formed dark-red needles (from absolute ethanol), m. p. 177.2–179.0°. *Anal.* Calcd. for $C_{26}H_{15}N_3O_7$: N, 8.7. Found: N, 8.8. A picrate of the dibenzoxanthene could not be formed.

The mother liquors of the neutral fraction were intensively investigated by chromatography and crystallization of the material and of its trinitrofluorenone complexes, but no pure material could be isolated. The possible presence of the isomeric dinaphtho[1,2-b,1',2'-d]furan, VI, was established by means of ultraviolet spectra, in the same manner as discussed above for the product obtained by cyclodehydrogenation of 2-(1'-naphthyl)-1-naphthol.

The alkali-soluble portion (Fraction A above) was a red oil that was exceedingly soluble in hexane and in alcohol. It could not be obtained in crystalline form, did not form a picrate, and was recovered unchanged after treatment with acetyl chloride; its properties were not improved by chromatography. The ultraviolet absorption spectrum (Fig. 3) was identical with that of the phenolic fraction obtained in the following experiment and is compatible with the spectrum to be expected of 2-(1'-naphthyl)-1-naphthol, III.

2-(1'-Naphthyl)-1-naphthol, III, from Tetralylidenetetralone, I.—A mixture of 10.00 g. I, 1.00 g. palladium-on-charcoal[13] and 100 cc. 1- and 2-methylnaphthalene was refluxed twenty-eight hours.[9] The product was taken up in benzene filtered and extracted first with 10% aqueous sodium hydroxide and then with Claisen alkali.[5] The Claisen-alkali extract gave 0.95 g. of a red oil which could not be crystallized.

Cyclodehydrogenation of III.—The presumed 2-(1'-naphthyl)-1-naphthol, III, was treated with palladium-on-charcoal[13] at 325–350° for 30 minutes; 26 cc. (S. T. P.) of gas was evolved. The product was separated into neutral and Claisen alkali-soluble fractions. There was obtained 0.27 g. of apparently unchanged starting material (ultraviolet absorption spectrum) and 0.46 g. of neutral material. The neutral fraction was chromatographed on alumina–celite; the product was converted to the trinitrofluorenone[14] complex, which was recrystallized from benzene–ethanol (m. p. 236.5–238.5°) and then chromatographed on alumina. There was obtained 0.061 g. of material, m. p. 117–127°. Recrystallization from alcohol gave 0.045 g. of yellow needles, m. p. 120–132°. The ultraviolet absorption spectrum indicated the presence of a large amount of dibenzo[c,kl]xanthene, IV; evidence for the presence of another compound, probably dinaphtho-[1,2-b,1',2'-d]furan, VI, has been discussed above.

Summary

1-Keto-2-(1'-tetralylidene)-1,2,3,4-tetrahydronaphthalene, I, has been prepared from 1-tetralone. The location of the double bond was established by infrared absorption spectra.

Hydrogenation of I gave 1-keto-2-(1',2',3',4'-tetrahydro-1'-naphthyl)-1,2,3,4-tetrahydronaphthalene.

Liquid-phase cyclodehydrogenation of I with a palladium catalyst at 300° gave a compound of the probable structure of dibenzo[c,kl]xanthene, IV. Evidence was obtained for the presence of dinaphtho[1,2-b,1',2'-d]furan, VI, and 2-(1'-naphthyl)-1-naphthol, III. III is probably formed as an intermediate in the conversion of I to IV and VI.

U. S. DEPARTMENT OF INTERIOR
PITTSBURGH, PA.
RECEIVED JANUARY 19, 1949

[CONTRIBUTION FROM THE WHITMORE LABORATORY OF THE SCHOOL OF CHEMISTRY AND PHYSICS, THE PENNSYLVANIA STATE COLLEGE]

Synthesis and Properties of Compounds with a Framework of Alternate Silicon and Carbon Atoms[1]

BY LEO H. SOMMER, FRANK A. MITCH AND GERSHON M. GOLDBERG

In extension of previous work,[2] the present paper deals with the synthesis and physical properties of compounds of the type $CH_3[(CH_3)_2SiCH_2]_nSi(CH_3)_3$ in which n is 1 to 4. As methylene analogs of the well-known family of trimethylsilyl end-blocked linear methylpolysiloxanes, $CH_3[(CH_3)_2SiO]_nSi(CH_3)_3$,[3] these compounds should provide valuable data concerning the relative effects of Si-O-Si and Si-CH_2-Si on physical properties.

While the unusual physical properties of the linear methylpolysiloxanes have in previous discussions been taken as indicative of low intermolecular forces resulting from the influence of siloxane linkages, complete proof of this hypothesis was formerly unavailable. With the exception of 2,2,4,4-tetramethylpentane and di-*t*-butyl ether, hydrocarbon and ether analogs of the methylpolysiloxanes are unknown. Since the effect of branching of a carbon chain on physical properties is known to be very pronounced, the possibility existed that the extensive branching found in the methylpolysiloxanes might be responsible for their unusual physical properties. Furthermore, while the effect of one silicon atom on physical properties in the tetraalkylsilanes was shown to be slight,[4] nothing was known of the effect on physical properties of chains containing alternate silicon and carbon atoms as compared to chains of alternate silicon and oxygen atoms in the methylpolysiloxanes.

One of the major objectives of the present work was to determine whether the siloxane linkages in the methylpolysiloxanes are indeed largely responsible for the unusual physical properties of these compounds. The physical properties of the compounds herein reported furnish a direct answer to this question, since the structural features of the methylpolysiloxanes are held

---

[1] XXII in a series on organosilicon chemistry. For XXI see THIS JOURNAL, **71**, 1509 (1949).

[2] Sommer, Goldberg, Gold and Whitmore, *ibid.*, **69**, 980 (1947).

[3] (a) Patnode and Wilcock, *ibid.*, **68**, 358 (1946); (b) Hurd, *ibid.*, **68**, 364 (1946); (c) Wilcock, *ibid.*, **68**, 691 (1946); (d) Hunter, Warrick, Hyde and Currie, *ibid.*, **68**, 2284 (1946).

[4] Whitmore, Sommer, DiGiorgio, Strong, Van Strien, Bailey, Hall, Pietrusza and Kerr, THIS JOURNAL, **68**, 475 (1946).

TABLE I

Compd. No.	Formula	Name
I	$CH_3[(CH_3)_2SiCH_2]_1Si(CH_3)_3$	Hexamethyldisilmethylene[a]
II	$CH_3[(CH_3)_2SiCH_2]_2Si(CH_3)_3$	Octamethyltrisilmethylene[a]
III	$CH_3[(CH_3)_2SiCH_2]_3Si(CH_3)_3$	Decamethyltetrasilmethylene
IV	$CH_3[(CH_3)_2SiCH_2]_4Si(CH_3)_3$	Dodecamethylpentasilmethylene
V	$ClCH_2[(CH_3)_2SiCH_2]_1Si(CH_3)_3$	Chloromethylpentamethyldisilmethylene
VI	$ClCH_2[(CH_3)_2SiCH_2]_2Si(CH_3)_3$	1-Chloromethylheptamethyltrisilmethylene
VII	$ClCH_2[(CH_3)_2SiCH_2]_3Si(CH_3)_3$	1-Chloromethylnonamethyltetrasilmethylene
VIII	$[(CH_3)_3SiCH_2(CH_3)_2SiCH_2(CH_3)_2Si]_2O$	2,2,4,4,6,6,8,8,10,10,12,12-Dodecamethyl-7-oxa-2,4,6,8,10,12-hexasilatridecane

[a] The oxa-aza names for compounds I and II are 2,2,4,4-tetramethyl-2,4-disilapentane and 2,2,4,4,6,6-hexamethyl-2,4,6-trisilaheptane.

constant except for the replacement of oxygen by methylene.

In Table I are given formulas and names by two systems of nomenclature for the compounds being reported. The silmethylene type of naming[2] is seen to be somewhat simpler and is analogous to naming of organopolysiloxanes. However, as has been pointed out,[5] the more general "oxa-aza" nomenclature is applicable to compounds having chains of mixed Si-O-Si and Si-CH_2-Si linkages where the silmethylene naming cannot be used, *i.e.*, compound VIII.

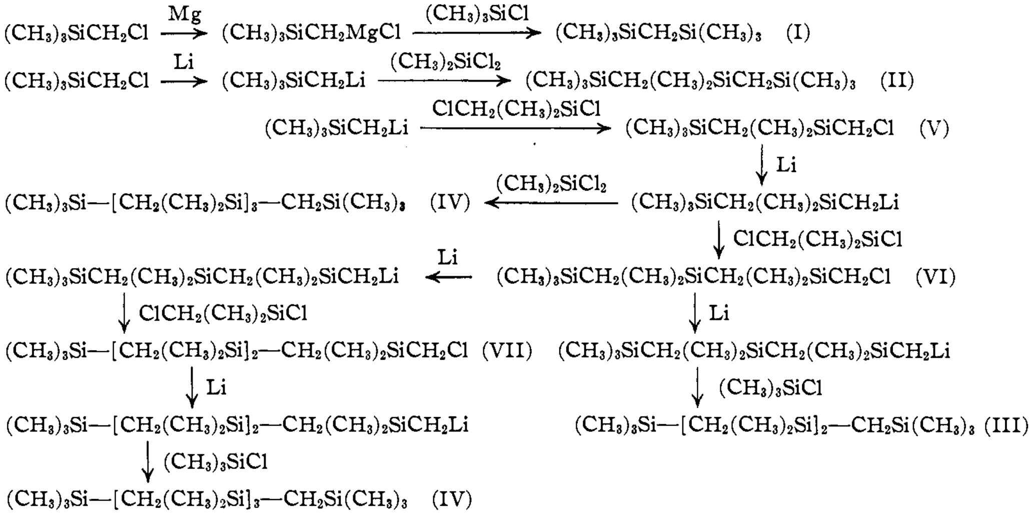
Synthesis of Methylpolysilmethylenes

Compounds I and II have been synthesized by the reaction of the Grignard reagent derived from chloromethyltrimethylsilane with trimethylchlorosilane and dimethyldichlorosilane, respectively.[2] However, continued use of the Grignard reagent for the synthesis of higher members was undesirable in view of the low yield of compound V (32%) which results from reaction of the above Grignard reagent with chloromethyldimethylchlorosilane.[2] Compound V is a necessary intermediate for lengthening the silmethylene chain by our procedure.

The successful synthesis of *t*-butylsilicon compounds by the use of *t*-butyllithium, despite the failure of the Grignard synthesis,[6] and the excellent yields of organosilicon compounds obtained with organolithium compounds by Gilman and co-workers,[7] suggested the possible use of trimethylsilylmethyllithium in place of the Grignard reagent.

It was found that addition of chloromethyltrimethylsilane to a suspension of thin lithium foil in refluxing unsaturate-free pentane gives trimethylsilylmethyllithium in yields which average 86%. Reaction with chloromethyldimethylchlorosilane gave compound V in 82% yield. The yield of compound II from dimethyldichlorosilane was also increased, from 65 to 86%, by the use of trimethylsilylmethyllithium in place of the Grignard reagent.

REACTION CHART



The reactions involved in the silmethylene preparations are summarized in the form of a reaction chart. Unsaturate-free pentane was used as a solvent in all of the preparations and reactions of the lithium compounds. The lithium compounds were synthesized in yields of 85–90%.

---

(5) Bluestein, THIS JOURNAL, **70**, 3068 (1948).

(6) Tyler, Sommer and Whitmore, *ibid.*, **70**, 2876 (1948).

(7) Gilman and Clark, *ibid.*, **68**, 1675 (1946); Gilman and Clark, *ibid.*, **69**, 1499 (1947).

TABLE II

PHYSICAL PROPERTIES OF SILMETHYLENES AND SILOXANES[f]

Compd.	B. p., °C. 200 mm.	B. p., °C. 760 mm.	$\Delta H_{\text{vap.}}$, kcal./mole	$\Delta S_{\text{vap.}}$ cal./deg. mole	n^{20}D	Density in g./ml. d^0	Density in g./ml. d^{20}	Density in g./ml. d^{69}	*MR*D Obs.	*MR*D Calcd.	Absolute viscosity, centipoises 0°	Absolute viscosity, centipoises 20°	Absolute viscosity, centipoises 60°	E_{vis} kcal.
I	91	134	9.20	22.6	1.4172	0.7682	0.7520	0.7176	53.67	53.65	0.987	0.736	0.457	2.32
MM[a,b]		100	8.30	22.4	1.3774		.7616					0.52[c]		2.17
II	159	206	11.4	23.8	1.4420	.8141	.7987	.7679	77.03	77.02	2.726	1.788	0.965	3.13
MDM		153	9.45	22.2	1.3848		.8200					0.91		2.45
III	208	259	13.4	25.1	1.4552	.8396	.8245	.7955	100.30	100.39	5.995	3.590	1.682	3.83
MD_2M		194	11.5	24.6	1.3895		.8536					1.41		2.67
IV	254	309	14.9	25.6	1.4640	.8549	.8408	.8124	123.66	123.76	11.87	6.514	2.737	4.42
MD_3M		229	12.7	25.3	1.3925		.8755					1.99[d]		2.78[e]

[a] The methylpolysiloxanes, hexamethyldisiloxane (MM) to dodecamethylpentasiloxane (MD_3M) are represented above according to the shorthand notation in ref. 3(a). [b] Data for the siloxanes are taken from ref. 3(c). [c] Viscosities at 20° for the siloxanes are taken from their curves in Fig. 2 which are based on data for other temperatures given in ref. 3(c). [d] Abs. viscosity at 20° for MD_4M and MD_5M are 4.27 and 7.59 centipoises, respectively. [e] E_{vis} in kcal. for MD_4M and MD_5M are 3.04 and 3.10, respectively. [f] Data for the preparation of the methylsilmethylenes are as follows: Compounds I and II were prepared in yields of 63 and 86%, respectively. Compound III was prepared in 51% yield by heating trimethylchlorosilane, 0.32 mole, with the appropriate RLi compound, 0.25 mole, for twenty-four hours at reflux temperature. Compound IV was prepared in 74% yield in the following manner: dimethyldichlorosilane, 0.2 mole, and the RLi compound, 0.54 mole, were heated at reflux temperature for four hours, and then the pentane was distilled from the reaction mixture until the temperature of the flask reached 150 where it was kept for eight hours. Compound IV was prepared in 64% yield by another method which involved the following procedure: trimethylchlorosilane, 0.184 mole, and the appropriate RLi compound, 0.11 mole, were heated at reflux temperature for twenty-four hours. *Anal.* Calcd. for compds. I, II, III and IV, respectively: Si, 35.0, 36.2, 36.9, 37.2. Found: Si, 34.9, 36.1, 36.6, 37.1.

Their reactions with chloromethyldimethylchlorosilane, trimethylchlorosilane, and dimethyldichlorosilane, gave yields of 65–82%, 51–64%, and 74–86%, respectively.

In one preparation of compound IV, a low reaction temperature resulted in reaction of only one silicon–chlorine bond in dimethyldichlorosilane. Hydrolysis and condensation gave compound VIII.

Subsequent to our publication on the synthesis of compounds I, II and V, McGregor and coworkers have reported the use of sodium for the preparation of compounds containing silmethylene and siloxane linkages.[8] Bluestein[5] has utilized the Grignard reagent derived from chloromethylpentamethyldisiloxane for the preparation of siloxane-silmethylene compounds.

Physical Properties

Table II gives physical properties of the methylpolysilmethylenes and analogous methylpolysiloxanes. Boiling points of the silmethylenes at 760 mm. are extrapolated from vapor-pressure curves drawn from five or more points covering the range 10–740 mm.; 50 mm. and 200 mm. values are taken from the curves. Heats of vaporization were calculated by use of the Clausius–Clapeyron equation for the range 200 to 730 mm. Molecular refraction was calculated by use of the Lorentz–Lorenz equation.

Boiling Point, Heat of Vaporization and Entropy of Vaporization.—If tetramethylsilane (b. p. 27°) is considered to be the common first member of the methylpolysilmethylenes and methylpolysiloxanes, Table II shows that the change in boiling point at 760 mm. on ascending the series to compound IV in the silmethylenes is 282° as compared to an increase of 202° for a corresponding change of structure in the siloxanes; an increase in boiling point which is 40% greater for the silmethylenes than for the siloxanes. Stated another way, the average increase in boiling point per $(CH_3)_2SiCH_2$ unit in this series is 70.5° as compared to 50.5° for $(CH_3)_2SiO$; an average increase of 20° for replacement of oxygen by methylene. Moreover, the average increase per methylene group in the straight-chain hydrocarbon series from *n*-pentane, b. p. 36°, to *n*-octadecane, b. p. 317°, is 21.6°. Thus the effect of oxygen on the contributions to boiling point of silicon and methyl in methylpolysiloxanes is of such large magnitude as to result in almost zero contribution of oxygen if the (incorrect) assumption is made that the other groups contribute normally.

TABLE III

BOILING POINTS OF SILICON AND CARBON COMPOUNDS OF SIMILAR STRUCTURE

Silicon compound	B. p., °C.	Carbon compound	B. p., °C.
$(CH_3)_3SiOSi(CH_3)_3$	100	$(CH_3)_3COC(CH_3)_3$	107[a]
$(CH_3)_3SiCH_2Si(CH_3)_3$	134	$(CH_3)_3CCH_2C(CH_3)_3$	122[b]
$(CH_3)_3SiSi(CH_3)_3$	112	$(CH_3)_3CC(CH_3)_3$	107[b]

[a] Erickson and Ashton, THIS JOURNAL, **63**, 1769 (1941). [b] Doss, "Physical Constants of the Principal Hydrocarbons," The Texas Company, 1943.

The data of Table III indicate the following relations between boiling point and structure: (1) Replacement of two carbon atoms by silicon atoms results in an increase in boiling point except in the case of di-*t*-butyl ether as compared to hexamethyldisiloxane. (2) Replacement of methylene by oxygen results in a decrease of 15° for the change from 2,2,4,4-tetramethylpentane

---

(8) Goodwin, Baldwin and McGregor, THIS JOURNAL, **69**, 2247 (1947).

to di-*t*-butyl ether and a decrease of 34° for the change from hexamethyldisilmethylene to hexamethyldisiloxane. (3) The insertion of oxygen between the quaternary carbon atoms in hexamethylethane to give di-*t*-butyl ether results in no appreciable change in boiling point, while the change from hexamethyldisilane to hexamethyldisiloxane gives a boiling point decrease of 12°.

All of the above data thus offer evidence for the unusual lowering effect of siloxane linkages on boiling point relative to carbon–carbon and carbon–oxygen–carbon linkages.

The low heats of vaporization of the methylpolysiloxanes as compared to the methylpolysilmethylenes, taken in conjunction with the low boiling points of the former, indicate that the intermolecular forces are indeed unusually low in the siloxanes due to the presence in these compounds of Si–O–Si linkages.

Entropies of vaporization are seen from Table II to be closely similar in the two classes of compounds.

Figure 1 graphically illustrates the greater effect on boiling point of $(CH_3)_2SiCH_2$ as compared to $(CH_3)_2SiO$.

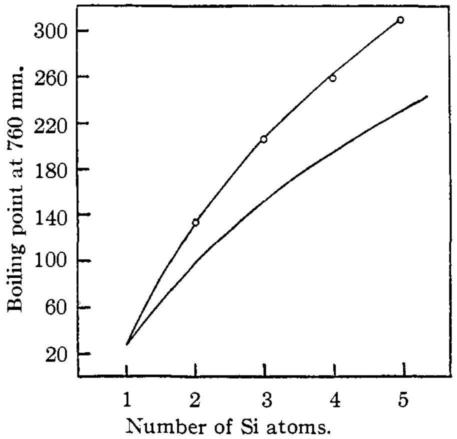


Fig. 1.—Change of boiling point with number of silicon atoms: O—O, silmethylenes; —, methylpolysiloxanes.

Density, Refractive Index and Molar Refraction.—As can be seen from Table II, densities of the silmethylenes are lower than those of the siloxane analogs by 0.0096–0.0347 unit, or an approximate lowering of 0.009 unit for replacement of one $(CH_3)_2SiO$ unit by $(CH_3)_2SiCH_2$. Refractive indices are higher in the siloxanes.

Table II also gives experimental values for molar refractions of the silmethylenes and also the values found by the bond refraction method of Warrick,[9] after applying a correction of −0.15 ml. for each silmethylene linkage. The latter is of the same order as the correction applied by Sauer,[10] −0.12 ml., to account for the difference between the bonds to an alpha carbon and other carbon atoms in a chain attached to silicon.

Viscosity.—In Fig. 2 are plotted the logarithms of the centipoise viscosities of silmethylenes and siloxanes as a function of reciprocal absolute temperature. These straight line plots indicate that the viscosities of the silmethylenes are considerably greater than those of analogous siloxanes at corresponding temperatures. Table II compares viscosities for the silmethylenes and siloxanes at 20°. From these data it is evident that the viscosity of dodecamethylpentasilmethylene exceeds that of hexadecamethylheptasiloxane (see footnote *d*). These data comprise further evidence that the low intermolecular forces in methylpolysiloxanes are largely due to the siloxane linkages. The viscosity of a liquid, like the boiling point and heat of vaporization, is related to intermolecular forces. It is a measure of the resistance due to such forces which opposes the passage of one molecule past another.

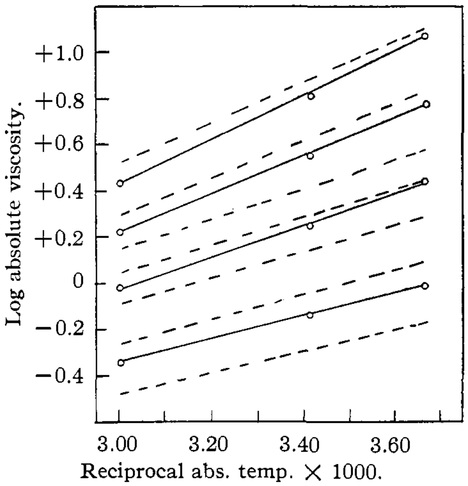


Fig. 2.—Change of absolute viscosity with temperature: O—O, bottom to top, compounds I, II, III and IV; - - -, bottom to top, methylpolysiloxanes from hexamethyldisiloxane to octadecamethyloctasiloxane.

Figure 2 also shows that the change of viscosity with temperature is greater for the silmethylenes. Table II lists energies of activation of viscous flow, E_{vis}, for silmethylenes and siloxanes. The former values were calculated from the viscosities at 0° and 60° by means of the Arrhenius equation[11]

$$\eta_T = \eta_\infty e^{E_{vis}/RT}$$

and are equal to $2R$ times the slope of the lines of Fig. 2.

Experimental

Starting Materials.—Chloromethyldimethylchlorosilane was prepared by the photochemical chlorination of trimethylchlorosilane as reported by Krieble and Elliott.[12] Chloromethyltrimethylsilane was prepared by the method of Whitmore, Sommer and Gold.[13]

All of the pentane for the following preparations was first freed of unsaturated compounds by stirring for forty-

---

[9] Warrick, THIS JOURNAL, **68**, 2455 (1946).

[10] Sauer, *ibid.*, **68**, 954 (1946).

[11] Arrhenius, *Meddel. Vetenskapad. Nobelinst.*, **3**, 20 (1916).

[12] Krieble and Elliott, THIS JOURNAL, **67**, 1810 (1945).

[13] Whitmore, Sommer and Gold, *ibid.*, **69**, 1976 (1947).

TABLE IV

CHLOROMETHYLSILMETHYLENES

Compd. no.	B. p., °C. 200 mm.	760[a] mm.	n^{20}_D	d^{20}	MR_D Calcd.	Obs.	Chlorine, % Calcd.	Found	Yield, %
V	141	186	1.4480	0.8950	58.49	58.30	18.2	18.1	81
VI	197	246	1.4630	.9000	81.86	81.69	13.3	13.4	72[b]
VII	242	297	1.4706	.9029	105.23	104.92	10.5	10.5	66[c]

[a] Boiling points at 760 mm. are extrapolated from vapor-pressure curves drawn from five or more points covering the range 10–740 mm. Boiling points at 200 mm. are extrapolated from the curves. [b] The reactants were heated at the reflux point for twelve hours; ratio of RLi to $ClCH_2(CH_3)_2SiCl$ was 0.6 to 0.5 mole. [c] The reactants were heated at the reflux point for forty-eight hours; ratio of RLi to $ClCH_2(CH_3)_2SiCl$ was 0.36 to 0.4 mole.

eight hours with one-fifth its volume of concentrated sulfuric acid, and was then fractionated; pentane obtained in this way had b. p. 36–37°.

The lithium was in the form of small pieces of very thin foil, prepared by careful pounding of the metal or use of a hand-operated roller. During the preparation of the foil, the lithium was at all times coated with a thin film of mineral oil to prevent reaction with the air. The mineral oil was removed by washing twice with pentane and the foil had a bright and shiny appearance.

The preparation of trimethylsilylmethyllithium will be described as representative of the procedure for the higher organolithium compounds. In a 2-liter, three-necked flask fitted with a mercury-sealed stirrer, a dropping funnel, and a large bulb-type condenser, there were placed one liter of pentane and 14 g. (2.0 moles)of lithium foil. After heating to reflux, 125 g. (1.0 mole) of chloromethyltrimethylsilane was added with vigorous stirring, over a two-hour period, giving a pale purple-colored solution. On refluxing for an additional ten hours, reaction continued and the solution became deep purple in color. The colored material, however, settled to the bottom on standing, leaving a water-white organic layer. The average yield for ten runs was 86%.

Chloromethylsilmethylenes.—The synthesis of compound V will be described as representative of the procedure used for the higher compounds. To a solution of trimethylsilylmethyllithium (0.86 mole) in one liter of pentane there was added 120 g. (0.80 mole) of chloromethyldimethylchlorosilane over a period of two hours, giving a precipitate of lithium chloride, and evolving sufficient heat to maintain reflux. The reaction mixture was heated at the reflux point for an additional eight hours and the pentane solution was then decanted from lithium chloride and excess lithium onto cracked ice. After separation of the layers, the water layer was extracted with 100 cc. of pentane and the combined pentane solution of the product was dried over potassium carbonate. The product was then distilled in a glass-helix packed fractionating column of about twenty theoretical plates. Table IV gives pertinent data on the preparations and properties of the chloromethylsilmethylenes.

Methylpolysilmethylenes.—The synthesis of compound I by reaction of the Grignard reagent from chloromethyltrimethylsilane with trimethylchlorosilane has been described.[2] The synthesis of compound II will be described as representative of the procedure used for the higher silmethylenes. Dimethyldichlorosilane, 20 g. (0.155 mole) was added to a solution of 0.5 mole of trimethylsilylmethyllithium in 500 cc. of pentane during forty-five minutes. This was followed by refluxing of the reaction mixture for twelve hours. Pentane was then slowly distilled until the flask temperature reached 90°, where it was maintained for twelve hours. After cooling, 200 cc. of pentane was added, the contents of the flask poured onto 500 g. of crushed ice, and the flask rinsed with 50 cc. of pentane. The layers were separated and the water layer extracted twice with 100-cc. portions of pentane. After drying over anhydrous potassium carbonate the product was fractionally distilled. There was obtained 31.3 g. (0.134 mole) of somewhat impure compound II, b. p. 110–112° at 40 mm., n^{20}_D 1.4410–1.4415, d^{20} 0.8003 (middle fraction). Treatment of this material with 50 cc. of concd. sulfuric acid removed a small amount of siloxane impurity, 2,2,4,4,6,6,8,8-octamethyl-5-oxa-2,4,6,8-tetrasilanonane. Refractionation gave pure compound II. Table II (see footnote *f*) gives pertinent data on the preparations of the polysilmethylenes.

Synthesis of Compound VIII.—Lithiomethylpentamethyldisilmethylene was prepared in the usual manner in 94% yield from 72.4 g. (0.372 mole) of compound V and 5.2 g. (0.744 mole) of lithium foil in 500 cc. of pentane. To the lithium alkyl there was added 24.6 g. (0.186 mole) of dimethyldichlorosilane over a period of one hour. After twelve hours of heating at reflux temperature, the contents of the flask were poured onto 500 g. of cracked ice. The layers were separated, the water layer extracted with 200 cc. of pentane, and the combined organic layers dried over anhydrous potassium carbonate. Fractionation gave 36.7 g. (0.082 mole) of compound VIII, b. p. 145 at 2 mm., n^{20}_D 1.4542, d^{20} 0.8601, an 88% yield based on the dimethyldichlorosilane.

Anal. Calcd. for $C_{18}H_{50}Si_6O$: Si, 37.2; mol. wt., 450; MD, 143. Found: Si, 37.3; mol. wt. in benzene, 457; MD 142.

Physical Properties.—Boiling points were determined in a modified Cottrell apparatus.[14] Refractive indices were measured with an Abbe type refractometer. Densities were measured with pycnometers of about 5-cc. capacity. Determinations were checked by running each compound in two different pycnometers. The instruments were calibrated at the three temperatures using triple-distilled water. All densities are corrected to the vacuum values. Viscosities were measured in Cannon–Fenske viscometers.[15] All determinations were checked by running each compound in two different instruments.

Summary

1. Eight silmethylene compounds have been synthesized and their physical properties studied.

2. The unusual physical properties of the methylpolysiloxanes were shown to be largely due to their siloxane linkages.

STATE COLLEGE, PA. RECEIVED FEBRUARY 25, 1949

---

(14) Quiggle, Tongberg and Fenske, *Ind. Eng. Chem., Anal. Ed.*, **6**, 466 (1934).

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