[CONTRIBUTION FROM THE RESEARCH LABORATORY OF THE GENERAL ELECTRIC COMPANY]

Methylphenylpolysiloxanes

BY RICHARD N. LEWIS

Many compounds in the series of methylpolysiloxanes and phenylpolysiloxanes have been reported in the literature[1]; polymers containing both methyl and phenyl groups on the same silicon atom[2] and copolymers of methyl and phenylpolysiloxanes[3] have also been reported. However, few pure compounds containing both methyl and phenyl groups have been described. Kipping[4] has prepared dimethyltetraphenyldisiloxane, a solid melting at 51–52°. Daudt[5] has disclosed tetramethyldiphenyldisiloxane without describing its properties and has prepared pentamethylphenyldisiloxane, b. p. 206°.[6] Hexamethyldiphenyltrisiloxane was studied by Hurd[7] but has not been fully characterized.

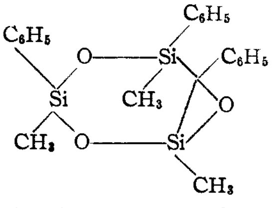
The shorthand notation used in this paper is based on that of Wilcock,[8] in which M and D represent mono- and difunctional units; primes are used to indicate phenyl groups, thus:

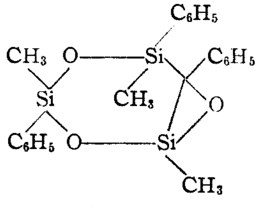
Unit	Formula	Unit	Formula
M	$(CH_3)_3SiO_{1/2}$	D	$(CH_3)_2SiO$
M′	$(CH_3)_2C_6H_5SiO_{1/2}$	D′	$CH_3C_6H_5SiO$
M″	$CH_3(C_6H_5)_2SiO_{1/2}$	D″	$(C_6H_5)_2SiO$

According to this system, the compounds mentioned above may be written, M''_2, M'_2, MM′, M_2D'', respectively.

A series of cyclic compounds was made by hydrolyzing methylphenyldichlorosilane[2] and distilling the resultant oil at a pressure of 2 mm. During the distillation the liquid was heated to 460°, at which temperature there is a strong possibility of thermal rearrangement of silicon–oxygen bonds.[9,10] The fact that there was no appreciable residue, therefore, does not mean that the original hydrolyzate was composed entirely of low molecular weight products. There was no indication, however, of rearrangement of the carbon–silicon bonds or of any other type of decomposition.

On fractional distillation of this oil there were obtained two forms of the cyclic trimer, D'_3, both solid at room temperature, and a cyclic tetramer, D'_4, as well as a non-volatile residue consisting of higher polymers of unusual thermal stability. Since the two forms of the trimer can be separated by distillation, they are apparently two distinct compounds. A type of *cis–trans* isomerism, in which the phenyl groups may or may not all lie on the same side of the ring, appears to be a reasonable explanation. The *cis*-configuration, which has a threefold axis of symmetry, is assigned to the higher melting isomer. This type of isomerism probably occurs with the tetramer as well. However, it was not possible to obtain any crystalline material from it, although four stereoisomers are theoretically present.


cis-Trimer, m. p. 99.5°


trans-Trimer, m. p. 39.5°

It is to be expected that these cyclic polysiloxanes can be converted to linear ones by equilibration with monofunctional units or "chain-stoppers." In the methyl series, M_2 and D_4, for instance, when shaken with sulfuric acid, produce compounds of the general formula M_2D_x.[9] Since the phenyl–silicon bond is known to be somewhat unstable toward acidic reagents,[11] it was considered desirable to use an alkaline catalyst in the present work. (Methods involving alkaline equilibration have recently been patented.[6,12])

It was found that compounds of the type D'_x, could be equilibrated with M'_2 and with M_2 by means of potassium hydroxide in isopropyl alcohol containing a small amount of water. In the first case, no other solvent was required, but when M_2 was used, it was necessary to add toluene because of the limited miscibility of D'_x with M_2 and isopropyl alcohol. This lack of solubility must be due to the presence of higher polymers as the tetramer is miscible with M_2. The phenyl–silicon bond is apparently quite inert toward this treatment as no appreciable quantity of benzene was produced.

In the reaction of D'_x with M_2 small amounts of dimethylphenylsilanol and dimethylphenylisopropoxysilane were formed; this means that the condensation of silanols and the hydrolysis of silyl ethers are reversible. Because of the acidic nature of silanols[13] some of the potassium salt must also have been formed. The following types of bonds are therefore present at equilibrium:

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(1) C. A. Burkhard, E. G. Rochow, H. S. Booth and J. Hartt, *Chem. Rev.*, **41**, 97 (1947).

(2) J. F. Hyde and R. C. DeLong, THIS JOURNAL, **63**, 1194 (1941).

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

(4) F. S. Kipping, *J. Chem. Soc.*, 104 (1927).

(5) W. H. Daudt, U. S. Patent 2,397,727; *C. A.*, **40**, 3938 (1946).

(6) W. H. Daudt and J. F. Hyde, British Patent 583,878; *C. A.*, **41**, 3115 (1947).

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

(8) D. F. Wilcock, *ibid.*, **69**, 477 (1947).

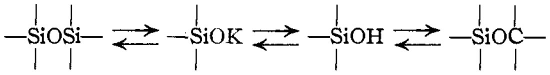
(9) W. Patnode and D. F. Wilcock, *ibid.*, **68**, 358 (1946).

(10) D. W. Scott, *ibid.*, **68**, 356 (1946).

(11) F. S. Kipping and L. L. Lloyd, *J. Chem. Soc.*, **79**, 449 (1901).

(12) J. F. Hyde, British Patent 583,875; *C. A.*, **41**, 3115 (1947).

(13) L. H. Sommer, E. W. Pietrusza and F. C. Whitmore, THIS JOURNAL, **68**, 2282 (1946).



$$-\mathrm{SiOSi}- \rightleftarrows -\mathrm{SiOK} \rightleftarrows -\mathrm{SiOH} \rightleftarrows -\mathrm{SiOC}-$$

Alkoxysilane formation, which might have been predicted, has not been observed before. The formation of silanols from siloxanes was reported by Kipping and Robison.[14]

Experimental[15]

Hydrolysis of Methylphenyldichlorosilane.—Eleven and six-tenths moles (2210 g.) of redistilled methylphenyldichlorosilane (*Anal.* Calcd.: Cl, 37.10. Found: Cl, 36.69) was hydrolyzed in six portions by running it into ice water with vigorous stirring. The oil which was produced was distilled rapidly at 2 mm. from a Claisen flask, which was completely surrounded by an electric heater. The temperature outside the flask reached 460° while the vapor (probably superheated) reached 295°. No appreciable residue was left. The distillate (1318 g., 9.7 moles of D′) was redistilled at 1.5 mm. through a 1.5 inch by 18-inch column packed with stainless steel helices, and the resulting fractions were grouped as follows: I, forerun, 3%; II, 12% boiling at 165–185°; III, another 12% boiling chiefly at 190°; IV, 48% boiling chiefly at 237°; and V, 24% of residue.

Fraction II crystallized on cooling and was recrystallized from alcohol; flat plates, m. p. 99.5°; yield, 60 g.

Anal. Calcd. for $C_{21}H_{24}Si_3O_3$ (D'_3): C, 61.73; H, 5.92; mol. wt., 408. Found: C, 61.7, 61.7; H, 6.0, 5.9; mol. wt., 390.

Several fractions of the material boiling at 190° (1.5 mm.) were left at 0°. The first of these, apparently contaminated with the previous material, developed crystals in a few hours. After one week, however, the entire mass crystallized, and a portion of it was used successfully to seed the other fractions. Upon recrystallization from alcohol there were obtained small needles, m. p. 39.5°; yield, 137 g. There were also some intermediate fractions containing considerable amounts of both II and III. The following properties of III were determined on an unrecrystallized sample: n^{20}_D 1.5397, d^{20}_4 1.1062, R_D 0.2835, R_D (calcd.) 0.2826.

Anal. Calcd. for $C_{21}H_{24}Si_3O_3$ (D'_3): C, 61.73; H, 5.92; mol. wt., 408. Found: C, 61.6, 61.2; H, 6.2, 5.9; mol. wt., 437.

IV remained a viscous liquid well below 0° and could not be made to crystallize. It was miscible with *n*-heptane, acetone, M_2 and D_4, but not with alcohol. A middle fraction had the following properties: n^{20}_D 1.5461, d^{20}_4 1.1183, R_D 0.2832, R_D (calcd.) 0.2826. The yield of pure material was 453 g.

Anal. Calcd. for $C_{28}H_{32}Si_4O_4$ (D'_4): C, 61.73; H, 5.92; mol. wt., 544. Found: C, 61.8, 61.5; H, 6.0, 6.1; mol. wt., 545.

V was not characterized; it was assumed to consist of higher polymers of D′. It is a viscous liquid of high thermal stability as the following experiment shows: A 3-cc. portion was heated in a 6-cc. beaker in contact with zinc metal. There was no change, except for some fuming above 240°, until the melting point of zinc (419.4) was reached. After two hours in contact with molten zinc (average temperature about 450°) some thickening occurred; the material was then cooled to room temperature, at which point it was rubbery.

Dimethylphenylchlorosilane and Dimethylphenylbromosilane.—These two compounds were obtained together from the reaction of phenylmagnesium bromide with dimethyldichlorosilane.[16] From 3.0 moles of bromobenzene and 3.0 moles of dimethyldichlorosilane there were obtained 1.44 moles of the chloride, b. p. 197° at 766 mm., and 0.53 mole of the bromide, b. p. 215° at 766 mm. The combined yield of both halides was 65%. The chloride had a pleasant odor like that of the silanol described below, while the bromide was almost odorless.

Anal. Calcd. for $C_8H_{11}SiCl$: Cl, 20.77. Found: Cl, 20.5.

Anal. Calcd. for $C_8H_{11}SiBr$: Br, 37.15. Found: Br, 36.8.

Tetramethyl-1,3-diphenyldisiloxane (M'_2).—The above halides (1.93 moles) were hydrolyzed in ice water with vigorous stirring, and the product was diluted with ether, washed well, dried and distilled. The major portion of it distilled at 140–144° (5.7 mm.); yield, 250.5 g. (91%). A sample was redistilled at 110–111° (1.0 mm.); n^{20}_D 1.5122, d^{20}_4 0.9763, R_D 0.30745, R_D (calcd.) 0.3096.

Anal. Calcd. for $C_{16}H_{22}Si_2O$: C, 67.08; H, 7.74. Found: C, 66.2, 66.0; H, 7.6, 7.8.

Pentamethyl-1,3,5-triphenyltrisiloxane (M'_2D').—M'_2 (245 g., 0.857 mole) was mixed with 75 cc. of isopropyl alcohol and 38.8 g. (0.275 mole of D′) of cyclic polymers, D'_x, from which most of the tetramer had been distilled. A homogeneous solution resulted, although the cyclic compounds alone were immiscible with isopropyl alcohol. A solution of 10 g. of potassium hydroxide in 8 cc. of water was added and all but 5.3 cc. dissolved. The mixture was heated thirty-nine hours at 71°. After cooling it was washed, first with 10% sodium chloride (to help break the emulsion), then with 10% ammonium chloride and dried. On distillation the following fractions were obtained: 15.1 g., 60–119° at 1.8 mm.; 166.5 g., 120–138° at 2.0 mm. (recovered M'_2); 59.3 g., 130–173° at 0.5 mm. (0.140 mole, 51%, of M'_2D'); and a 25.3 g. residue of much lower viscosity than the original D'_x, presumably polymeric material of the general formula $M'_2D'_x$. The third fraction was redistilled at 169° and 0.7 mm.; n^{20}_D 1.5280, d^{20}_4 1.0227, R_D 0.3011, R_D (calcd.) 0.3009.

Anal. Calcd. for $C_{23}H_{30}Si_3O_2$ (M'_2D'): C, 65.36; H, 7.15. Found: C, 64.5, 64.9; H, 7.1, 7.2.

Dimethylphenylsilanol and Dimethylphenylisopropoxysilane.—The low-boiling fraction from the preceding preparation had a strong, pleasant odor similar to that of dimethylphenylchlorosilane and was therefore believed to contain the corresponding silanol. On redistillation 2.8 g. of material was obtained; b. p. 65–66° (3.5 mm.), n^{20}_D 1.4714, d^{20}_4 0.9074, R_D 0.3082, R_D (calcd. for silanol) 0.3034. The only other compound which seemed at all likely to be present was the isopropyl derivative; its calculated specific refraction, 0.3091, is closer to the observed value. A test-tube portion treated with sodium liberated hydrogen. Another portion treated with potassium hydroxide and potassium triiodide (the iodoform test) gave a precipitate, slowly on standing, more rapidly on warming to 70°, as would be expected from the slow formation of isopropyl alcohol. Similar tests with M'_2 and D_4 gave no precipitate. It was therefore concluded that the material was a difficultly separable mixture of dimethylphenylsilanol and dimethylphenylisopropoxysilane.

Heptamethyl-3-phenyltrisiloxane (M_2D').—A mixture of unfractionated cyclic methylphenylpolysiloxanes (13.6 g., 0.1 mole of D′) was dissolved in 48 g. (0.3 mole) of M_2 by adding 50 cc. of toluene and 25 cc. of isopropyl alcohol. To this was added 6.6 g. of 50% aqueous potassium hydroxide solution of which all but 1.5 cc. dissolved. The mixture was heated twenty-four hours at 60°. It was washed with water to remove alkali and alcohol, then dried and distilled through a 9-inch packed column. One cc. distilled from 76.4 to 89.5°. Of this only the first few drops had any odor of benzene; the rest appeared to be a mixture of water and M_2. The amount of benzene produced in the reaction was therefore considered to be negligible. A large fraction with an odor of toluene

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(14) R. Robison and F. S. Kipping, *J. Chem. Soc.*, **103**, 40 (1913); F. S. Kipping and R. Robison, *ibid.*, **105**, 484 (1913).

(15) Melting points and boiling points are corrected. Molecular weights were determined cryoscopically in cyclohexane. Specific refractions were calculated according to R. O. Sauer, THIS JOURNAL, **68**, 954 (1946).

(16) For a similar reaction see R. N. Lewis, *ibid.*, **69**, 717 (1947).

distilled at 99.6° (750 mm.); n^{20}_{D} 1.3910. It was assumed to be an azeotrope between M_2 (b. p. 100.4°) and toluene (b. p. 110.8°). After the excess toluene was removed, the next fraction (10 g., 0.036 mole) was distilled at about 250°, leaving as a residue a low viscosity oil, which was assumed to consist of linear compounds of the type $M_2D'_x$. The 250° fraction was redistilled; b. p. 95° (5.0 mm.), n^{20}_{D} 1.4468, d^{20}_{4} 0.9080, R_D 0.2941, R_D (calcd.) 0.2929.

Anal. Calcd. for $C_{13}H_{26}Si_3O_2$ (M_2D'): C, 52.30; H, 8.78. Found: C, 52.8, 52.6; H, 8.9, 8.7.

Acknowledgment.—The author is indebted to Miss Mary L. Caldwell, who carried out the microanalyses for carbon and hydrogen.

Summary

1. Two stereoisomeric cyclic trimers and a cyclic tetramer have been obtained by the hydrolysis of methylphenyldichlorosilane.

2. Linear methylphenylpolysiloxanes have been prepared from the cyclic ones by means of hexamethyldisiloxane or tetramethyl-1,3-diphenyldisiloxane and an alkaline catalyst.

3. Evidence for an equilibrium between siloxanes, silanols and silyl ethers has been found.

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Preparation and Properties of Trimethylsilylmethanol

BY JOHN L. SPEIER, B. F. DAUBERT AND R. R. MCGREGOR

Organo-silicon compounds containing organic functional groups such as the carbinol group are not readily prepared by the usual methods of synthesis of organo-silicon compounds. The literature records the preparation of only two compounds in which this group is contained. The first is triethylsilylethanol of uncertain structure[1] obtained by the chlorination of tetraethylsilane, conversion of the chloride to the acetate and hydrolysis of the acetate. The second is 1-trimethylsilyl-2-propanol prepared from trimethylsilylmethylmagnesium chloride and acetaldehyde.[2]

Since it was desired to investigate the properties of an α-hydroxyalkylsilane, trimethylsilylmethanol was synthesized in good yield through the sequence of reactions:

$$\mathrm{Me_3SiCH_2Cl}^{3} \xrightarrow[190\,^{\circ}\mathrm{C.}]{\mathrm{KOAc}\atop\mathrm{HOAc}}$$

$$\mathrm{Me_3SiCH_2OAc} \xrightarrow[\mathrm{H_2SO_4}]{\mathrm{MeOH}} \mathrm{Me_3SiCH_2OH}$$

The trimethylsilylmethanol so prepared was found to be approximately six times as reactive in forming a phenylurethan as its carbon analog, neopentyl alcohol, and approximately three times as reactive as methanol in the same reaction.

Experimental

Preparation of Trimethylsilylmethyl Acetate.—Chloromethyltrimethylsilane[4] (3.1 moles), potassium acetate (3.8 moles), and glacial acetic acid (420 ml.) were charged into a stainless steel high-pressure reactor and shaken at 190–192° for eighteen hours. The contents of the reactor were then washed thoroughly with distilled water. The water-insoluble liquid, after drying over anhydrous sodium carbonate, was slightly amber in color and weighed 416.5 g. (92%). The mixture was distilled through a three-foot Stedman column and was found to boil entirely between the temperatures of 136.2–136.8° at 748 mm., all but 5 ml. distilling at the higher temperature. The ester has the following constants: b. p. 136.8° at 748 mm., $[n]^{25}_{D}$ 1.4060, $[d]^{25}_{4}$ 0.8667. Molar refraction: Calcd.[5] for Me_3SiCH_2OAc, 41.31. Found: 41.37. Sapn. equiv.: Calcd., 146.2. Found: 146.5, 146.6. *Anal.* Calcd. for $C_6H_{14}O_2Si$: Si, 19.2. Found: Si, 19.3, 19.1.

Preparation of Trimethylsilylmethanol.—Trimethylsilylmethyl acetate (420 ml., 2.5 moles) was dissolved in absolute methanol (9 moles) and acidified with 10 drops of concentrated sulfuric acid. After standing at room temperature for two days, 165 ml. of the azeotropic mixture of methanol and methyl acetate was removed by distillation. The charge was then diluted with methanol (4 moles) and permitted to stand four days at room temperature before fractionation to yield 268 ml. (80%) of constant boiling trimethylsilylmethanol, b. p. 121.6° at 729 mm. The alcohol redistilled from lime had the following properties: b. p. 121.7–121.9° at 751 mm., $[n]^{25}_{D}$ 1.4169, $[d]^{25}_{4}$ 0.8261. Molar refraction: Calcd.[5] for Me_3SiCH_2OH, 31.83. Found, 31.71. The alcohol has a strong odor resembling that of menthol.

Preparation of Trimethylsilylmethyl 3,5-Dinitrobenzoate.—Trimethylsilylmethanol (1.1 g.) was added dropwise to 3,5-dinitrobenzoyl chloride (2.5 g.) and heated to 90° until no more hydrogen chloride was evolved. The mixture was cooled, and ground into a fine powder in the presence of two portions of warm 5–6% sodium carbonate solution. It was heated with a third portion of sodium carbonate solution until it fused. On stirring vigorously as it cooled, solidification occurred. The solids were washed with water in a suction filter, dissolved in boiling 95% ethanol, and filtered while hot. On cooling to room temperature, 2.3 g. of crystalline product was obtained which melted at 69.5–70°. The mother liquor was heated to boiling and diluted with water to the point of incipient turbidity. Again on cooling, 0.9 g. of crystalline product formed, m. p. 68.5–70°. The two crops of crystals were combined and recrystallized once from 95% ethanol. The recrystallized product melted at 70–70.5°. Further recrystallizations did not change this melting point.

Anal. Calcd. for $C_{11}H_{14}O_6N_2Si$: C, 44.26; H, 4.73; N, 9.33; Si, 9.41. Found: C, 44.04; H, 4.41; N, 9.33; Si, 9.47, 9.45.

Preparation of (Trimethylsilylmethoxy)-trimethylsilane.—Trimethylsilylmethanol (19.7 g.) dissolved in dry

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(1) Friedel and Crafts, *Compt. rend.*, **61**, 792 (1865).

(2) Whitmore, Sommer, Gold and Van Strien, THIS JOURNAL, **69**, 1551 (1947).

(3) Whitmore and Sommer, *ibid.*, **68**, 481 (1946), first prepared chloromethyltrimethylsilane and showed that it reacted with potassium acetate in glacial acetic acid.

(4) Chloromethyltrimethylsilane was prepared for use in this work by the method of Whitmore, Sommer and Gold, *ibid.*, **69**, 1976 (1947).

(5) Warrick, *ibid.*, **68**, 2455 (1946).