(30%) of a yellow solid, m.p. 60–63°. Recrystallization from ethanol–water gave a crystalline solid of m.p. 65–67%.

Anal. Calcd. for $C_{13}H_9NO_4S$: C, 56.80; H, 3.32. Found: C, 56.82; H, 3.54.

A solution of the product, m.p. 65–67°, in ethanol was hydrolyzed with 10% sodium hydroxide and the resulting solution concentrated to dryness. The residue was dissolved in 10% sodium hydroxide and treated with excess 3% hydrogen peroxide to produce a dark brown solid, m.p. 153–160°. Recrystallization from ethanol–water gave a brown crystalline solid,[12] m.p. 174–177°. Since no diphenyl disulfide could be obtained, it was concluded that the rearrangement product, m.p. 65–67°, was the phenyl S-(*p*-nitrophenyl) thiolcarbonate and not the isomeric *p*-nitrophenyl S-phenyl thiolcarbonate.

Phenyl S-(*p*-Chlorophenyl) Thiolcarbonate.—Phenyl *p*-chlorophenyl thioncarbonate did not yield crystalline products when heated at 285° for 30 min. The rearrangement was, however, effected in the following way. The thioncarbonate (150 mg.) was heated at 240° for 30 min.; the ethanolic solution of the product deposited upon slow cooling, 95 mg. of the starting thioncarbonate, m.p. 122–124°, as shown by mixed m.p. Dilution of the ethanolic filtrate yielded 45 mg. (30%) of product, m.p. 90–96°, which, after recrystallization from 30% ethanol, yielded white phenyl S-(*p*-chlorophenyl) thiolcarbonate, m.p. 97–98°.

Anal. Calcd. for $C_{13}H_9ClO_2S$: C, 58.97; H, 3.40. Found: C, 58.84; H, 3.65.

Alkaline hydrolysis of this compound followed by peroxide oxidation yielded 4,4'-dichlorodiphenyl sulfide,[16] m.p. and mixed m.p. 72–74°. Isolation of this disulfide proves that the chlorophenyl group was the one which migrated in the rearrangement.

2,6-Dimethylthiophenol.—This was prepared from 40 g. of 2,6-dimethylaniline by diazotization and coupling with potassium ethyl xanthate[17]; the product (17 g.) had the following properties: b.p. 91° (50 mm.), $n^{20}D$ 1.5712.

Anal. Calcd. for $C_8H_{10}S$: C, 69.51; H, 7.29. Found: C, 69.26; H, 7.53.

2,6,2',6'-Tetramethyldiphenyl disulfide, prepared by peroxide oxidation of the thiophenol, melted at 103–104°.[18]

Acknowledgment.—One of us (H. R. A.-K.) is indebted to the Royal Iraquian Government for a Fellowship, during tenure of which this work was performed.

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[16] R. Otto, *Ann.*, **143**, 111 (1867), reports the m.p. of the disulfide as 71°.

[17] The procedure of Tarbell and Fukushima, *Org. Syntheses*, **27**, 81 (1947), for *m*-thiocresol was followed.

[18] R. M. Pierson, A. J. Costanza and A. H. Weinstein, *J. Polymer Sci.*, in press (1955), report the m.p. as 105.5–106°. We are indebted to Dr. Weinstein for information about this paper.

ROCHESTER, N. Y.

[CONTRIBUTION FROM THE COLLEGE OF CHEMISTRY AND PHYSICS, THE PENNSYLVANIA STATE UNIVERSITY]

Hybrid Paraffin-siloxanes Containing the 1,6-Disilahexane Grouping[1]

BY LEO H. SOMMER AND GERALD R. ANSUL

RECEIVED OCTOBER 9, 1954

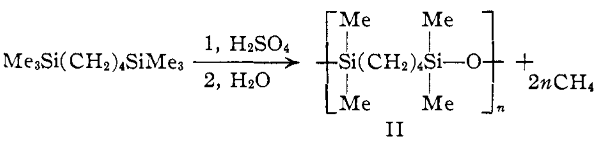
Four organosiloxanes conforming to the general formula $Me_3SiO(SiMe_2CH_2CH_2CH_2CH_2SiMe_2O)_nSiMe_3$, with n = 1, 2, 3 and 4, have been synthesized. A study of the physical properties of these substances has shown that they are intermediate between the linear methylpolysiloxanes and the paraffin hydrocarbons.

Because of the important and unusual physical properties of the organosiloxanes,[2] the synthesis of a family of compounds intermediate in structure between the linear methylpolysiloxanes and the paraffin hydrocarbons was of interest. The present paper reports the synthesis and physical properties of four hybrid paraffin-siloxanes containing the 1,6-disilahexane group.

Monomers

In the present study which deals with substances containing the 1,6-disilahexane system, 1,4-bis-(trimethylsilyl)-butane (I) may be termed a "monomer" from the fact that this compound can be converted to polysiloxanes by the sulfuric acid cleavage of one methyl group from each Me_3Si- grouping. Compound I was prepared in the present work by reaction of the di-Grignard reagent from 1,4-dibromobutane with trimethylchlorosilane, using tetrahydrofuran as a solvent. Use of tetrahydrofuran as the solvent in this preparation has several advantages over the more conventional ethyl ether. In preliminary experiments performed with ether as the solvent, the di-Grignard reagent separated as an oily lower layer and the yield of desired product was only 32%. In contrast, the di-Grignard reagent is soluble in tetrahydrofuran and compound I was obtained in yields of 52–69%. Tetrahydrofuran has the additional advantage of providing a higher reaction temperature.[3]

$$Me_3SiCH_2CH_2CH_2CH_2SiMe_3 \quad \text{I}$$



$$Me_3Si(CH_2)_4SiMe_3 \xrightarrow[2,\ H_2O]{1,\ H_2SO_4} \left[-\overset{Me}{\underset{Me}{Si}}(CH_2)_4\overset{Me}{\underset{Me}{Si}}-O- \right]_n + 2nCH_4$$

II

$$BrMg(CH_2)_4MgBr + 2Me_3SiCl \xrightarrow{\text{T.H.F.}} \text{I}$$

Treatment of a small sample of compound I with concentrated sulfuric acid gave 92% of the theoretical amount of methane (2 moles of methane per mole of I), thus indicating that silicon–carbon cleavage took place at both silicon atoms. On the basis of the above result it appeared that while Me–Si cleavage was the main reaction, about 8% of the reaction gave cleavage between silicon and methylene. In view of the latter fact, polymers II as obtained from the cleavage reaction would contain small amounts of products not having the 1,6-disila-

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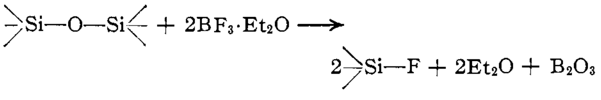
[1] Paper 47 in a series on organosilicon chemistry. For paper 46 see THIS JOURNAL, **77**, 1677 (1955).

[2] For an excellent treatment of the rapidly expanding organosiloxane field see E. G. Rochow, "An Introduction to the Chemistry of the Silicones," second edition, John Wiley and Sons, Inc., New York, N. Y., 1951.

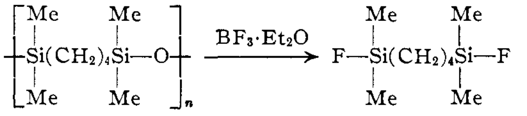
[3] R. West and E. G. Rochow, *J. Org. Chem.*, **18**, 1739 (1953), have reported the synthesis of compound I in 63% yield from reaction of the di-lithium reagent with trimethylchlorosilane in a pentane solvent.

hexane system. This difficulty was resolved by utilizing boron fluoride etherate as a reagent for converting organosiloxanes to organofluorosilanes. This reaction has been investigated extensively in this Laboratory[4] and takes the course



$$\geq Si—O—Si \leq + 2BF_3 \cdot Et_2O \longrightarrow 2 \geq Si—F + 2Et_2O + B_2O_3$$

In the present work, reaction of boron fluoride etherate with the mixture of organopolysiloxanes obtained from compound I gave three organofluorosilanes. The desired product, 2,7-dimethyl-2,7-difluoro-2,7-disilaoctane (III) was obtained in yields of 65–78%. From the yields of trimethyl-

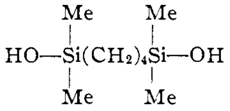


$$\left[-Si(Me)_2(CH_2)_4Si(Me)_2—O-\right]_n \xrightarrow{BF_3 \cdot Et_2O} F—Si(Me)_2(CH_2)_4Si(Me)_2—F$$

III

fluorosilane and *n*-butyldimethylfluorosilane the amount of silicon–methylene cleavage was estimated to be about 10%.

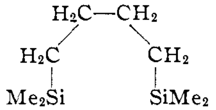
Hydrolysis of compound III with aqueous potassium hydroxide gave a white, crystalline substance, m.p. 66.5–67°, which was identified as 2,7-dimethyl-2,7-dihydroxy-2,7-disilaoctane (IV) (94% yield).



$$HO—Si(Me)_2(CH_2)_4Si(Me)_2—OH$$

IV

Since organosilicon compounds containing a seven-membered ring were unknown, it was of interest to determine whether compound IV would undergo intramolecular condensation. Refluxing of a dilute benzene solution of compound IV in the presence of a small amount of trifluoroacetic acid gave the theoretical quantity of water and resulted in the formation of an 85% yield of the desired product, 2,2,7,7-tetramethyl-1-oxa-2,7-disilacycloheptane (V).

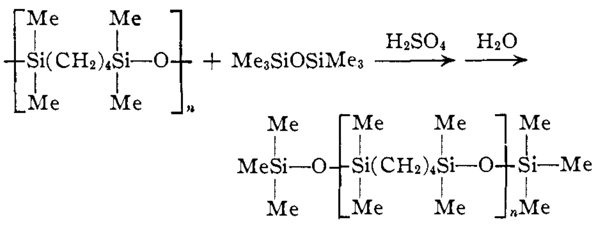


V

Compound V is a liquid and has an infrared absorption maximum for its siloxane linkage at 9.86 μ. Open-chain organodisiloxanes usually have siloxane absorption maxima in the range of 9.4–9.5 μ. Hunter and co-workers[5] have shown in studies of methyl-, ethyl- and phenylcyclosiloxanes that this absorption maximum is shifted to shorter or longer wave lengths depending on ring-size. Thus, the cyclotrisiloxanes have absorption maxima for the siloxane linkage in the range 9.8–9.9 μ, while the cyclotetrasiloxanes have maxima at 9.15–9.25 μ.

Polymers

Treatment of the pure diol IV with trifluoroacetic acid in fairly concentrated benzene solution gave a mixture of compound V and polymers II. This then was equilibrated with hexamethyldisiloxane through the use of a small amount of concentrated sulfuric acid.



$$\left[-Si(Me)_2(CH_2)_4Si(Me)_2—O-\right]_n + Me_3SiOSiMe_3 \xrightarrow{H_2SO_4} \xrightarrow{H_2O} MeSi(Me)_2—O-\left[-Si(Me)_2(CH_2)_4Si(Me)_2—O-\right]_n-Si(Me)_2—Me$$

VI

Polymers VI, n = 1, 2, 3 and 4, are colorless liquids whose structures are intermediate between the methylpolysiloxanes and paraffin hydrocarbons, *i.e.*, the main chains of atoms in these substances are composed of alternate siloxane and carbon–carbon groupings. Physical properties of these new fluids are therefore of considerable interest and some of these have been measured in the present work and are given in Table I.

Discussion of the Physical Properties

Boiling Point and Melting Point.—Comparing compounds 1–4 in Table I with normal paraffins it is seen that the former have a considerably lower dependence of boiling point on molecular weight. The "low" boiling points of compounds 1–4 may be shown by noting that compound 3 (mol. wt. 727) has nearly the same boiling point as *n*-pentacosane (mol. wt. 353) and that compound 3 contains 26 atoms in its longest chain. A count of only the atoms in the main chain of compound 3 ignores 16 methyl groups. The "low" boiling points of compounds 1–4, relative to *n*-paraffins, doubtless are due to the siloxane linkages and the branching present in these compounds.

On the other hand, comparison of compound 3 with the linear methylpolysiloxane, $Me_3SiO(Me_2SiO)_9SiMe_3$, having 23 atoms in the main chain, a molecular weight of 828 and b.p. 201.8° (4.7 mm.), shows that the linear methylpolysiloxanes have, as expected, a lower dependence of boiling point on molecular weight than compounds 1–4. A count of the atoms in the main chain of the linear methylpolysiloxane ignores 22 methyl groups.

In common with the linear methylpolysiloxanes, compounds 1–4 have "low" melting points relative to the *n*-paraffins of similar molecular weights. Thus, *n*-hexacontane has m.p. 98.9°. The linear methylpolysiloxane $Me_3SiO(Me_2SiO)_6SiMe_3$ has m.p. −63°.

Refractive Index and Density.—Refractive index and density both increase with increase in molecular weight. The refractive index and density for compound 4 may be compared with the corresponding properties for linear methylsiloxanes. The latter also give an increase in refractive index with increasing molecular weight as Me_2SiO units are progressively introduced into hexamethyldisiloxane ($n^{20}D$ 1.3771), but a limiting value of $n^{20}D$ 1.40–1.41

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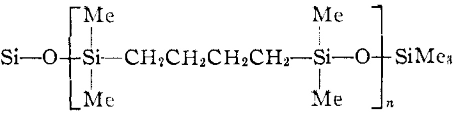
[4] L. H. Sommer and G. H. Barnes, unpublished work. *Cf.* E. Wiberg and U. Kruerke, *Z. Naturforschung*, **80**, 608 (1953) for reactions of boron halides with compounds containing the Si–O linkage.

[5] C. W. Young, P. C. Servais, C. C. Currie and M. J. Hunter, THIS JOURNAL, **70**, 3758 (1948).

TABLE I

ORGANOSILOXANES CONTAINING THE 1,6-DISILAHEXANE GROUPING



$$Me_3Si{-}O{-}\left[\overset{Me}{\underset{Me}{Si}}{-}CH_2CH_2CH_2CH_2{-}\overset{Me}{\underset{Me}{Si}}{-}O\right]_n{-}SiMe_3$$

Cmpd.	n	Mol. wt.	B.p. °C.	B.p. Mm.	M.p.,[a] °C.	$n^{20}D$	Density in g./ml. d^0	d^{20}	d^{50}	Viscosity, centipoises 0°	20°	60°	E_{vis}[b] kcal.
1	1	350.7	139	16	−35	1.4169	0.8563	0.8389	0.8057	4.73	2.97	1.49	3.84
2	2	539.0	196	6	−62	1.4292	.8780	.8622	.8311	14.36	7.84	3.31	4.42
3	3	727.4	250	6	−56	1.4349	.8891	.8738	.8436	29.50	14.75	5.60	4.92
4	4	915.8	276	5	−66	1.4377	.8958	.8799	.8503	42.02	19.65	7.08	5.41

[a] Melting points are accurate to ±2°. [b] E_{vis}, energy of activation for viscous flow over the temperature range 0 to 60° with viscosities in centipoises, obtained from the slopes of *linear* log abs. viscosity *vs.* $1/T$ plots.

is approached in the high-molecular-weight range. Further, d^{20} for a linear methylpolysiloxane of molecular weight 754 is 0.93 (extrapolated from d^{25}). Thus, compounds 1–4 as a class have higher refractive indices and lower densities than the methylpolysiloxanes. Refractive index and density differences between the paraffins and methylpolysiloxanes are in the same directions.

Excellent agreement was found between the experimental refractive index-density relationships for the individual compounds and the molar refraction values calculated by the bond refraction method of Warrick.[6]

Viscosity.—In sharp contrast to the linear methylpolysiloxanes which reach a limiting value of 3.8 kcal. for the energy of activation of viscous flow, E_{vis}, in the high molecular-weight range, compound 4 has E_{vis} 5.41. Thus, the structure change from a main chain composed entirely of alternate silicon and oxygen atoms, *e.g.*, the linear methylpolysiloxanes, to one having both paraffinic and siloxane units, *e.g.*, compounds 1–4, has a very marked effect on viscosity–temperature coefficients. The limiting value of E_{vis} for hydrocarbons is of the order of 6–7 kcal.

Infrared Spectra.—The close similarity of their infrared spectra leave no doubt that the four compounds studied belong to a homologous series. Of further interest is the fact that the maxima for the methyl–silicon and siloxane groupings are found in the usual positions of 8 and 9.5 μ, respectively.

Conclusions.—With reference to their physical properties, compounds 1–4 are intermediate between the linear methylpolysiloxanes and the paraffin hydrocarbons. They are stable, colorless liquids of low boiling point and low melting point in comparison to n-paraffins, but have viscosity–temperature coefficients which correspond more closely to those of the paraffins than to the linear methylpolysiloxanes.

If the low viscosity–temperature coefficients of the linear methylpolysiloxanes are correctly attributed to the ability of the siloxane chain to assume the shape of a coiled helix, which elongates with increased temperature and thus leads to increased dipole–dipole interaction between the siloxane groups in different chains,[7] it may be concluded that the presence of carbon–carbon bonds in the main chain of an organosiloxane results in considerable inhibition of this type of intramolecular motion.

Experimental

Monomers

1,4-Bis-(trimethylsilyl)-butane.—In a 5-liter three-necked flask equipped with a mercury-sealed stirrer, dropping funnel and reflux condenser, were placed magnesium turnings (150 g., 6.1 moles) and tetrahydrofuran, 500 ml. To this was added (11 hours) a solution of 1,4-dibromobutane (604 g., 2.8 moles) in 1500 ml. of tetrahydrofuran while maintaining the reaction temperature at 30–35° by means of a water-bath. At the end of the addition, almost all of the magnesium had reacted and trimethylchlorosilane, 981 g., 9 moles, was added during one hour. After heating at reflux temperature for 9 hours, the reaction mixture was cooled, added to ice and dilute hydrochloric acid, followed by separation of the organic layer and extraction of the aqueous layer with pentane. The organic layer and pentane extract were washed once with dilute sodium bicarbonate, once with water, and then dried over anhydrous calcium chloride. Fractionation gave compound I, b.p. 193° (732 mm.), $n^{20}D$ 1.4260, d^{20} 0.7651, 376 g., 1.86 moles, 67% yield.

Anal. Calcd. for $C_{10}H_{26}Si_2$: Si, 27.7; *MR*D, 67.7. Found: Si, 27.9; *MR*D, 67.8.

2,7-Dimethyl-2,7-difluoro-2,7-disilaoctane.—In a 3-liter three-necked flask fitted with a mercury-sealed stirrer and a gas-outlet tube were placed 486 g., 2.4 moles, of compound I and 2000 g. of concentrated sulfuric acid. This reaction mixture was vigorously stirred at room temperature for 41 hours until gas evolution ceased, and was then stirred for an additional 24 hours. The homogeneous solution which resulted was poured on ice and stirred. The upper organic layer was separated after adding 500 ml. of pentane and the aqueous acid layer was further extracted with five 100-ml. portions of pentane. The combined extracts and organic layer were washed twice with aqueous sodium bicarbonate and once with water. Drying over anhydrous calcium chloride followed by distillation of the pentane gave 444 g. of polysiloxane. The latter (188 g., 1 mole) and boron fluoride etherate (142 g., 1 mole) were placed in a 500-ml. round-bottom flask which was then attached to a fractionating column. On heating to 100°, distillation of trimethylfluorosilane and ethyl ether began. The flask temperature then was increased gradually (3 hours) to the boiling point of boron fluoride etherate (125°) and then the reaction mixture was cooled. Hexamethyldisiloxane (86 g., 0.53 mole) was added for the purpose of effecting reaction of the excess boron fluoride etherate and the reaction flask was then heated. Trimethylfluorosilane and ethyl ether distilled when the flask temperature reached 75° and continued to be formed until the reaction temperature reached 167°. Fractionation gave compound III, 164 g., 0.78 mole, b.p. 176° (730 mm.), in 78% yield.

Anal. Calcd. for $C_8H_{20}Si_2F_2$: F, 18.1. Found: F, 17.9 (gravimetric, lead chlorofluoride method), 18.2 (volumetric, tritration with standard base).

In order to determine the amount of silicon–methylene cleavage, the mixture of trimethylfluorosilane and ether obtained before addition of hexamethyldisiloxane was titrated with standard base for determination of the quantity of trimethylfluorosilane present. In this manner it was found for a number of preparations of compound III that silicon–methylene cleavage amounts to 5–10%.

2,7-Dihydroxy-2,7-dimethyl-2,7-disilaoctane.—Compound III (314 g., 1.5 moles) was added to a solution of 196 g., 3.5 mole, of potassium hydroxide in 700 ml. of water and

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(6) E. L. Warrick, THIS JOURNAL, **68**, 2455 (1946).

(7) E. L. Warrick, M. J. Hunter and A. J. Barry, *Ind. Eng. Chem.*, **44**, 2196 (1952).

the reaction mixture was stirred vigorously for 5 hours and cooled by means of a water-bath. A white solid separated, was removed by filtration and dried in a vacuum desiccator giving 292 g., 1.42 moles, of compound IV, m.p. 64–66°, 95% yield. After one recrystallization from hexane, white needles, m.p. 66.5–67°, were obtained.

Anal. Calcd. for $C_8H_{22}Si_2O_2$: Si, 27.2. Found: Si, 27.4.

Additional conclusive proof of structure for the diol is afforded by an experiment (see below) in which the theoretical amount of water was obtained from treatment of a benzene solution of the diol with trifluoroacetic acid. Further, conversion of the diol to 2,7-dichloro-2,7-dimethyl-2,7-disilaoctane, b.p. 112° (15 mm.), was achieved in 30% yield by treatment with thionyl chloride and pyridine.

Anal. Calcd. for $C_8H_{20}Si_2Cl_2$: Cl, 29.2. Found: Cl, 28.9.

2,2,7,7-Tetramethyl-1-oxa-2,7-disilacycloheptane.—In a 2-liter round-bottom flask fitted with a Stark and Dean water trap and a reflux condenser were placed 75 g., 0.364 mole, of compound IV, 1300 ml. of benzene and 0.5 g. of trifluoroacetic acid. The reaction mixture was heated to reflux and the theoretical amount of water, 6.6 g., was collected in the Stark and Dean tube after one-half hour. After cooling, the reaction mixture gave on fractionation 57.7 g., 0.31 mole, 85% yield of compound V, b.p. 169° (730 mm.), $n^{20}D$ 1.4340, d^{20} 0.8794.

Anal. Calcd. for $C_8H_{20}Si_2O$: Si, 29.8; *MR*D, 56.0; mol. wt., 188. Found: Si, 29.5; *MR*D, 55.8; mol. wt., 190.

Additional experiments showed the yield of 7-ring compound was greatly dependent on dilution. For example, 15.0 g. of diol in 125 ml. of benzene gave only 43% of compound V while 20 g. of diol in 400 ml. of benzene gave the 7-ring compound in 70% yield.

Polymers

Synthesis of Trimethylsiloxy End-blocked Polymers.—In a 2-liter round-bottom flask fitted with a Stark and Dean water trap and reflux condenser were placed 275 g., 1.33 moles, of compound IV, 700 ml. of benzene and 0.5 g. of trifluoroacetic acid. The reaction mixture was heated to reflux and 22.9 g. of water (theoretical, 23.9 g.) was collected during 5 hours. After cooling, the reaction mixture was washed once with aqueous sodium bicarbonate and once with water. The benzene–water azeotrope and the benzene were then distilled leaving 249 g. of a mixture of linear and cyclic organosiloxanes. This was placed in a 1-liter flask fitted with a mercury-sealed stirrer and 324 g., 2 moles, of hexamethyldisiloxane plus 20 ml. of concentrated sulfuric acid were added. The reaction mixture was stirred for 18 hours at room temperature. At the end of this time a small brown viscous layer was present at the bottom of the flask. This was separated and the reaction mixture was washed once with 75 ml. of water. Then, 10 ml. of concd. sulfuric acid and 3 ml. of fuming sulfuric acid (30% SO_3) were added and the reaction mixture was again stirred at room temperature for 9 hours. After washing once with water, twice with aqueous sodium bicarbonate, and once again with water, the product was dried overnight with calcium chloride. Fractionation gave: hexamethyldisiloxane, 168.3 g., 1.04 moles, 52% recovery; (1) octamethyl-3,10-dioxa-2,4,9,11-tetrasiladodecane, 150 g., 0.43 mole, 32.4% yield based on starting polymers (II). *Anal.* Calcd. for $C_{14}H_{38}Si_4O_2$: Si, 32.01; *MR*D, 104.97. Found: Si, 32.02; *MR*D, 105.10.

(2) Dodecamethyl-3,10,17-trioxa-2,4,9,11,16,18-hexasilanonadecane 87.2 g., 0.16 mole 24.5% yield. *Anal.* Calcd. for $C_{22}H_{58}Si_6O_3$: Si, 31.23; *MR*D, 161.02. Found: Si, 31.48; *MR*D, 161.24.

(3) Hexadecamethyl-3,10,17,24-tetraoxa-2,4,9,11,16,-18,23,25-octasilahexacosane, 44.6 g., 0.06 mole, 13.9% yield. *Anal.* Calcd. for $C_{30}H_{78}Si_8O_4$: Si, 30.86; *MR*D, 217.07. Found: Si, 31.11; *MR*D, 217.18.

(4) Eicosamethyl-3,10,17,24,31-pentaoxa-2,4,9,11,16,-18,23,25,30,32-decasilatritriacontane, 13.9 g., 0.02 mole, 4.6% yield. *Anal.* Calcd. for $C_{38}H_{98}Si_{10}O_5$: Si, 30.64; *MR*D, 273.12. Found: Si, 30.82; *MR*D, 273.05.

Acknowledgment.—We thank W. D. English of this Laboratory for the melting point determinations.

UNIVERSITY PARK, PENNSYLVANIA

[CONTRIBUTION FROM THE COLLEGE OF CHEMISTRY AND PHYSICS, THE PENNSYLVANIA STATE UNIVERSITY]

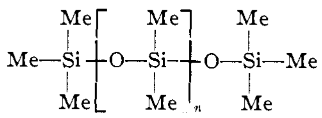
Aliphatic Organo-functional Siloxanes. III. Synthesis and Physical Properties of Organopolysiloxane Diesters[1]

BY L. H. SOMMER, W. D. ENGLISH, G. R. ANSUL AND D. N. VIVONA

RECEIVED OCTOBER 9, 1954

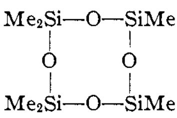
The synthesis and physical properties of three families of organopolysiloxane diesters are described. In harmony with the fact that the main chains of the high molecular weight members of these families are largely composed of Me_2SiO units, it was found that these substances have in large measure the important and unusual physical properties characteristic of the linear methylpolysiloxanes. The *decrease* in energy of activation for viscous flow, E_{vis}, with an *increase* in molecular weight in a single family is one example of the interesting effects on physical properties produced by the introduction of Me_2SiO units into an organic structure such as a diester. Taken as a whole the physical property data lead to the important conclusion that the presence of organic ester functions in the end-groups of linear organopolysiloxanes does not interfere with the "organosiloxane" properties conferred on these substances by the presence of Me_2SiO units in the main chain.

The methylpolysiloxanes have important and unusual physical properties which set them sharply apart from ordinary organic monomers and polymers. Typical examples of these structures are provided by the linear organosiloxanes A and the cyclic structure B.[2]



$$\mathrm{Me}-\underset{\mathrm{Me}}{\overset{\mathrm{Me}}{\mathrm{Si}}}\left[-\mathrm{O}-\underset{\mathrm{Me}}{\overset{\mathrm{Me}}{\mathrm{Si}}}-\right]_n-\mathrm{O}-\underset{\mathrm{Me}}{\overset{\mathrm{Me}}{\mathrm{Si}}}-\mathrm{Me}$$

A



B

In extension of previous work,[3,4] on the synthesis and study of organosiloxanes having functional groups linked to carbon, the present paper reports the synthesis and properties of sixteen organopolysiloxane diesters.

Monomers and Dimers.—The present study deals with three organofunctional silanes which may be called "monomers" from the fact that these compounds (I–III) are converted to dimers by the sulfuric acid cleavage of one methyl group from Me_3Si–.

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[1] Paper 48 in a series on organosilicon chemistry. For Paper 47, see THIS JOURNAL, **77**, 2482 (1954).

[2] For an excellent treatment of the rapidly expanding organosiloxane field the reader is referred to E. G. Rochow, "An Introduction to the Chemistry of the Silicones," second edition, John Wiley and Sons, Inc., New York, N. Y., 1951.

[3] L. H. Sommer, R. P. Pioch, N. S. Marans, G. M. Goldberg, J. Rockett and J. Kerlin, THIS JOURNAL, **75**, 2932 (1953).

[4] L. H. Sommer and R. P. Pioch, *ibid.*, **75**, 6337 (1953).