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.), $n^{20}\mathrm{D}$ 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.

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[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

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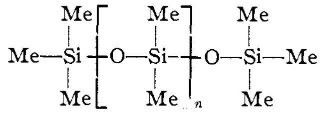
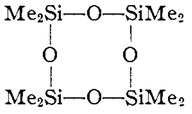
The synthesis and physical properties of three families of organopolysiloxane diesters are described. In harmony with the fact that the main chains of the high molecular weight members of these families are largely composed of $Me_2SiO$ units, it was found that these substances have in large measure 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]



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

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).

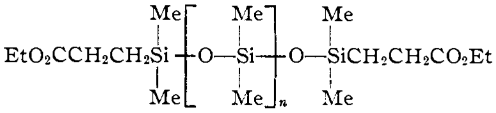
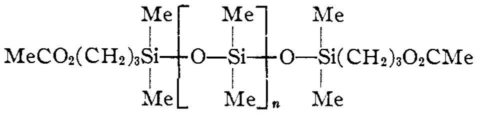
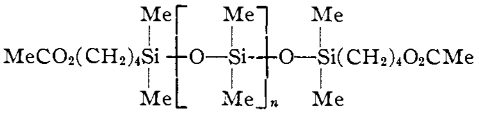
[2] For an excellent treatment of the rapidly expanding organosiloxane field the reader is referred to E. G. Rochow, "An Introduction to the Chemistry of the Silicones," second edition, John Wiley and Sons, Inc., New York, N. Y., 1951.

[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).

TABLE I

ORGANOSILOXANE DIESTERS

| Cmpd. | $n$ | Mol. wt. | B.p., °C. (39 mm.) | $n^{20}D$ | Density in g./ml. $d^0$ | $d^{20}$ | $d^{60}$ | Viscosity, centipoises 0° | 20° | 60° | A.S.T.M.[a] slope | $E_{vis}$,[b] kcal. |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
|  $\mathrm{EtO_2CCH_2CH_2\overset{Me}{\underset{Me}{Si}}\left[O\text{—}\overset{Me}{\underset{Me}{Si}}\right]_n O\text{—}\overset{Me}{\underset{Me}{Si}}CH_2CH_2CO_2Et}$ | | | | | | | | | | | | |
| 1 | 0 | 334.6 | 203 | 1.4330 | 0.9984 | 0.9802 | 0.9453 | 8.10 | 4.51 | 2.07 | 0.748 | 4.11 |
| 2 | 1 | 408.6 | 217 | 1.4288 | 0.9986 | .9808 | .9442 | 8.58 | 5.09 | 2.36 | .669 | 3.88 |
| 3 | 2 | 482.8 | 238 | 1.4256 | 1.0020 | .9812 | .9446 | 9.05 | 5.42 | 2.56 | .634 | 3.79 |
| 4 | 3 | 556.8 | 255 | 1.4248 | 0.9945 | .9776 | .9418 | 10.21 | 6.06 | 2.83 | .611 | 3.79 |
| 5 | 4 | 630.9 | 265 | 1.4231 | .9951 | .9785 | .9426 | 10.99 | 6.54 | 3.07 | .594 | 3.80 |
| 6[c] | 5 | 704.9 | 272 | 1.4212 | .9989 | .9813 | .9451 | 12.91 | 7.71 | 3.54 | .569 | 3.79 |
|  $\mathrm{MeCO_2(CH_2)_3\overset{Me}{\underset{Me}{Si}}\left[O\text{—}\overset{Me}{\underset{Me}{Si}}\right]_n O\text{—}\overset{Me}{\underset{Me}{Si}}(CH_2)_3O_2CMe}$ | | | | | | | | | | | | |
| 7 | 0 | 334.6 | 207 | 1.4342 | 0.9957 | 0.9777 | 0.9430 | 11.48 | 5.94 | 2.41 | 0.772 | 4.49 |
| 8 | 1 | 408.6 | 223 | 1.4290 | .9958 | .9795 | .9442 | 11.03 | 6.00 | 2.57 | .718 | 4.31 |
| 9 | 2 | 482.8 | 242 | 1.4253 | .9962 | .9802 | .9444 | 11.64 | 6.57 | 2.87 | .660 | 4.22 |
| 10 | 3 | 556.8 | 268 | 1.4230 | .9943 | .9787 | .9429 | 13.56 | 7.78 | 3.42 | .602 | 4.17 |
|  $\mathrm{MeCO_2(CH_2)_4\overset{Me}{\underset{Me}{Si}}\left[O\text{—}\overset{Me}{\underset{Me}{Si}}\right]_n O\text{—}\overset{Me}{\underset{Me}{Si}}(CH_2)_4O_2CMe}$ | | | | | | | | | | | | |
| 11 | 0 | 362.6 | 221 | 1.4366 | 0.9817 | 0.9645 | 0.9308 | 12.84 | 6.51 | 2.60 | 0.754 | 4.770 |
| 12 | 1 | 436.7 | 237 | 1.4320 | .9851 | .9675 | .9337 | 13.11 | 6.78 | 2.82 | .711 | 4.690 |
| 13 | 2 | 510.8 | 256 | 1.4285 | .9876 | .9694 | .9356 | 13.58 | 7.27 | 3.14 | .659 | 4.490 |
| 14 | 3 | 584.9 | 269 | 1.4260 | .9879 | .9708 | .9363 | 14.22 | 7.85 | 3.42 | 622 | 4.320 |
| 15 | 4 | 659.1 | 287 | 1.4240 | | .9702 | | | | | | |

[a] Viscosity–temperature chart modified from A.S.T.M. (D 341-39), U. S. Naval Research Laboratory. [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. [c] In addition to the six diethyl esters given in the above table, compound 16, the di-2-ethylhexyl ester analog of compound 1 was prepared and had the following physical properties: mol. wt. 502.9; b.p.; 294° (39 mm.), $n^{20}D$ 1.4468, $d^0$ 0.9455, $d^{20}$ 0.9305, $d^{60}$ 0.8980; viscosity in centipoises, at 0°, 36.44; 20°, 15.42; 60°, 4.88 A.S.T.M. slope, 0.752, $E_{vis}$ 5.98.

$Me_3Si(CH_2)_2CO_2H$ I $Me_3Si(CH_2)_3Br$ II $Me_3Si(CH_2)_4Br$ III

$$Me_3Si(CH_2)_2CO_2H \xrightarrow[2,\ H_2O]{1,\ H_2SO_4} O(SiMe_2(CH_2)_2CO_2H)_2 + 2CH_4$$

IV

$$Me_3Si(CH_2)_3Br \xrightarrow[2,\ H_2O]{1,\ H_2SO_4} O(SiMe_2(CH_2)_3Br)_2 + 2CH_4$$

V

$$Me_3Si(CH_2)_4Br \xrightarrow[2,\ H_2O]{1,\ H_2SO_4} O(SiMe_2(CH_2)_4Br)_2 + 2CH_4$$

VI

Monomers I and II have been prepared previously and the present synthesis of III requires no comment here. The syntheses of dimers V and VI are of interest because these furnish examples of the application of the sulfuric acid methyl–silicon cleavage reaction to heterogeneous systems. Dimer IV has been reported in an earlier publication.

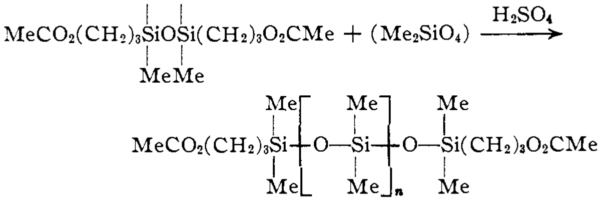
Compound IV was converted to the known diethyl ester by conventional esterification and compounds V and VI gave the acetoxy-ended dimers in good yield on treatment with potassium acetate in glacial acetic acid, *e.g.*, for V

$$O(SiMe_2(CH_2)_3Br)_2 \xrightarrow[HOAc]{KOAc} O(SiMe_2(CH_2)_3O_2CMe)_2$$

The ethyl ester of IV was converted to the 2-ethylhexyl ester by base-catalyzed ester interchange.

$$O(SiMe_2(CH_2)_2CO_2C_2H_5)_2 + 2CH_3(CH_2)_3CH(C_2H_5)CH_2OH \xrightarrow{Na} O(SiMe_2(CH_2)_2CO_2C_8H_{17})_2 + 2C_2H_5OH$$

**Organofunctional Siloxane Polymers.**—In Table I are listed eleven new organofunctional siloxanes and some of their physical properties. Also included are four previously reported compounds together with new physical property data for these substances: (compounds 1–4). Thus, Table I gives physical properties for fifteen new-type organosiloxanes with ester end-groups and dimethylsiloxy units as the difunctional portion of the siloxane chain. These substances were prepared by equilibration of the disiloxane diesters with octamethylcyclotetrasiloxane (as the source of $Me_2SiO$



$$\mathrm{MeCO_2(CH_2)_3\overset{MeMe}{\underset{MeMe}{SiOSi}}(CH_2)_3O_2CMe + (Me_2SiO_4) \xrightarrow{H_2SO_4} MeCO_2(CH_2)_3\overset{Me}{\underset{Me}{Si}}\left[O\text{—}\overset{Me}{\underset{Me}{Si}}\right]_n O\text{—}\overset{Me}{\underset{Me}{Si}}(CH_2)_3O_2CMe}$$

units[5]) using concd. sulfuric acid as the reagent.

## Discussion of the Physical Properties

**Boiling Point.**—In comparison with normal paraffins and a limited number of branched alkanes, the organopolysiloxane diesters have, as expected from their siloxane structures, a much lower dependence of boiling point on molecular weight. Thus, the average increase in boiling point of the diesters for the inclusion of one additional $Me_2SiO$ unit (mol. wt. 74) is 17°. A similar increase in molecular weight (5 methylene groups) in the $C_{30}$–$C_{40}$ molecular-weight range causes an increase of 58° for the *n*-paraffins. The remarkably "low" boiling points of the organopolysiloxane diesters may be illustrated by reference to the fact that compounds 6 and 15 (Table I) have nearly the same boiling point as *n*-pentacosane (mol. wt. 353), b.p. 259° (15 mm.), and that compounds 6 and 15 contain 25 atoms in their longest chains. With reference to compound 6, a count of only the atoms in the long chain ignores 14 methyl groups.

The methylpolysiloxanes exhibit a parallel low dependency of boiling point on molecular weight.

**Refractive Index and Density.**—Examination of the refractive index data in Table I gives clear indication of some of the interesting effects on physical properties resulting from introduction of dimethylsiloxy units into the main chain of organic structures such as diesters. The *decrease* in refractive index with an *increase* in molecular weight for the three families of diesters is reasonably ascribed to the fact that the structure changes which increase molecular weight also modify structure in the direction of making the diesters more like methylpolysiloxanes and less like purely organic compounds.

For the open-chain methylpolysiloxanes, there is an increase in refractive index as dimethylsiloxy units are progressively introduced into hexamethyldisiloxane ($n^{20}$D 1.3771). However, a limiting value of $n^{20}$D 1.40–1.41 is approached in the higher molecular weight methylpolysiloxanes.

The relative small change in density with increasing molecular weight for the three families of diesters is likely caused by the operation of two opposing factors. On the one hand, the normal effect of molecular weight increase, in a range short of approaching a limiting value of the density, would result in an increased density. On the other hand, $d^{20}$ for an open-chain methylpolysiloxane of molecular weight 754 is 0.93 (extrapolated from $d^{25}$).

The refractive index–density relationships in the individual compounds give excellent agreement between the experimental molar refraction values and those calculated by the bond-refraction method of Warrick.[6]

**Viscosity.**—Perhaps the most interesting data in Table I are those showing the change in energy of activation for viscous flow ($E_{vis}$) as additional $Me_2SiO$ units are introduced. Again, as noted above for refractive index–molecular weight relationships, the approach of the diesters to a pure organopolysiloxane structure as more $Me_2SiO$ units are introduced completely overbalances the expected increase in $E_{vis}$ with increased molecular weight. The activation energy of viscous flow for high molecular weight open-chain methylpolysiloxanes approaches a limiting value of 3.8 kcal. In comparison, the limiting value of $E_{vis}$ for hydrocarbons is 6–7 kcal.

In common with the open-chain methylpolysiloxanes, the diesters here reported have "low" viscosities. For example, the main chain in di-(2-ethylhexyl) sebacate consists of 24 atoms and this substance has a kinematic viscosity at 0° of 60.9 centistokes.[7] In comparison, compounds 6 and 14 have kinematic viscosities at 0° of 12.9 and 14.2 centistokes, respectively, with the former having a main chain of 25 atoms and the latter a chain of 23 atoms. Di-(2-ethylhexyl) sebacate has molecular weight 427, and an A.S.T.M. slope of 0.71.

**Vapor Pressure–Viscosity Relationships and the Unit of Flow.**—Eyring and co-workers[8] found that for small molecules the energy of vaporization at the normal boiling point, $\Delta E_{vap}$, is either three or four times the energy of activation for viscous flow, $E_{vis}$. For molecules which have spherical or approximately spherical symmetry, the factor is three, while long-chain compounds, *e.g.*, long-chain hydrocarbons give a factor of about 4. The energy of vaporization can be calculated from the heat of vaporization $\Delta H_{vap}$ through use of the relationship

$$\Delta E_{vap} = \Delta H_{vap} - RT_{b.p.}$$

where $RT_{b.p.}$ is computed from the constants of the equations which correspond to the linear plots obtained from plotting log $p$ *vs.* $1/T$ by setting $p$ equal to 760 mm. The ratios of $\Delta E_{vap}$ to $E_{vis}$ for compounds 1–6 are given in Table II. These data for the organosiloxane diesters parallel a similar increase of $\Delta E_{vap}/E_{vis}$ to a value above 4 in the hydrocarbon series[9] and in the linear methylpolysiloxane series.[10]

TABLE II

VAPOR PRESSURE–VISCOSITY RELATIONSHIPS

| Cmpd. | $\Delta E_{vap}$, kcal. | $E_{vis}$, kcal. | $\Delta E_{vap}/E_{vis}$ |
|---|---|---|---|
| 1 | 13.9 | 4.11 | 3.38 |
| 2 | 15.6 | 3.88 | 4.02 |
| 3 | 16.4 | 3.79 | 4.32 |
| 4 | 17.2 | 3.79 | 4.54 |
| 5 | 18.0 | 3.80 | 4.73 |
| 6 | 18.3 | 3.79 | 4.83 |

If the ratio is usually four for thin non-spherical molecules of low molecular weight, the longer hydrocarbons, methylpolysiloxanes and the diester polysiloxanes must move in segments during flow, the activation energy for movement of a segment being only a fraction of that required for motion of the entire molecule. The size of the flow unit for a specific compound in a series of compounds is estimated to correspond to the size of that member of

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(5) For the use of this procedure in the preparation of trimethylsiloxy end-blocked dimethylpolysiloxanes see W. I. Patnode and D. F. Wilcock, THIS JOURNAL, **68**, 361 (1946).

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

(7) E. M. Bried, H. F. Kidder, C. M. Murphy and W. A. Zisman, *Ind. Eng. Chem.*, **39**, 484 (1947).

(8) R. E. Powell, W. E. Roseveare and H. Eyring, *ibid.*, **33**, 430 (1941); R. H. Ewell and H. Eyring, *J. Chem. Phys.*, **5**, 726 (1937); S. Glasstone, K. J. Laidler and H. Eyring, "Theory of Rate Processes," McGraw-Hill Book Co., Inc., New York, N. Y., 1941.

(9) W. Kauzmann and H. Eyring, THIS JOURNAL, **62**, 3113 (1940).

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

the series whose $\Delta E_{vap}$ equals four times the value of $E_{vis}$ for the specific compound.[8] Therefore, since $E_{vis}$ for compounds 3–6 has an almost constant value of 3.79, the unit of flow in these diesters should approximate the size of that member of the series which has $\Delta E_{vap}$ of 15.2. Thus, the unit of flow for compounds 3–6 corresponds approximately to the size of compound 2. The latter should also represent the limiting size of the unit of flow for longer-chain homologs. In this connection it is interesting to note that the high molecular weight linear methylpolysiloxanes and paraffin hydrocarbons have maximum units of flow of 7 $Me_2SiO$ units and 20–25 $CH_2$ units,[10] respectively. These may be compared with compound 2 which has a main chain of 17 atoms with 6 methyl groups as substituents.

**Conclusions.**—From consideration of the physical properties of the compounds here reported it seems likely that organosiloxane diesters of higher molecular weight should closely approximate the more conventional methylpolysiloxanes in physical properties. Further, the present work shows that the presence of organic ester functions in the end-groups does not markedly hinder the introduction of desirable "organosiloxane" properties through the incorporation of dimethylsiloxy units into the chain. Thus, the data show that the effects of such structural modifications on physical properties are evident on introduction of only a few $Me_2SiO$ units.

## Experimental

**Monomers and Dimers.**—Compounds I[11] and II[12] were prepared previously and require no experimental details.

Compound III was synthesized readily from the known ω-hydroxy-*n*-butyltrimethylsilane[13] by treatment of the latter with phosphorus tribromide. Compound III, ω-bromo-*n*-butyltrimethylsilane, b.p. 85° (26 mm.), $n^{20}D$ 1.4551, $d^{20}$ 1.0932, was obtained in 94% yield.

*Anal.* Calcd. for $C_7H_{17}BrSi$: Si, 13.4; *MR*D, 51.9. Found: Si, 13.5; *MR*D, 51.9.

Compound IV and its diethyl ester have been reported previously.[4]

The synthesis of compound VI will be described as representative of the procedure used for both V and VI. Concentrated sulfuric acid, 560 g., was placed in a 3-liter three-necked flask equipped with a mercury-sealed stirrer, thermometer and gas outlet tube. The reaction flask was then cooled in a water-bath (18°) and compound III, 147 g., 0.7 mole, was added with vigorous stirring during one-half hour. Stirring was continued for 16 hours until the system was homogeneous, the temperature being maintained at 20–26°. At the end of this time the methane collected corresponded to 99% of the theoretical amount for cleavage of one methyl group from $Me_3Si$–. The reaction mixture was then added to 1 kg. of ice and the resulting organic layer was separated. Ether extraction of the aqueous layer, washing of the product with sodium bicarbonate solution and drying, were followed by fractional distillation which gave compound VI, bis-(ω-bromo-*n*-butyl)-tetramethyldisiloxane, b.p. 143° (1.7 mm.), $n^{20}D$ 1.4747, $d^{20}$ 1.2369, in 87% yield.

*Anal.* Calcd. for $C_{12}H_{28}Br_2OSi_2$: Si, 13.9; *MR*D, 92.1. Found: Si, 14.0; *MR*D, 92.0.

By a procedure similar to that described above, compound V, bis-(γ-bromopropyl)-tetramethyldisiloxane, b.p. 115° (1 mm.), $n^{20}D$ 1.4751, $d^{20}$ 1.281, was obtained from II in 64% yield.

*Anal.* Calcd. for $C_{10}H_{24}Br_2OSi_2$: Si, 14.9; Br, 42.5; *MR*D, 82.8. Found: Si, 15.0; Br, 42.4; *MR*D, 82.7.

Compound VI was converted to the diacetoxydisiloxane by the following procedure. Anhydrous potassium acetate (380 g., 3.87 moles), compound VI (510 g., 1.26 moles) glacial acetic acid (500 ml.) and acetic anhydride (20 ml.), were heated at reflux temperature for 62 hours. After cooling, 200 ml. of pentane was added and the mixture was filtered. The solid obtained was dissolved in water and the aqueous solution extracted with pentane. The pentane extract was combined with the filtrate and the resulting solution washed with 400 ml. of aqueous saturated sodium chloride solution. Removal of the last traces of acid was then achieved by washing with aqueous sodium bicarbonate. Drying over anhydrous magnesium sulfate followed by fractional distillation gave bis-(ω-acetoxy-*n*-butyl)-tetramethyldisiloxane, compound 11, in 91% yield.

*Anal.* Calcd. for $C_{16}H_{34}Si_2O_5$: Si, 15.5; sapn. equiv., 181; *MR*D, 98.8. Found: Si, 15.6; sapn. equiv., 182; *MR*D, 98.4.

By a similar procedure, compound V was converted to bis-(γ-acetoxypropyl)-tetramethyldisiloxane, compound 7, in 84% yield.

*Anal.* Calcd. for $C_{14}H_{30}Si_2O_5$: Si, 16.8; sapn. equiv., 167.3; *MR*D, 89.5. Found: Si, 16.9; sapn. equiv., 169.1; *MR*D, 89.3.

Compound 16 was prepared by an ester interchange reaction from compound 1. To 270 g., 2.08 moles, of 2-ethylhexanol-1 was added 4 g. of metallic sodium. The mixture was heated until all the sodium dissolved, the solution was cooled and 67 g., 0.2 mole, of ethyl bis-(β-carboxyethyl)-tetramethyldisiloxane added. The solution was refluxed under a fractionating column for 2 hours, in which time 17 g. of ethanol distilled off (theoretical, 19 g.). The solution was cooled, washed with water, dilute hydrochloric acid, water and dried on calcium sulfate. The washings were extracted with ether and the ether solution combined with the organic material and dried. Benzene, 50 ml., was added, and the remaining water removed by azeotropic distillation. Unreacted 2-ethylhexanol-1, 176 g., was recovered by fractional distillation. The residue was fractionally distilled at reduced pressure. Unreacted ethyl ester, 32 g., and 58 g. (58%) of 2-ethylhexyl bis-(β-carboxyethyl)-tetramethyldisiloxane were obtained, b.p. 242–4° (3.5 mm.), $n^{20}D$ 1.4456.

*Anal.* Calcd. for $C_{26}H_{54}Si_2O_5$: Si, 11.2; sap. equiv., 251.7; *MR*D, 144.8. Found: Si, 11.2; sap. equiv., 250.2; *MR*D, 144.7.

**Organo-Functional Siloxane Polymers.**—The synthesis of compounds 1–4 by sulfuric acid equilibration of the diethyl ester of compound IV with octamethylcyclotetrasiloxane has been described in a previous publication.[4] In the present work equilibration of a mixture of compounds 2 and 3 with octamethylcyclotetrasiloxane by the same procedure gave: Compound 5, 1,11-bis-(β-carboethoxyethyl)-dodecamethylhexasiloxane. *Anal.* Calcd. for $C_{22}H_{54}Si_6O_9$: Si, 26.7; sapn. equiv., 316; *MR*D, 165. Found: Si, 26.7; sapn. equiv., 315; *MR*D, 165.

Compound 6, 1,13-bis-(β-carboethoxyethyl)-tetradecamethylheptasiloxane. *Anal.* Calcd. for $C_{24}H_{60}Si_7O_{10}$: Si, 27.9; sapn. equiv., 353; *MR*D, 184. Found: Si, 27.8; sapn. equiv., 354; *MR*D, 183.

The equilibration of compound 11 with octamethylcyclotetrasiloxane will be described as representative of the procedure used for the synthesis of both acetoxybutyl- and acetoxypropylsiloxanes. Octamethylcyclotetrasiloxane (98.3 g., 0.332 mole), bis-(ω-acetoxy-*n*-butyl)-tetramethyldisiloxane (480 g., 1.33 moles) and 13 ml. of concentrated sulfuric acid were placed in a 1-liter three-necked flask equipped with a mercury-sealed stirrer and protected from atmospheric moisture by a Gilman sulfuric acid trap. The reaction mixture was then stirred at room temperature for 15.5 hours. Removal of the sulfuric acid by addition of water and washing of the organic layer with bicarbonate was followed by drying over calcium chloride. Fractional distillation gave: Bis-(ω-acetoxy-*n*-butyl)-tetramethyldisiloxane, compound 11, 119 g. (0.33 mole), 25% recovery.

1,5-Bis-(ω-acetoxy-*n*-butyl)-hexamethyltrisiloxane, compound 12, 115 g. (0.24 mole), 18% yield based on starting disiloxane diester. *Anal.* Calcd. for $C_{18}H_{40}Si_3O_6$: Si, 19.3; sapn. equiv., 219; *MR*D, 117.4. Found: Si, 19.3; sapn. equiv., 222; *MR*D, 117.1.

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[11] L. H. Sommer, J. Gold, G. M. Goldberg and N. S. Marans, THIS JOURNAL, **71**, 1509 (1949).

[12] L. H. Sommer, R. E. Van Strien and F. C. Whitmore, *ibid.*, **71**, 3056 (1949).

[13] J. L. Speier, *ibid.*, **74**, 1003 (1952).

1,7-Bis-(ω-acetoxy-*n*-butyl)-octamethyltetrasiloxane, compound 13, 62 g. (0.12 mole), 9% yield. *Anal.* Calcd. for $C_{20}H_{46}Si_4O_7$: Si, 22.0; sapn. equiv., 256; *MR*D, 136.0. Found: Si, 22.0; sapn. equiv., 253; *MR*D, 135.7.

1,9-Bis-(ω-acetoxy-*n*-butyl)-decamethylpentasiloxane, compound 14, 36 g. (0.06 mole), 5% yield. *Anal.* Calcd. for $C_{22}H_{52}Si_5O_8$: Si, 24.0; sapn. equiv., 293; *MR*D, 154.7. Found: Si, 24.2; sapn. equiv., 293; *MR*D, 154.4.

1,11-Bis-(ω-acetoxy-*n*-butyl)-dodecamethylhexasiloxane, compound 15, 8.1 g. (0.01 mole), 1% yield. *Anal.* Calcd. for $C_{24}H_{58}Si_6O_9$: Si, 25.55; sapn. equiv., 330; *MR*D, 173.3. Found: Si, 25.59; sapn. equiv., 331; *MR*D, 173.3.

By a procedure similar to that described above, bis-(γ-acetoxypropyl)-tetramethyldisiloxane, compound 7 (499 g., 1.5 moles), was equilibrated with octamethylcyclotetrasiloxane (148 g., 0.5 mole), in the presence of 14.5 ml. of concentrated sulfuric acid and gave: Bis-(γ-acetoxypropyl)-tetramethyldisiloxane, compound 7, 142 g., 28% recovery based on the amount of starting diester.

1,5-Bis-(γ-acetoxypropyl)-hexamethyltrisiloxane, compound 8, 76 g., 12.5% yield. *Anal.* Calcd. for $C_{16}H_{36}Si_3O_6$: Si, 20.6; sapn. equiv., 204; *MR*D, 108. Found: Si, 20.8; sapn. equiv., 205; *MR*D, 108.

1,7-Bis-(γ-acetoxypropyl)-octamethyltetrasiloxane, compound 9, 28 g., 4% yield. *Anal.* Calcd. for $C_{18}H_{42}Si_4O_7$: Si, 23.3; sapn. equiv., 241; *MR*D, 127. Found: Si, 23.6; sapn. equiv., 246; *MR*D, 127.

1,9-Bis-(γ-acetoxypropyl)-decamethylpentasiloxane, compound 10, 8 g., 1% yield. *Anal.* Calcd. for $C_{20}H_{48}Si_5O_8$: Si, 25.2; sapn. equiv., 278; *MR*D, 145. Found: Si, 24.9; sapn. equiv., 278; *MR*D, 145.

**Physical Properties.**—Boiling points were determined in a modified Cottrell apparatus.[14] The boiling points at 39 mm. given in Table I for compounds 1–10 are taken from vapor pressure *vs.* temperature plots covering the range 15–100 mm. Boiling points for compounds 10–15 were determined at 39 mm.

Refractive indices were determined with an Abbe refractometer. Densities were measured with pycnometers of about 5-ml. capacity. Viscosities were determined in Cannon–Fenske viscometers.[15]

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(14) D. Quiggle, C. O. Tongberg and M. R. Fenske, *Ind. Eng. Chem., Anal. Ed.*, **6**, 466 (1934).

(15) M. R. Cannon and M. R. Fenske, *ibid.*, **10**, 297 (1938).

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[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF NORTHWESTERN UNIVERSITY]

# Organoboron Compounds. V. The Preparation of an Unsymmetrical Diarylborinate[1]

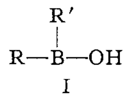
BY ROBERT L. LETSINGER AND NATHANIEL REMES

RECEIVED NOVEMBER 19, 1954

The preparation and some properties of aminoethyl phenyl-α-naphthylborinate and aminoethyl di-α-naphthylborinate are described.

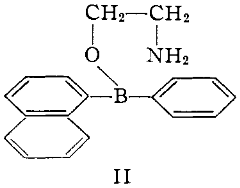
The limited range of known organoboron compounds is well illustrated by the fact that no unsymmetrical borinic acids (I, $R \neq R'$) have been described. With the development of practical procedures for isolating and characterizing the symmetrical borinic acids,[2] however, the synthesis of such compounds seemed feasible. We therefore undertook to make a compound of this class, phenyl-α-naphthylborinic acid. An aromatic borinic acid was selected for investigation since it was expected to be more stable and less prone to disproportionation than an unsymmetrical aliphatic borinic acid.

Butyl benzeneboronate was treated with an equimolar amount of α-naphthylmagnesium bromide in an ether solution at −60 to −70°. After acid hydrolysis, the organic layer was warmed to distil the ether and then mixed with ethanolamine dissolved in alcohol and water. A white precipitate, II, assigned the structure, β-aminoethyl phenyl-α-naphthylborinate, separated (75% yield) from the solution. The ethanolamine served, therefore, as an agent to remove the borinic acid selectively from the other organoboron compounds present in the reaction mixture. In another experiment this borinate also was prepared (80% yield) from the alternate pair of reagents, phenylmagnesium bromide and butyl α-naphthaleneboronic acid.



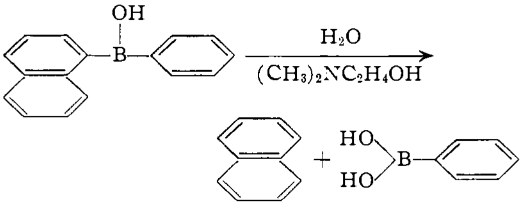
$$R-\overset{R'}{\overset{|}{B}}-OH$$

I



II

Compound II was a high melting solid (m.p. 228°) stable indefinitely in air at room temperature. In this respect it differed markedly from the unsymmetrical alkylborines.[3] With dilute hydrochloric acid it hydrolyzed rapidly to an oil, no doubt phenylnaphthylborinic acid, which could be re-esterified with ethanolamine, or converted to the β-aminoisobutyl ester (92% yield from the aminoethyl ester) with 2-amino-2-methyl-1-propanol. An attempt to prepare a solid ester with β-dimethylaminoethanol was unsuccessful. Instead of forming the derivative, the borinic acid partially decomposed with the formation of naphthalene. At steam-bath temperatures, the cleavage reaction was virtually quantitative within ten minutes (reaction 1); naphthalene and benzeneboronic acid were isolated from this reaction in yields of 86 and 82%, respectively.



(1)

Melnikov found that diarylborinic acids reacted with bromine to give aryl bromides and boric acid.[4]

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[1] Presented at the 126th Meeting of the American Chemical Society in New York, September, 1954. A portion of this material appeared in a preliminary publication, THIS JOURNAL, **76**, 4047 (1954).

[2] R. L. Letsinger and I. Skoog, *ibid.*, **77**, 2491 (1955); **76**, 4147 (1954).

[3] T. Parsons and D. Ritter, *ibid.*, **76**, 1710 (1954).

[4] H. Melnikov, *J. Gen. Chem.* (*U.S.S.R.*), **6**, 636 (1936); *C. A.*, **30**, 5571 (1936).