent of chloromethylheptamethylcyclotetrasiloxane was prepared for the first time, and the yield of Grignard reagent was 84%.

The hydrolytic stability of the cyanomethyl compounds was studied by refluxing each of the compounds with aqueous reagents for 24 hours. Silicon-carbon bond cleavage took place with loss of the cyanomethyl group. The results are summarized in Table I.

TABLE I  
PERCENTAGE SILICON-CARBON BOND CLEAVAGE AFTER REFLUXING FOR 24 HOURS

	Water	5% HCl	5% NaOH
I	100	100	100
II	58	86	100
III	0	38	100

Silicon-carbon bond cleavage is greatest with base, least with water, and intermediate with acid. The electronegative nitrile group renders the silicon more electropositive through an inductive effect. Therefore, silicon undergoes nucleophilic attack by hydroxyl ion, resulting in extensive silicon-carbon cleavage. Hauser and Hance<sup>2</sup> have reviewed the base-catalyzed cleavage of substituted methyl silicon compounds. Acid also promotes silicon-carbon bond cleavage. A possible mechanism is



The ketenimine then rearranges to acetonitrile.<sup>6</sup>

The preparation of 1,3-bis-(cyanomethyl)-tetramethyldisiloxane was attempted by demethylation of I with concd. sulfuric acid,<sup>7</sup> but loss of the cyanomethyl group took place and hexamethyldisiloxane was formed. The desired nitrile was obtained by equilibrating II with one-half volume per cent. of sulfuric acid.<sup>8</sup> When higher concentrations of acid were used it was very difficult to isolate the pure dinitrile because of close boiling siloxanes produced by silicon-carbon bond cleavage. Loss of cyanomethyl groups also took place when III was equilibrated with hexamethyldisiloxane or octamethylcyclotetrasiloxane using four volume per cent. sulfuric acid.<sup>8</sup>

The effect of the polar nitrile group on the intermolecular forces was examined by measuring the change of viscosity with temperature. Gener-

(5) V. Grignard, E. Bellet and C. Courtot, *Ann. chim.*, **12**, 364 (1919).

(6) G. D. Cooper, *THIS JOURNAL*, **76**, 3713 (1954).

(7) J. R. Gold, L. H. Sommer and F. C. Whitmore, *ibid.*, **70**, 2874 (1948).

(8) W. I. Patnode and D. F. Wilcock, *ibid.*, **68**, 361 (1946).

ally, the greater the change of viscosity with temperature, the greater the intermolecular forces. The activation energies of viscous flow for the cyanomethyl compounds and the parent silicon compounds are given in Table II.

TABLE II  
ACTIVATION ENERGY OF VISCOUS FLOW

(I)	Compound	Activation energy, kcal./mole
(I)	Tetramethylsilane	3.1
(II)	Hexamethyldisiloxane	3.2
(III)	Octamethylcyclotetrasiloxane	2.2 <sup>9</sup>
		4.5
		3.4 <sup>10</sup>

It is apparent from these figures that the activation energy of viscous flow is increased appreciably by introducing the nitrile group.

The vapor pressures of the nitriles were measured and the heats of vaporization, calculated from the Clausius-Clapeyron equation, are listed in Table III. The entropies of vaporization are also presented. The entropies of vaporization of the cyanomethyl compounds are significantly higher than those of the parent silicon compounds, indicating once again higher intermolecular forces.

TABLE III  
HEATS AND ENTROPIES OF VAPORIZATION

Compound	Heat of vaporization, kcal./mole	Entropy of vaporization, kcal./mole/°
(I)	10.8	24.9
Tetramethylsilane	5.8 <sup>11</sup>	19.4
(II)	12.0	25.4
Hexamethyldisiloxane	8.3 <sup>9</sup>	22.2
(III)	14.0	27.6
Octamethylcyclotetrasiloxane	10.0 <sup>9</sup>	24.8

Miscellaneous physical properties were also measured. The coefficient of cubical expansion for I, II, and III, derived from the density data, was  $1.1 \times 10^{-3}$  cc./°, which is also similar to that of the corresponding siloxanes.<sup>9</sup>

The dielectric constant of III at 1 kilocycle varied from 9.64 to 8.15 over the range 10 to 50°. The dielectric behavior is that of a typical polar liquid. Unlike octamethylcyclotetrasiloxane, III does not undergo a solid state transition. Very probably, this results from the hindering effect of the cyano group. The dipole moment of III is 3.54. This value is comparable to the moments for aliphatic nitriles in benzene solution.<sup>12</sup>

The infrared absorption curves for I, II and III show a single, sharp absorption band for nitrile at  $4.48 (2242 \pm 5 \text{ cm.}^{-1})$ . This is in the low end of the range for saturated nitriles.<sup>13</sup>

### Experimental

**Cyanomethyltrimethylsilane (I).** A. **Reaction of Cyanogen and Grignard Reagent.**—The cyanogen was prepared

(9) C. B. Hurd, *THIS JOURNAL*, **68**, 364 (1946).

(10) D. F. Wilcock, *ibid.*, **68**, 691 (1946).

(11) J. G. Aston, R. M. Kennedy and G. H. Messerly, *ibid.*, **63**, 2343 (1941).

(12) L. G. Wesson, "Tables of Electric Dipole Moments," Technology Press, Cambridge, Mass., 1948, pp. 14, 17.

(13) R. E. Kitson and N. E. Griffith, *Anal. Chem.*, **24**, 334 (1952).

according to the procedure of Migrdichian,<sup>14</sup> and purified by simple distillation. Cyanogen, 66 g. (1.28 moles, 10% excess) was distilled into 400 ml. of dry ether (at  $-78^\circ$ ). With the bath temperature at  $-40$ – $-50^\circ$ , 1.17 moles of the Grignard reagent of chloromethyltrimethylsilane in 1.5 l. of ether was added dropwise to the stirred solution. Stirring was continued overnight, and the bath temperature allowed to rise slowly to room temperature. The reaction slurry was poured into cold ammonium chloride solution. A very bad emulsion formed and it was necessary to centrifuge the mixture in order to see the ether-water interface. The solution was dried over calcium chloride, the solvent removed, and the residue vacuum distilled, yielding 130 ml., b.p. 59–89° at 51 mm. The distillate was rectified, yielding 71.1 g., 0.628 mole, b.p. 84–85° at 54 mm.,  $n_D^{20}$  1.4203,  $d_4^{20}$  0.827,  $M_R D$  (calcd.)<sup>15</sup> 34.63,  $M_R D$  (obsd.) 34.66.

*Anal.* Calcd. for  $C_5H_{11}NSi$ : C, 53.04; H, 9.79; N, 12.34. Found: C, 52.9; H, 9.8; N, 12.3, 12.4.

**B. Reaction of Chloromethyltrimethylsilane and Sodium Cyanide.**—A stainless steel bomb was charged with 61.3 g. (0.500 mole) of chloromethyltrimethylsilane and 29.4 g. (0.600 mole) of sodium cyanide and shaken at 200° for eight hours. Ten one-half inch steel balls were placed in the bomb to promote mixing. The liquid reaction product was decanted, the salts washed with dry ether, and the solution rectified. There were obtained (a) 6.1 g. of hexamethyldisiloxane and 31.8 g. of chloromethyltrimethylsilane, b.p. 96–100° (composition established by infrared and chlorine analyses); (b) 4.5 g. of cyanomethyltrimethylsilane, b.p. 84–85° at 56 mm.,  $n_D^{20}$  1.4200, infrared spectrum identical with that prepared by the cyanogen reaction; (c) 3.0 g. of residue.

*Anal.* Calcd. for  $C_5H_{11}NSi$ : C, 53.04; H, 9.79; N, 12.37. Found: C, 53.2; H, 9.7; N, 12.8.

**Reaction of Silver Cyanide and Iodomethyltrimethylsilane.**—A solution of 50.0 g. (0.234 mole) of iodomethyltrimethylsilane in 75 ml. of distilled diphenyl ether (added to raise the reaction temperature) was stirred with 50.0 g. (0.373 mole) of silver cyanide at a bath temperature at 175°. The reflux temperature dropped, and 22 ml. of distillate, b.p. 110–170°, was collected. The distillate was rectified yielding 11.0 g. (49% yield) of isocyanotrimethylsilane, b.p. 69–71° at 168 mm., 117–118° at atmospheric pressure, m.p. 11–12°,  $n_D^{20}$  1.3922; reported<sup>16</sup> b.p. 117.8°, m.p. 10.5–11.5°,  $n_D^{20}$  1.3891. The observed infrared curve was similar to that reported. There was a 2.5-g. forerun and 2.5-g. residue which had characteristic isocyanide odors.

*Anal.* Calcd. for  $C_4H_9NSi$ : C, 45.58; H, 9.12. Found: C, 45.8; H, 9.0.

**Cyanomethylpentamethyldisiloxane (II).**—The cyanogen-Grignard procedure for I was followed. From 225.0 g. (1.30 moles) of chloromethylpentamethyldisiloxane, there was obtained 18.2 g. of unreacted chloromethyl compound and 92.5 g. (0.494 mole, 38% yield) of cyanomethylpentamethyldisiloxane, b.p. 82–83° at 14 mm.,  $n_D^{20}$  1.4118,  $d_4^{20}$  0.875,  $M_R D$  (calcd.) 53.32,  $M_R D$  (obsd.) 53.21.

*Anal.* Calcd. for  $C_7H_{17}NSi_2$ : C, 44.88; H, 9.15; N, 7.48. Found: C, 45.2, 44.7; H, 9.4, 9.2; N, 7.2, 7.4.

**Cyanomethylheptamethylcyclotetrasiloxane (III).**—The cyanogen-Grignard procedure for I was followed. From 770.4 g. (2.40 moles) of chloromethylheptamethylcyclotetrasiloxane there was obtained 52.6 g. of octamethylcyclotetrasiloxane, 43.8 g. of unreacted chloromethylheptamethylcyclotetrasiloxane and 397.7 g. (1.242 moles, 52% yield) of cyanomethylheptamethylcyclotetrasiloxane, b.p. 92–93° at 2.0–2.5 mm.,  $n_D^{20}$  1.4155,  $d_4^{20}$  1.021,  $M_R D$  (calcd.) 79.22,  $M_R D$  (obsd.) 78.94.

*Anal.* Calcd. for  $C_9H_{23}O_4NSi_4$ : C, 33.62; H, 7.21; N, 4.36. Found: C, 33.7; H, 7.2; N, 4.4, 4.5.

When the nitrile was isolated by steam distillation, thereby avoiding the emulsion difficulties, the yield was 37%.<sup>17</sup>

(14) V. Migrdichian, "The Chemistry of the Organic Cyanogen Compounds," Reinhold Publishing Co., New York, N. Y., 1947, p. 10.

(15) A. I. Vogel, W. T. Cresswell and J. Leicester, *J. Phys. Chem.*, **58**, 174 (1954); A. I. Vogel, W. T. Cresswell, G. H. Jeffrey and J. Leicester, *J. Chem. Soc.*, 531 (1952).

(16) J. J. McBride, Jr. and H. C. Beachell, *THIS JOURNAL*, **74**, 5247 (1952); S. Sujishi, Paper 31 P, Abstracts of Meeting of The American Chemical Society, April 1951, and private communication from Dr. Sujishi.

(17) This modification was carried out by Dr. J. R. Ladlaud and Mr. C. Kumienski in this Laboratory.

The Grignard reagent was prepared by priming with small quantities of methyl Grignard. The ether solution should not be stirred until the ether is refluxing vigorously. If stirring is begun too early, the reaction ceases. The yield of Grignard reagent was determined in the usual manner.<sup>18</sup>

**Hydrolytic Stability.**—The nitrile, 5.00 g., was refluxed for 24 hours with 25 ml. of each reagent. The upper organic layer was removed, washed with water, weighed, dried, and refractive indices and infrared absorptions were obtained. Approximately 95 mole per cent. was accounted for. In the hydrolysis of III with acid and base, the organic layer was dispersed in small droplets. The emulsion was shaken with benzene, and the solvent then removed by evaporation. The losses through volatility account for the lower recoveries (70–80%) in these two cases.

The percentage of unreacted nitrile was obtained by comparison of the intensity of the C≡N band with that of the pure compound. The organic phase did not contain any acetonitrile, a possible cleavage product. The decrease in C≡N is due to silicon-carbon bond cleavage. It does not result from hydrolysis to CONH<sub>2</sub> or CO<sub>2</sub>H with retention of the silicon-carbon bond since there are no infrared absorption bands corresponding to C=O, N-H or O-H.

In a larger scale hydrolysis of I with water acetonitrile was isolated.

The results of Table I seem to indicate that III possesses the greatest hydrolytic stability. This is surprising since hydrolytic stability is decreased by increasing the number of siloxane bonds attached to the functional group silicon.<sup>9</sup> The explanation for the observed order of reactivity may be a solubility effect, since these hydrolyses were heterogeneous reactions, and III is least soluble.

**Attempted Demethylation of Cyanomethyltrimethylsilane.**—I (5.00 g.) was added slowly to 15 ml. of stirred concd. sulfuric acid. No gas was evolved, and the solution was stirred overnight at room temperature. The solution was poured into 100 ml. of ice-water, and there was obtained 2.8 g. (78% yield) of hexamethyldisiloxane, b.p. 100–101°, *n*<sub>D</sub><sup>20</sup> 1.3788, infrared curve identical with that of an authentic sample.

**Equilibration of Cyanomethylpentamethyldisiloxane.**—II (57.7 g., 0.294 mole) and 0.05 ml. of concd. sulfuric acid were shaken gently for 20 hours. The siloxanes then were shaken vigorously with water, dried over calcium chloride, and rectified. There was obtained 8.3 g. (0.051 mole) of hexamethyldisiloxane, 26.3 g. (0.140 mole) of cyanomethylpentamethyldisiloxane and 11.0 g. (0.052 mole) of 1,3-bis-(cyanomethyl)-tetramethyldisiloxane, b.p. 97–99° at 0.1 mm., *n*<sub>D</sub><sup>20</sup> 1.4393.

*Anal.* Calcd. for C<sub>5</sub>H<sub>15</sub>ON<sub>2</sub>Si<sub>2</sub>: C, 45.23; H, 7.59; N, 13.19. Found: C, 44.8; H, 7.3; N, 13.4.

**Equilibration of Cyanomethylheptamethylcyclotetrasiloxane.**—A mixture of 32.15 g. (0.100 mole) of III and 1.40 g. (0.00832 mole) of hexamethyldisiloxane (molar ratio, 12:1) was shaken with 1.2 ml. of concentrated sulfuric acid at room temperature for 24 hours. The sulfuric acid went into solution with slight warming. The solution was then shaken with water but a bad emulsion developed, which contained solid. Benzene was added to break the emulsion. The solution was filtered, washed with water until neutral, and dried over calcium chloride plus calcium carbonate. The solvent was removed and the residue was pumped at 2 mm. for 2 hours at 160 to 170°. This oil has a viscosity of 575.3 cp. at 37.8°, 303.5 cp. at 65.0° and 158.1 cp. at 98.9°; a viscosity temperature coefficient of 0.72 compared to 0.6 for a dimethylpolysiloxane.<sup>19</sup> Infrared analysis indicated a loss of 10% of the cyanomethyl groups. There was no CO<sub>2</sub>H or CONH<sub>2</sub> absorption.

In an equilibration of III with octamethylcyclotetrasiloxane and hexamethyldisiloxane (molar ratio 2:5:1) using 4 volume per cent. sulfuric acid 37% of cyanomethyl groups were lost. This oil has a viscosity temperature coefficient of 0.62.

**Viscosity and Density.**—The viscosities were measured with calibrated Ostwald-Cannon-Fenske viscometers, the densities with 10-ml. pycnometers. The bath temperature was constant to ±0.1°. The energy of activation for viscous flow was calculated from a least squares treatment of the data.

(18) H. Gilman, E. A. Zoellner and J. B. Dickey, *THIS JOURNAL*, **51**, 1576 (1929).

(19) E. G. Rochow, "Chemistry of the Silicones," 2nd Ed., John Wiley and Sons, Inc., New York, N. Y., p. 87.

		I	II	III
37.8°	Kin. viscosity	1.33	1.69	4.86
	Density, <i>d</i> <sup>37.8</sup> <sub>4</sub>	0.811	0.858	1.002
	Viscosity, cp.	1.08	1.45	4.87
65.0°	Kin. viscosity	0.91	1.14	2.82
	Density, <i>d</i> <sup>65.0</sup> <sub>4</sub>	.788	0.834	0.979
	Viscosity, cp.	.72	0.95	2.74
98.9°	Kin. viscosity	0.62	0.80	1.66
	Density, <i>d</i> <sup>98.9</sup> <sub>4</sub>	.757	.802	0.938
	Viscosity, cp.	.47	.64	1.48

**Vapor Pressure.**—The vapor pressures were measured by distillation using a procedure similar to that of Wilcock.<sup>10</sup> The heat of vaporization was calculated from a straight line least squares treatment of the data.

Compound	Vapor pressure, mm.	Temp., °C.
I	13.0	54.9
	22.5	66.3
	45.5	81.4
	84.5	96.8
II	9.4	75.7
	24.2	95.6
	47.3	111.3
	92.3	128.3
III	11.6	118.5
	23.2	133.1
	43.5	148.7
	83.7	166.1

The heat of vaporization of octamethylcyclotetrasiloxane recently has been shown to vary somewhat with temperature.<sup>20</sup> However the figure reported by Wilcock<sup>10</sup> has been used for comparison in Table III, since his measurements were carried out in the same temperature range as those of the corresponding nitrile.

**Dielectric Measurements.**—The static dielectric constant (1 kilocycle) is plotted in Fig. 1.

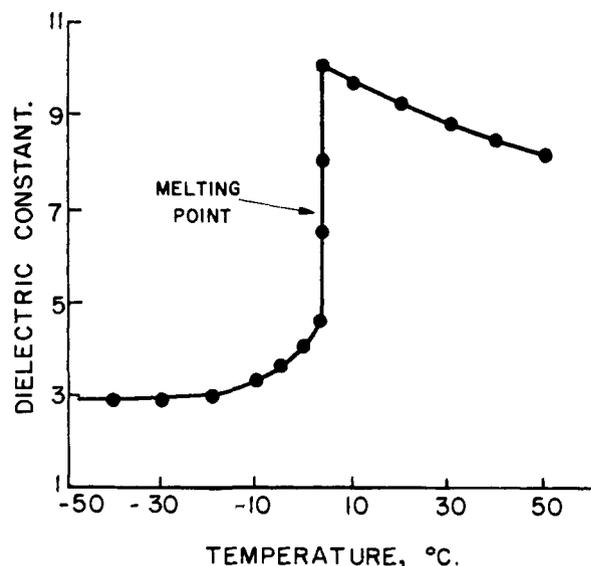


Fig. 1.—Dielectric constant vs. temperature for cyanomethylheptamethylcyclotetrasiloxane.

The curve below the melting point undoubtedly is due to some impurity in this sample. The dipole moment was calculated using the Onsager equation in the form

$$\frac{4\pi N\mu^2}{9kT} = \frac{M}{d} \frac{(\epsilon_0 - \epsilon_\infty)(2\epsilon_0 + \epsilon_\infty)}{\epsilon_0(\epsilon_\infty + 2)^2}$$

(20) R. C. Osthoff and W. T. Grubb, *THIS JOURNAL*, **76**, 399 (1954).

where  $N$  is the Avogadro number;  $k$ , the Boltzmann constant;  $T$ , the absolute temperature, 293.2°;  $M$ , the molecular weight, 321.5;  $d$ , the density, 1.021;  $\epsilon_0$  the static dielectric constant; and  $\epsilon_\infty$ , that part of the dielectric constant due to atomic and electronic polarization.<sup>21</sup>

(21) J. D. Hoffman, *THIS JOURNAL*, **75**, 6313 (1953), has demonstrated that  $\epsilon_\infty$  calculated from the usual equation  $\epsilon_\infty = n^2$ , is unsatisfactory for silicones because of the large atomic polarization. He has developed the equation  $\epsilon_\infty = 1.177n^2$ , and this value of  $\epsilon_\infty$  was used above.

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## Some Organotin Compounds Containing Water-solubilizing Groups

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Methodides and methosulfates of some organotin compounds containing tertiary amino groups have been prepared. A few of these compounds have remarkable solubilities in water. The solubility increases with an increase in the number of quaternary ammonium groups in the molecule. The methodide of triphenyl- $\gamma$ -diethylaminopropyltin is more soluble than that of triphenyl- $p$ -dimethylaminophenyltin. Triphenyl- $p$ -bromophenyltin was found to have a much lower melting point than that described in the literature.

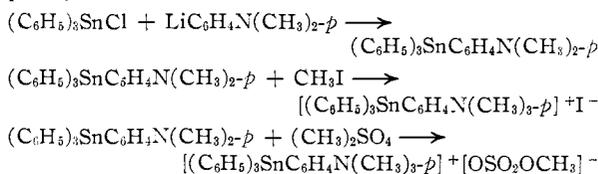
The evaluation of an organotin compound as a chemotherapeutic agent would be rendered more feasible by adequate masking of the tin and the addition of water-solubilizing groups to the molecule.<sup>1</sup> Some organolead compounds containing tertiary amino groups have been converted into their methodides and methosulfates, thus enhancing their solubility in water.<sup>2</sup> In this investigation a number of new organotin compounds were prepared and their solubilities were studied.

The organotin compounds containing one or more tertiary amino groups were prepared by treating an organotin halide with an organolithium compound containing a substituted amino group or by treating a dialkylaminoalkyl halide with triphenyltin-lithium.<sup>3</sup> The conversion of organotin compounds containing substituted amino groups to their methodides or methosulfates was carried out by treating the organotin compounds with methyl iodide or with dimethyl sulfate. Tetra- $p$ -dimethylaminophenyltin was treated with an excess of methyl iodide to give the tetramethiodide which could be recrystallized from water, but the product obtained from the reaction of tetra- $p$ -dimethylaminophenyltin with dimethyl sulfate was too soluble in water to be purified from this solvent. Triphenyl- $p$ -dimethylaminophenyltin gave the methodide and the methosulfate in good yields, but they are only slightly soluble in hot water. Attempts to prepare diphenyldi- $p$ -dimethylaminophenyltin resulted in an oily product, the identity of which was shown by its conversion to the methodide derivative. The solubility of these quaternary ammonium salts appears to increase with an increase in the number of the quaternary ammonium groups. Also, the methosulfates seem to have a better solubility than the corresponding methodides.

Organotin compounds containing dialkylaminoalkyl groups also were considered as possible intermediates for introducing water-solubilizing groups into the molecule. Triphenyl- $\gamma$ -diethylaminopropyl-

tin was obtained as an oily product from the reaction of triphenyltin-lithium with  $\gamma$ -diethylaminopropyl chloride. The methodide of triphenyl- $\gamma$ -diethylaminopropyltin is somewhat soluble in hot water while the methosulfate derivative is too soluble to be isolated. Here again, it appears that the methosulfate is more soluble than the corresponding methodide.

As an illustration, the preparation of quaternary ammonium salts of triphenyl- $p$ -dimethylaminophenyltin is outlined as



Some of these quaternary ammonium salts decompose on heating and it is difficult to judge the purity based on the melting point determination. A few methodides can be recrystallized from water to give crystalline products.

In order to synthesize some tetraaryltin compounds containing water-solubilizing groups in the  $p$  position of one of the aryl groups, triphenyl- $p$ -bromophenyltin was considered as a possible intermediate compound. This compound was prepared in a high yield by the reaction of  $p$ -bromophenylmagnesium iodide with triphenyltin chloride. However, when  $p$ -bromophenyllithium was used instead of the Grignard reagent, no triphenyl- $p$ -bromophenyltin was isolated. The failure to obtain the desired product probably is due to the cleavage of the carbon-tin bond of the organotin compound by the organolithium compound. It has been observed that tetraphenyltin<sup>4</sup> and tetraphenyllead<sup>5</sup> can be cleaved by  $n$ -butyllithium to give tetra- $n$ -butyltin and tetra- $n$ -butyllead, respectively. The corresponding metal-metal interconversion reaction with tetraphenyllead and  $n$ -butylmagnesium bromide does not occur in the same length of

(1) H. Gilman and C. F. Arntzen, *J. Org. Chem.*, **15**, 994 (1950).

(2) H. Gilman and L. Summers, *THIS JOURNAL*, **74**, 5924 (1952).

(3) H. Gilman and S. D. Rosenberg, *ibid.*, **74**, 531 (1952).

(4) H. Gilman, F. W. Moore and R. G. Jones, *ibid.*, **64**, 2482 (1942).

(5) H. Gilman and F. W. Moore, *ibid.*, **62**, 3206 (1940).