TABLE IV

INTERATOMIC DISTANCES IN $(NH_4)_2[InCl_5H_2O]$

$In-Cl_I$	2.52 Å.	Cl_I-Cl_{II}	3.70 Å.	$2(NH_4-Cl_I)$	3.27 Å. 3.43
$In-Cl_{II}$	2.71	$Cl_{II}-Cl_{III}$	3.61	$2(NH_4-Cl_{II})$	3.51 3.52
$In-Cl_{III}$	2.60	$2(Cl_I-Cl_{IV})$	3.62	$2(NH_4-Cl_{III})$	3.56 3.48
$2(In-Cl_{IV})$	2.54	$2(Cl_{II}-Cl_{IV})$	3.68	Average	3.46
Average	2.58	$2(Cl_{III}-Cl_{IV})$	3.58		
		Average	3.63		
$In-H_2O$	2.23				
H_2O-Cl_I	3.60	$2(NH_4-H_2O)$	4.21 3.87	$4(NH_4-Cl_{IV})$	3.35 3.53 3.72 3.82
H_2O-Cl_{III}	3.32				
$2(H_2O-Cl_{IV})$	3.42	Average	4.04		
Average	3.44			Average	3.61

the indium than by the NH_4^+ ions, and the bond radii hold accurately only where each kind of atom is octahedrally coördinated by the opposite kind. The observed value, 2.58 Å., is thus a reasonable one, and the bond is doubtless partly ionic and partly covalent.

Lindqvist's average non-bonded Cl–Cl distance in the ferrate was 3.39 Å. The value of 3.63 Å. observed is about what would be expected as a result of the exchange of the larger In^{3+} ion (radius = 0.81 – 0.92 Å.) for Fe^{3+} (radius = 0.67 Å.). Similarly the $Fe-H_2O$ distance in the ferrate was 2.08 Å. in comparison with 2.23 Å. for $In-H_2O$.

There are more data available for comparison of the NH_4-Cl distances. This distance is 3.35 Å. in low ammonium chloride. In the somewhat more similar compound, $(NH_4)_2ZnCl_4 \cdot NH_4Cl$,[6] there are two kinds of ammonium ions from the standpoint of the coördination about them. Eight of them are surrounded by six chlorine atoms at the corners of a trigonal prism (average distance, 3.44 Å.), with three additional chlorine atoms at a little greater distance (average, 3.63 Å.). The remaining four ammonium groups are surrounded by eight chlorine atoms at the corners of an irregular polygon with the distances varying from 3.14 to 3.68 Å., average, 3.32 Å. Thus the observed average NH_4-Cl distances of 3.46 and 3.61 Å. in the indate are about as expected.

Summary

A complete structure determination of the salt $(NH_4)_2InCl_5 \cdot H_2O$ has been carried out by single crystal X-ray diffraction methods in order to study the stereochemistry of its 1:5 stoichiometry. The structure is orthorhombic with a_0 = 14.10 Å., b_0 = 10.17 Å., c_0 = 7.16 Å. and is an example of the $J1_8$ structure type, of which $Cl_2[Rh(NH_3)_5Cl]$ and $(NH_4)_2[FeCl_5H_2O]$ are already known. The structure is a packing of spherical NH_4^+ ions and octahedral $[InCl_5H_2O]^=$ ions. The water molecule occupies a definite corner of the octahedron, which is distorted because of the unequal sizes of Cl^- and H_2O. The NH_4^+ ions are surrounded by a distorted cube of six chlorine atoms and two water molecules. The sixteen parameters fixing the positions of the atoms in the cell have been determined, and the various interatomic distances calculated. The formula of the salt should be written $(NH_4)_2[InCl_5H_2O]$.

PITTSBURGH 13, PA. RECEIVED MAY 24, 1948

[CONTRIBUTION FROM THE RESEARCH LABORATORY, GENERAL ELECTRIC COMPANY]

Polysilmethylene Compounds and their Siloxy Derivatives

BY BEN A. BLUESTEIN

The thermal and hydrolytic stability of methyl groups attached directly to silicon has been well established in the now commercially important "silicones." However, the siloxane bonds present in silicones are susceptible to thermal and to catalytic rearrangements.[1] Since the substitution of a methylene group for an oxygen atom of a siloxane would eliminate the possibility of these rearrangements, it seemed of interest to study the chemical and physical properties of compounds containing silicon–methylene–silicon linkages.

Compounds containing disilmethylene groups, $[\equiv Si-CH_2-Si\equiv]$ were first prepared by Patnode and Schiessler[2] who obtained hexachlorodisilmethylene as a product of the reaction between methylene chloride and silicon–copper. Rochow[3] has disclosed the possibility of preparing polymers containing silmethylene groups but gives no details. Sommer, *et al.*,[4] have recently reported the

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(1) Patnode and Wilcock, THIS JOURNAL, **68**, 356 (1946).

(2) Patnode and Schiessler, U. S. Patent 2,381,000, 2,381,002.

(3) Rochow, "Introduction to the Chemistry of the Silicones," John Wiley and Sons, Inc., New York, N. Y., 1946, p. 46.

(4) Sommer, Goldberg, Gold and Whitmore, THIS JOURNAL, **69**, 980 (1947).

TABLE I

Short formula	Formula	Oxa-aza name
$MODCH_2DOM$	$[(CH_3)_3SiOSi(CH_3)_2]_2CH_2$	2,2,4,4,6,6,8,8-octamethyl-3,7-dioxa-2,4,6,8-tetrasilanonane
$MODCH_2M$	$(CH_3)_3SiOSi(CH_3)_2CH_2Si(CH_3)_3$	2,2,4,4,6,6-hexamethyl-3-oxa-2,4,6-trisilaheptane
$MODCH_2DODCH_2DOM$	$[(CH_3)_3SiOSi(CH_3)_2CH_2Si(CH_3)_2]_2O$	2,2,4,4,6,6,8,8,10,10,12,12-dodecamethyl-3,7,11-trioxa-2,4,6,8,10,12-hexasilatridecane
$MODCH_2DCH_2DOM$	$[(CH_3)_3SiOSi(CH_3)_2CH_2]_2Si(CH_3)_2$	2,2,4,4,6,6,8,8,10,10-decamethyl-3,9-dioxa-2,4,6,8,10-pentasilahendecane
$MODCH_2DOH$	$(CH_3)_3SiOSi(CH_3)_2CH_2Si(CH_3)_2OH$	2-hydroxy-2,4,4,6,6-pentamethyl-5-oxa-2,4,6-trisilaheptane
$HODCH_2DOH$	$HOSi(CH_3)_2CH_2Si(CH_3)_2OH$	2,4-dihydroxy-2,4-dimethyl-2,4-disilapentane
$(—DCH_2DO—)_n$	$[—Si(CH_3)_2CH_2Si(CH_3)_2O—]_n$	Polymeric 2,2,4,4-tetramethyl-1-oxa-2,4-disiletane
$(—DCH_2DO—)_2$	$[—Si(CH_3)_2CH_2Si(CH_3)_2O—]_2$	2,2,4,4,6,6,8,8-octamethyl-1,5-dioxa-2,4,6,8-tetrasilocane
$FDCH_2DF$	$FSi(CH_3)_2CH_2Si(CH_3)_2F$	2,4-difluoro-2,4-dimethyl-2,4-disilapentane
$FDCH_2DCH_2DF$	$FSi(CH_3)_2[CH_2Si(CH_3)_2]_2F$	2,6-difluoro-2,4,4,6-tetramethyl-2,4,6-trisilaheptane
$FDCH_2DCl$	$FSi(CH_3)_2CH_2Si(CH_3)_2Cl$	2-chloro-4-fluoro-2,4-dimethyl-2,4-disilapentane
$ClDCH_2DCl$	$ClSi(CH_3)_2CH_2Si(CH_3)_2Cl$	2,4-dichloro-2,4-dimethyl-2,4-disilapentane

preparation of several completely alkylated silanes (hexamethyldisilmethylene and octamethyltrisilmethylene). More recently Goodwin, Baldwin and McGregor[5] have described the "preparation of compounds of the type $ASi(CH_3)_2[CH_2Si(CH_3)_2]_nB$ . . . where A and/or B may be methyl, chloride or ethoxy."

While the class name "polysilmethylenes," proposed by Sommer,[4] may be appropriate for the particular series they have prepared, the more general "oxa-aza" nomenclature system is recommended where no simple name is feasible.[6] The modified shorthand notation introduced in this Laboratory,[7] where $M = [(CH_3)_3Si—]$ and $D = [CH_3)_2Si=]$, will be used throughout this paper, and is given, with the appropriate oxa-aza name, in Table I.

The experiments described herein are concerned with the preparation and properties of compounds containing the di- and tri-silmethylene groupings, $—DCH_2D—$ and $—DCH_2DCH_2D—$, respectively. The important reactions involved are summarized in the equations below

$$MOM + Cl_2 \longrightarrow MODCH_2Cl + HCl \quad (1)$$

$$MODCH_2Cl + Mg \longrightarrow MODCH_2MgCl \quad (2)$$

$$MODCH_2MgCl + ClDCl \longrightarrow MODCH_2DCl \xrightarrow{H_2O} \text{siloxysilmethylenes} \quad (3)$$

$$\text{siloxysilmethylenes} + H_2SO_4 + HF \longrightarrow \text{fluorosilmethylenes} \quad (4)$$

$$FDCH_2DF + H_2O \longrightarrow HODCH_2DOH + (—DCH_2DO—)_n \quad (5)$$

$$FDCH_2DF + MCl \xrightarrow{AlCl_3} FDCH_2DCl + ClDCH_2DCl + MF \quad (6)$$

Experimental

I. Chloromethylpentamethyldisiloxane and its Grignard Derivative.—Chloromethylpentamethyldisiloxane, $MODCH_2Cl$, was prepared, with the assistance of Dr. J. R. Elliott, by the direct chlorination of hexamethyldisiloxane, using the chlorination technique of Krieble and Elliott.[8] A 58% yield of product (based on unrecovered **MOM**), b. p. 151–152°, was obtained.

The Grignard reagent of $MODCH_2Cl$ was readily prepared. To 126 g. (5.2 moles) of magnesium, 200 ml. dry ether, and a crystal of iodine, contained in a 3 l. Grignard set-up, was added a solution of 1080 ml. (5.0 moles) of $MODCH_2Cl$ in 1 l. of dry ether. The initial formation of the Grignard reagent was erratic and sometimes required the introduction of a few drops of ethyl iodide. The addition took about six hours and the mixture was kept at reflux temperature for another hour after the addition was complete.

II. Reaction of $MODCH_2MgCl$ with $(CH_3)_2SiCl_2$: A. $MODCH_2MgCl$ to DCl_2 Ratio of 1:1.—The Grignard reagent reacted readily with dimethyldichlorosilane to yield, after hydrolysis, a complex mixture of siloxanes and silmethylenes. To separate and identify the organic groups present in the mixture, it was found convenient to convert the siloxanes to fluorosilanes. Although sulfuric acid has been used previously in conjunction with calcium,[9a] sodium[9b] and ammonium[9b,c] fluoride it was found preferable to use anhydrous, gaseous hydrogen fluoride[10] as it eliminated the presence of a solid phase during the reaction. This treatment has been found to cleave siloxanes to fluorosilanes, leaving silmethylene groups intact.

The Grignard reagent prepared from 5.0 moles of $MODCH_2Cl$ was added to a solution of 665 ml. (5.5 moles) of dimethyldichlorosilane in 800 ml. of dry ether during a two-hour period. Some heat was evolved. The mixture was then heated for an additional fifteen minutes. The product was carefully poured over cracked ice, the ether layer separated, washed, dried with sodium sulfate, and distilled. After removal of the ether, 1130 g. of oil remained.

This oil was added slowly, with stirring, to 1100 ml. of concentrated sulfuric acid. Some hydrogen chloride was evolved during the solution process, probably by metathesis of unhydrolyzed high molecular weight chlorosilanes. The maximum temperature attained was 68°

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[5] Goodwin, Baldwin and McGregor, THIS JOURNAL, **69**, 2247 (1947).

[6] Thus, the compound, $FDCH_2DF$, is called 2,4-difluoro-2,4-dimethyl-2,4-disilapentane but could also have the alternative names bis-(fluorodimethylsilyl)-methane or 1,3-difluorotetramethyldisilmethylene.

[7] Price, THIS JOURNAL, **70**, 871 (1948).

[8] Krieble and Elliott, *ibid.*, **67**, 1810 (1945); *ibid.*, **68**, 2291 (1946).

[9] (a) Emeleus and Wilkins, *J. Chem. Soc.*, 454 (1944); (b) Flood, THIS JOURNAL, **55**, 1735 (1933); (c) Sommer, Pietrusza and Whitmore, *ibid.*, **68**, 2282 (1946).

[10] A general method for the conversion of siloxanes to fluorosilanes by the action of anhydrous hydrogen fluoride, fuming sulfuric acid, and a wetting agent has since been described by Booth in *Chem. Rev.*, **41**, 104 (1947).

and a homogeneous, amber solution resulted. The sulfuric acid solution, in a Pyrex flask, was cooled to room temperature and anhydrous hydrogen fluoride was introduced rapidly during a two-hour period. The copper inlet tube for the gas was bent upward at the orifice to prevent the gas from coming in direct contact with the glass container. The hydrogen fluoride was absorbed rapidly and the gas, trimethylfluorosilane, was evolved. After an initial, short reaction period, an organic layer appeared above the sulfuric acid solution. The completion of the reaction was evidenced by (1) no further increase in the volume of the organic layer and (2) the appearance of myriads of bubbles due to the attack of hydrogen fluoride on the glass container, which becomes only slightly etched during the reaction. The upper organic layer was separated quickly and distilled through a Vigreux column. Some trimethylfluorosilane was first obtained and then a fraction, b. p. 114–116°, 532 g., was distilled. Based on **MODCH$_2$Cl** initially used, this is a 63% yield of **FDCH$_2$DF**, n^{20}_D 1.3780, d^{20}_4 0.920, MR_D (calcd.) 41.74, (fd.) 42.16.

Anal. Calcd. for $C_5H_{14}Si_2F_2$: C, 35.68; H, 8.38; F, 22.6. Found: C, 35.7, 35.1, 35.3; H, 8.4, 8.5, 8.1; F, 22.1, 22.1.

A small amount of high boiling liquid remained. Dilution of the lower sulfuric acid layer showed that there was no residual organic material. The difluoro compound is an example of a difunctional silicon compound having only monofunctional silicons. It has a pleasant odor, reminiscent of silanols. It is not readily hydrolyzed and can be kept in stoppered glass vessels with little etching of the container.

B. MODCH$_2$MgCl to DCl$_2$ Ratio of 2:1, Experiment 1.—To the Grignard reagent prepared from 2.5 moles of **MODCH$_2$Cl** in 550 ml. of dry ether was added 145 ml. (1.2 moles) of dimethyldichlorosilane during one-half hour. Reflux temperature was maintained for an additional two and one-half hours. The reaction products were poured onto ice, the ether layer separated, washed and dried over sodium sulfate. The ether was distilled, together with some hexamethyldisiloxane formed as a by-product. The remaining oil was distilled rapidly at 50 mm. to a temperature of 235° and this distillate was rectified to yield the pure fractions: 1A, b. p. 99–101° (57 mm.), 18.6 g.; 1B, b. p. 132–133° (55 mm.), 80.3 g.; 1C, b. p. 175–177° (55 mm.), 43.9 g. Fraction 1A is **MODCH$_2$M**, 7% yield, n^{20}_D 1.4137, d^{20}_4 0.808, MR_D (calcd.) 72.56, (fd.) 72.43.

Anal. Calcd. for $C_9H_{26}Si_3O$: C, 46.10; H, 11.18. Found: C, 46.6, 46.5; H, 11.3, 11.1.

Fraction 1B is **MODCH$_2$DOM**, 22% yield, n^{20}_D 1.4121, d^{20}_4 0.845, MR_D (calcd.) 91.19, (fd.) 90.92.

Anal. Calcd. for $C_{11}H_{32}Si_4O_2$: C, 42.81; H, 10.45. Found: C, 42.9, 43.2; H, 10.6, 10.5.

Fraction 1C is **MODCH$_2$DCH$_2$DOM**, 10% yield, n^{20}_D 1.4276, d^{20}_4 0.855, MR_D (calcd.) 114.8, (fd.) 114.5.

Anal. Calcd. for $C_{14}H_{40}Si_5O_2$: C, 44.17; H, 10.59. Found: C, 44.8, 44.9; H, 10.8, 10.7.

The high-boiling residues from both distillations, 159 g., were dissolved in 160 ml. of concentrated sulfuric acid and treated with hydrogen fluoride as described above. Distillation yielded only 99 g. of liquid, b. p. 114–115°. This represents a 48% yield of the difluoride, **FDCH$_2$DF** (12 g. of tar remained).

Experiment 2.—This was identical with Experiment 1 except that a nineteen-hour reflux period was maintained after the addition of all the reagents. After removal of the ether and hexamethyldisiloxane, no flash distillation was carried out, but the oil was carefully fractionated at reduced pressure. The pure fractions obtained were: 2A, b. p. 96.5–97.5° (51 mm.), 43.7 g.; 2B, b. p. 118.5–120° (53 mm.), 62.9 g.; 2C, b. p. 129–130° (53 mm.), 35.2 g.; a residue, b. p. above 131° (54 mm.), 185 g.

Fractions 2A and 2C are **MODCH$_2$M** (16% yield) and **MODCH$_2$DOM** (10% yield), respectively, and are identified above. Water slowly separated from Fraction 2B upon standing at room temperature. It was believed to be an azeotrope of **MODCH$_2$DOH** with **MODCH$_2$DOM**, analogous to the azeotrope, trimethylsilanol–hexamethyldisiloxane.[11] The silanol seemed to be relatively stable in the dilute solution of the reaction products but condensed, with rearrangements, in the more concentrated solution. The liquid was heated to boiling, at atmospheric pressure, for two hours, the water formed (2.6 g.) was removed and the organic layer was rectified to yield: 2D, b. p. 127–129° (52 mm.), 11.2 g.; 2E, b. p. 184–185° (34 mm.), 32.7 g.

Some high boilers (7 g.) remained and were probably polysiloxanes. Fraction 2D is **MODCH$_2$DOM** (3% yield). Fraction 2E is **MODCH$_2$DODCH$_2$DOM**, 6% yield (accounts for 12% initial **DCl$_2$**), n^{20}_D 1.4243, d^{20}_4 0.872, MR_D (calcd.) 133.4, (fd.) 133.1.

Anal. Calcd. for $C_{16}H_{46}Si_6O_3$: C, 42.25; H, 10.20. Found: C, 42.9, 42.5; H, 10.3, 10.3.

Treatment of the high boiling residue, 185 g., from the first distillation, with concentrated sulfuric acid and hydrogen fluoride gave an oil from which was distilled: 2F, b. p. 115–116°, 89 g.; 2G, b. p. 187–188°; 102–102.5° (44 mm.), 14.2 g. Fraction 2F represents a 44% yield of **FDCH$_2$DF**. Fraction 2G is **FDCH$_2$DCH$_2$DF**, 5% yield, n^{20}_D 1.4150, d^{20}_4 0.926, MR_D (calcd.) 65.35, (fd.) 65.02.

Anal. Calcd. for $C_8H_{22}Si_3F_2$: C, 39.97; H, 9.23. Found: C, 39.6, 39.7; H, 9.4, 9.3.

III. Hydrolysis of FDCH$_2$DF. A. Hydrolysis at Room Temperature.—When 15 g. of the difluoro compound, **FDCH$_2$DF**, was shaken with excess dilute alkali, in the cold, both a solid and a liquid organic phase resulted. Filtration of the mixture yielded 7 g. of white needles. The solid, upon recrystallization from benzene, had a m. p. of 84–86°, and is the disilanol, **HODCH$_2$DOH**.

Anal. Calcd. for $C_5H_{16}Si_2O_2$: C, 36.55; H, 9.81. Found: C, 36.9, 36.6; H, 9.7, 9.7.

The disilanol is soluble in acetone and carbon tetrachloride, and somewhat soluble in water. It can be dehydrated to a polymeric oil by heating above the melting point or by acidifying its water solution.

B. Hydrolysis in Hot Alkali.—A rapidly stirred mixture of 220 g. (1.3 moles) of **FDCH$_2$DF** and 168 g. (3.0 moles) of potassium hydroxide in 1 liter of water was refluxed for three hours. The supernatant oil was washed with a saturated solution of sodium chloride, then with water. It was shaken with 10 ml. of concentrated sulfuric acid and again washed with water. After drying with anhydrous potassium carbonate and filtering, a clear, somewhat viscous oil, (—**DCH$_2$DO**—)$_n$, resulted, n^{20}_D 1.4436.

Anal. Calcd. for $(C_5H_{14}Si_2O)_n$: C, 41.05; H, 9.58. Found: C, 41.2, 41.2; H, 9.5, 9.7.

The oil has a number average molecular weight (cryoscopic) of 518, *i. e.*, an average chain length of about seven silicon atoms per molecule. It has a viscosity of 45 centistokes at 100° F., and a viscosity-temperature coefficient[12] (V. T. C.) of 0.66 compared to about 0.6 for the usual silicone oils and 0.8 for petroleum oils.

When the oil is vacuum-distilled, there is obtained a 50% yield of the cyclic dimer, (—**DCH$_2$DO**—)$_2$, b. p. 103–104° (20 mm.), m. p. 28–29°. (Goodwin, *et al.*,[5] have also isolated this compound.)

Anal. Calcd. for $(C_5H_{14}Si_2O)_2$: C, 41.05; H, 9.58. Found: C, 40.8, 41.0; H, 9.6, 9.6.

IV. Preparation of Chlorosilane Derivatives.—The difluoride, **FDCH$_2$DF**, was converted to the dichloride by metathesis with trimethylchlorosilane in the presence of aluminum chloride, according to equation 6.

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[11] Sauer, This Journal, **66**, 1707 (1944).

[12] Wilcock, *Mech. Eng.*, 739 (1944). V. T. C. = 1 − η210°F./η100°F.

A solution of 36.6 ml. (0.2 mole) of the fluorosilane and 63.5 ml. (0.5 mole) of trimethylchlorosilane was refluxed for three hours under a small fractionating column, equipped with a Dry Ice trap. Only traces of trimethylfluorosilane, b. p. 17°, were obtained. The addition of 1 g. of aluminum chloride still yielded only small amounts of product. However, when the temperature of the reaction mixture was raised by distilling about 75% of the trimethylchlorosilane, appreciable quantities of trimethylfluorosilane began to condense in the trap. The distilled trimethylchlorosilane was returned to the reaction mixture flask in small portions, keeping the take-off temperature below 30°. Distillation at reduced pressure yielded two compounds: A, b. p. 71–72° (50 mm.), 9.6 g.; B, b. p. 95–96° (50 mm.), 18.7 g. Fraction A is $FDCH_2DCl$, 26% yield.

Anal. Calcd. for $C_5H_{14}Si_2FCl$: Cl, 19.20. Found: Cl, 19.0, 18.9.

Fraction B is $ClDCH_2DCl$, 47% yield, n^{20}_D 1.4480, d^{20}_4 1.016, *MR*D (calcd.) 53.10, (fd.) 53.01.

Anal. Calcd. for $C_5H_{14}Si_2Cl_2$: Cl, 35.22. Found: Cl, 35.14.

The mixed chlorofluorosilane disproportionates into the dichloro and the difluoro-silane when distilled at atmospheric pressure.

Discussion

Of the silmethylene–siloxane compounds isolated in the above experiments, only $MODCH_2DCH_2DOM$ and $(MODCH_2D)_2O$ could have been formed as direct products of the synthetic method employed. The compound, $MODCH_2DOM$, must have resulted from siloxane rearrangements either during the course of the Grignard reaction or during the hydrolysis of the products thereof. To explain the presence of $MODCH_2M$, it is necessary to assume that the Grignard reagent, $MODCH_2MgCl$, reacted with Si–O bonds present in the reaction mixture,[11] possibly according to the equation

$$MODCH_2MgCl + MODCH_2Cl \longrightarrow MODCH_2M + ClMgODCH_2Cl$$

An analysis of the physical properties of the silmethylenesiloxanes prepared in this Laboratory and the compounds prepared by Sommer, *et al.*[4], shows that the substitution of a methylene group for an oxygen atom between two silicons results in the following changes in the physical properties of the lower members of the series: (1) an increase in the boiling point of 20–30°, (2) a lowering of the density by about 0.01 g./cc., and (3) an increase in the refractive index by 0.02–0.03. The introduction of a second silmethylene group has a somewhat smaller effect.

Chemically, the disilmethylene group is shown to be quite stable. During the course of this work, compounds containing this grouping have been subjected to treatment with cold concentrated sulfuric acid, gaseous, anhydrous hydrogen fluoride and aqueous, boiling potassium hydroxide with no apparent deleterious effects. They are somewhat susceptible to oxygen at elevated temperatures; one of the oxidation products is formaldehyde. Their thermal stability is, however, quite good in the absence of oxygen.

The investigation of other derivatives and of higher members of this interesting series of compounds is being continued.

Acknowledgment.—The author wishes to express his thanks to Dr. R. O. Sauer for his advice and interest in this work and to Mr. L. B. Bronk and Miss M. L. Caldwell for the analyses reported herein.

Summary

1. Organosilicon compounds, containing di- and tri-silmethylene linkages, have been prepared; and their chemical and physical properties have been investigated.

2. The use of hydrogen fluoride and concentrated sulfuric acid to convert complex siloxanes to fluorosilanes has led to the synthesis of two new organofluorosilanes.

3. Organofluorosilanes have been shown to undergo "halogen interchange" with trimethylchlorosilane.

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[CONTRIBUTION FROM THE CHEMISTRY LABORATORIES OF WASHINGTON SQUARE COLLEGE OF NEW YORK UNIVERSITY]

Nitrogen Analogs of Hexestrol.[1] The Synthesis of N,N′-Dimethyl-α,α′-bis-(4-hydroxyphenyl)-ethylenediamine and Derivatives

BY JOSEPH B. NIEDERL AND MARTIN I. DEXTER[2]

Intramolecular synchronization of molecular groupings possessing *a priori* divergent physiological properties, were extended to the hexestrol series. It was surmised that by replacing carbon atoms in the aliphatic portion of the hexestrol structure by nitrogen, compounds exhibiting interesting pressor action, or estrogenic activity, or both, might result. In the present paper account is given of the first of these types of compounds, namely, the N,N-dimethyl-α,α′-bis-(4-hydroxyphenyl)-ethylenediamine, a compound which incorporates the physiologically active phenylethylamine grouping into the hexestrol structure. The synthesis of this compound, from anisaldehyde as the starting material, involved the Decker and Becker[3] methylation procedure of the intermediate di-anisal derivative of the substituted ethylenediamine, in addition to conventional

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(1) Presented before the Division of Organic Chemistry of the American Chemical Society, Chicago, Ill., April 19–23, 1948.

(2) This paper has been abstracted from a portion of the thesis presented by Martin I. Dexter to the faculty of the Graduate School of New York University in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

(3) Fischer and Prause, *J. prakt. Chem.*, [2] **77**, 130 (1908).