Department of Synthetic Chemistry, Kyoto University
Kyoto, Japan

Some Methylpolysilicon Sulfates

Makoto Kumada and Sajiro Maeda

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Four methylpolysilicon sulfates, $(Me_3Si.SiMe_2)_2SO_4$, $[-(Me_2Si)_2-SO_4-]_x$, $\underline{|-(SiMe_2)_3SO_4-|}$, *and* $\underline{|-(SiMe_2)_4SO_4-|}$, *were prepared in good yield by reaction of the corresponding chloropolysilanes with the theoretical amount of 100 per cent sulfuric acid. Reactions of hexamethyltrisilylene sulfate with several reagents were studied, and found in most cases to proceed in normal ways without cleavage of the silicon-silicon bond. However, the reaction with an excess of triphenylsilyllithium for a many hour period led to the formation of dodecamethylcyclohexasilane and hexaphenyldisilane. A possible mechanism for this reaction is discussed.*

Introduction

In an earlier paper[1] we briefly described that in the synthesis of 1,3-dichlorohexamethyltrisilane by the action of concentrated sulfuric acid on octamethyltrisilane followed by treatment with ammonium chloride some amount of hexamethyltrisilylene sulfate, a product in the intermediate stage, was also isolated as crystals. This isolation prompted a further study on this sulfate and other organopolysilicon sulfates, since the literature of organosilicon chemistry contains no examples of such a type of compounds, despite a large number of publications dealing with organomonosilicon sulfates.[2-12]

Preparation

All the methylpolysilicon sulfates reported here (I)-(IV) were prepared most conveniently by the reaction of appropriate chlorosilanes with the theoretical amount of 100 per cent sulfuric acid, which has usually been employed for synthesis of monosilicon sulfates.

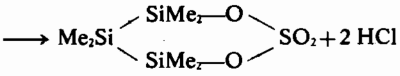
$$2\ Me_3SiSiMe_2Cl + H_2SO_4 \longrightarrow (Me_3SiSiMe_2)_2SO_4 + 2\ HCl$$

(I)

$$ClMe_2SiSiMe_2Cl + H_2SO_4 \longrightarrow [Me_2SiSiMe_2SO_4]_x + 2\ HCl$$

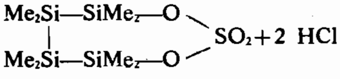
(II)

$$ClMe_2SiSiMe_2SiMe_2Cl + H_2SO_4 \longrightarrow$$



(III)

$$Cl(SiMe_2)_4Cl + H_2SO_4 \longrightarrow$$



(IV)

No appreciable cleavage of the silicon-silicon bond was observed to occur during the reaction. In general, the methylpolysilicon sulfates are relatively stable to heat and could be isolated by distillation or sublimation under reduced pressure. Yields were quite satisfactory.

Hexamethyltrisilylene sulfate (III) is a monomeric (by mass spectrometry) crystalline solid, readily soluble in most of inert organic solvents. It seems most likely that liquid octamethyltetrasilylene sulfate (IV) also is monomeric in view of its relatively high volatility. On the other hand, tetramethyldisilylene sulfate (II) is insoluble white powder and hence probably polymeric, although it could be sublimed at 160° under reduced pressure.

Yields, some physical properties, and analytical data for these sulfates are given in Table 1.

Reactions

All of these sulfates are extremely hygroscopic. We have studied chemical properties of hexamethyltrisilylene sulfate (III) in some detail and arrived at a conclusion that the sulfate, and most probably the other methylpolysilicon sulfates also, can undergo many of the reactions that are known to the monosilicon sulfates without appreciable cleavage of the silicon-silicon bond. Thus, hydrolysis of (III) gave an expected cyclic siloxane, i.e., 2,2,3,3,4,4,6,6,7,7,8,8-dodecamethyl-1,5-dioxa-2,3,4,6,7,8-hexasilacyclooctane (V) in 40% yield, along with higher polymers. The action of dry hydrogen chloride on (III) in the presence of ammonium chloride

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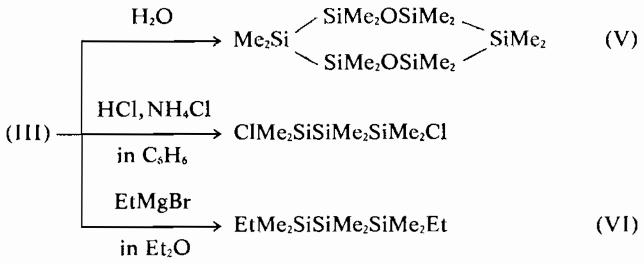
Table I. Yields, Physical Properties and Analytical Data for Methylsilicon Sulfates

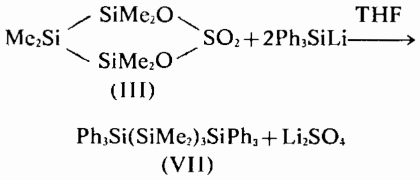
No.	Compound	Yield (%)	M.P. (°C)	B.P. (°C/mm)	Si % Found	Si % Calcd.	Neutral equiv. Found	Neutral equiv. Calcd.
(I)	Bis(pentamethyldisilanyl) sulfate	74		117-118/3	30.88	31.32	181	179
(II)	Tetramethyldisilylene sulfate[a]	96	172-177		26.21	26.45	107	106
(III)	Hexamethyltrisilylene sulfate[b]	79	82-83		30.89	31.15	135	135
(IV)	Octamethyltetrasilylene sulfate	83		125-130/0.8	33.79	34.18	163	164

[a] Probably polymeric; sublimes at 160°/3 mm. [b] Sublimes at 100-110°/7 mm; mol. wt. (by mass spectroscopy), 270 (calcd. 270).

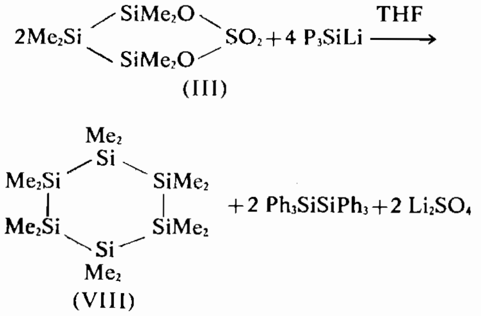
in benzene converted it into 1,3-dichlorohexamethyltrisilane in almost quantitative yield. The reaction with ethylmagnesium bromide produced 1,3-diethylhexamethyltrisilane (VI) in 85.5% yield.



However, the reaction of (III) with triphenylsilyllithium in tetrahydrofuran (THF) proceeded in a more complex fashion. When a greenish black solution of this reagent in tetrahydrofuran was added in the cold to a solution of (III) in the same solvent, reaction took place instantly with decoloration of the reagent until about 80 per cent of an equivalent amount of the latter was introduced. The reaction products obtained at this stage consisted mainly of the expected 1,1,1,5,5,5-hexaphenylhexamethylpentasilane (VII) (yield, 63.5%).



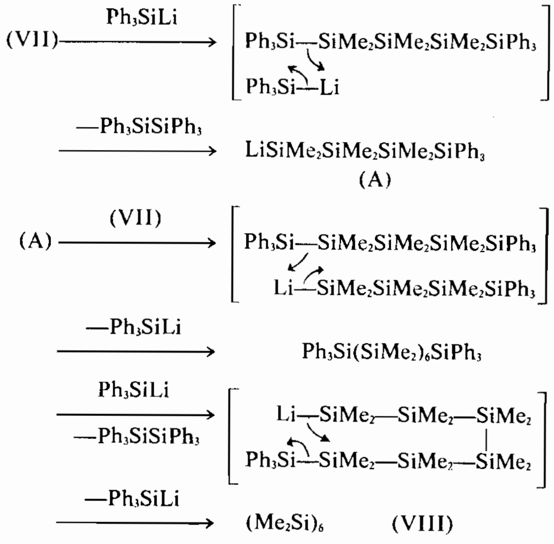
On the other hand, if the theoretical amount or an excess of the reagent was added to (III) and the reaction mixture was stirred at room temperature over a many hour period and finally heated to reflux, then dodecamethylcyclohexasilane (VIII) and hexaphenyldisilane were obtained as the main products. Yields were 67 and 83.5%, respectively.



The other two silylene sulfates, (II) and (IV), were also found to be converted to some extent into the cyclohexasilane (VIII) under analogous conditions.

Mechanism for the formation of $(Me_2Si)_6$

The formation of dodecamethylcyclohexasilane (VIII) upon treatment of hexamethyltrisilylene sulfate (III) with an excess of triphenylsilyllithium in tetrahydrofuran for a prolonged time can well be understood in terms of initial formation of 1,1,1,5,5,5-hexaphenylhexamethylpentasilane (VII), as described above, which subsequently undergoes a sequence of Si-Si/Si-Li redistribution. The pathway as illustrated below is analogous to that proposed by Gilman and Tomasi[13] for the formation of dodecamethylcyclohexasilane from lithium coupling of dimethyldichlorosilane in the presence of triphenylsilyllithium. In this mechanism, the formation of aliphatic polysilyllithium intermediates such as (A) is assumed. The assumption of the possible existence, at least transient, of such species would not be unreasonable in view of the facts in the literature that permethylated linear polysilanes higher than the disilane undergo cleavage by sodium-potassium alloy in tetrahydrofuran[14] and tetrakis(trimethylsilyl)silane is cleaved to give tris(trimethylsilyl)silyllithium when treated with methyllithium or triphenylsilyllithium in tetrahydrofuran.[15]



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[14] U. G. Stolberg, *Angew Chem.*, *75*, 206 (1963); *Z. Naturforsch.*, *186*, 765 (1963).

[15] H. Gilman, J. M. Holmes and C. L. Smith, *Chem. Ind.* (London), 848 (1965).

The mechanism obviously can also be applied with some modification to the reaction of two other silylene sulfates, (II) and (IV), with triphenylsilyllithium. Thus, in order to account for the formation of cyclohexasilane (VIII) from sulfate (IV) it is necessary to take into account the rearrangement at the Me_2Si-$SiMe_2$ bonding under reaction conditions to give rise to this most stable cyclic polysilane.

Recently, we have been able to demonstrate that the polysilanes of the general formula $Ph_3Si(SiMe_2)_nSiPh_3$ with $n = 1$-5 are, in fact, convertible into dodecamethylcyclohexasilane (VIII) in good yields on treatment with triphenylsilyllithium (free from metallic lithium) in tetrahydrofuran. These results will be published elsewhere.[16]

Experimental Section

Bis(pentamethyldisilanyl) sulfate (I). In a 100-ml three-necked flask provided with a motor-driven stirrer, a reflux condenser and a gas inlet tube there were placed 40 g (0.24 mole) of chloropentamethyldisilane[17, 18] and 11.8 g (0.24 mole) of 100 per cent sulfuric acid. The mixture was cooled to 0° and stirred vigorously under a stream of dry nitrogen. After about five hours' stirring the evolution of hydrogen chloride ceased, and so the mixture was gradually heated to 80° in 2 h. At this point the contents of the flask were distilled to give 29 g of a fraction boiling over the range of 120-128°/3 mm, along with 7 g of unchanged chlorodisilane and 3.5 g of residue. The distillate was redistilled under reduced pressure in a 1.0×30 cm column packed with glass helices to give 26 g of (I) in the pure state.

Tetramethyldisilylene sulfate (II). In essentially the same manner, 11.5 g (0.061 mole) of 1,2-dichlorotetramethyldisilane[17, 18] was allowed to react with 6 g (0.061 mole) of 100 per cent sulfuric acid. After seven hours' reaction (initially at 0° and finally at 80°) the content in the flask turned into a white solid mass. As this product was insoluble in many inert organic solvents, it was washed with petroleum ether and dried. It weighed 12 g. The product could be purified by sublimation at 160° under reduced pressure (3 mm).

Hexamethyltrisilylene sulfate (III). By the same procedure as above, 15 g (0.061 mole) of 1,3-dichlorohexamethyltrisilane[1, 18, 19] and 6 g (0.061 mole) of 100 per cent sulfuric acid were brought into reaction. In this case the solid product was easily soluble in hydrocarbons, and much more readily sublimable under reduced pressure than sulfate (II). Recrystallization from benzene-petroleum ether gave 13 g of white needles. Its molecular weight was satisfactorily determined by mass spectroscopy. The cryoscopic method in benzene gave only unreliable values probably because of the highly hygroscopic nature of this compound.

Octamethyltetrasilylene sulfate (IV). A mixture of 10 g (0.033 mole) of dichlorooctamethyltetrasilane[19] and 3.2 g (0.033 mole) of 100 per cent sulfuric acid was stirred for 7 h at 0°. The resulting colorless viscous oil was heated to 80° for 2 hr and then distilled to give 9 g of a pure sample of sulfate (IV).

Hydrolysis of (III). A solution of 9 g (0.03 mole) of sulfate (III) in 100 ml of ether was added to a stirred mixture of 100 ml of ether and 300 ml of water. The ether layer and ether extracts from the water phase were combined, washed to neutral, dried over anhydrous sodium carbonate, and distilled to give as a definite product 2.5 g (40% yield) of 2,2,3,3,4,4,6,6,7,7,8,8-dodecamethyl-1,5-dioxa-2,3,4,6,7,8-hexasilacyclooctane (V), b.p. 98-100°/2 mm, n_D^{20} 1.4841, d_4^{20} 0.9010, MR_D 121.00 (calcd. 121.34) (Found: C, 37.96; H, 9.35; mol. wt. 388. $C_{12}H_{36}O_2Si_6$ calcd.: C, 37.83; H, 9.53%; mol. wt. 381).

Action of hydrogen chloride on (III). In a 300-ml three-necked flask there were placed 10 g (0.037 mole) of sulfate (III), 4.0 g (0.074 mole) of ammonium chloride, and 70 ml of dry benzene. Through the stirred mixture was passed slowly dry hydrogen chloride at room temperature over a 10-h period. At this point the organic layer was separated by decantation and distilled to give 9 g (99% yield) of gas chromatographically homogeneous 1,3-dichlorohexamethyltrisilane, b.p. 98°/18 mm, n_D^{20} 1.4850, d_4^{20} 0.9854 (reported:[1] b.p. 82-83°/11 mm, n_D^{20} 1.4852, d_4^{20} 0.9865) (Found: Cl, 28.82. $C_6H_{18}Cl_2Si_3$ cacld.: Cl, 28.90%).

Action of ethylmagnesium bromide on (III). To a stirred solution of ethylmagnesium bromide prepared from 18.2 g (0.167 mole) of ethyl bromide, 4.05 g (0.167 g-atom) of magnesium in 170 ml of ether was added at room temperature over a 30-min period 15 g (0.056 mole) of sulfate (III) dissolved in a mixture of ether (130 ml) and benzene (70 ml). During the addition, white salts precipitated with gentle evolution of heat. The mixture was stirred first at room temperature for 2 h and then heated to reflux for 8 h. It was then hydrolyzed with dilute hydrochloric acid, and the resulting organic layer was separated, washed to neutral, dried over anhydrous calcium chloride, and fractionally distilled. Product (13 g, 85.5% yield) was collected with b.p. 97°/15 mm, n_D^{20} 1.4771, d_4^{20} 0.8052 and MR_D 81.64 (calcd. 81.38), and was identified as 1,3-diethylhexamethyltrisilane (Found: C, 51.44; H, 12.13. $C_{10}H_{28}Si_3$ calcd.: C, 51.64; H, 12.13%).

Action of tripenylsilyllithium on (III). Triphenylsilyllithium[20] was prepared from 39.4 g (0.13 mole) of triphenylchlorosilane and 3.0 g (0.43 g-atom) of lithium in 200 ml of tetrahydrofuran. Unchanged lithium was removed by filtration in dry nitrogen atmosphere. The solution of reagent thus obtained was gradually added with cooling to a stirred solution of 15 g (0.056 mole) of sulfate (III) in 100 ml tetrahydrofuran. The instant the reagent dropped its greenish black color vanished.

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(20) H. Gilman, D. J. Peterson and Wittenberg, *Chem. Ind.* (London), 1479 (1958); for a pertinent review, see D. Wittenberg and H. Gilman, *Quart Rev.*, *8*, 116 (1959).

But the rate of decoloration much decreased when about 80 per cent of the reagent had been introduced. At this point the reaction mixture was hydrolyzed with dilute hydrochloric acid. The resulting organic layer was washed, dried over calcium chloride, and distilled to give 27 g of a crystalline material boiling mainly over the range of 330-343°/0.15 mm. Recrystallization of it from a benzene-ethanol mixture gave 19 g (63.5% yield) of 1,1,1,5,5,5-hexaphenylhexamethylpentasilane (VII), m.p. 191-192° (reported value,[21] 190-191°) (Found: C, 72.34; H, 6.85. $C_{42}H_{48}Si_5$ calcd.: C, 72.76; H, 6.98%). In this case neither dodecamethylcyclohexasilane nor hexaphenyldisilane was detected.

In a second run in which identical quantities of materials were employed, all the triphenylsilyllithium reagent was added to the sulfate, and the colored mixture was stirred at room temperature for 14 h and then at refluxing temperature for 9 h. During these periods considerable quantities of white precipitate were produced, but the color of the liquid phase still survived. At this point, the contents of the flask were hydrolyzed with dilute hydrochloric acid. The organic solution and insoluble white mass were separated from the water layer in a separating funnel, and then the mass was separated by filtration. This solid was rinsed out in water and then in ether, and dried (24 g, 83.5%). It was identified as hexaphenyldisilane by comparison of its IR spectrum with that of an authentic sample[22] and by its m.p. and mixed m.p. 347-350°. The filtrate was washed to neutral, dried over anhydrous calcium chloride, and distilled to give 13 g of white crystals, along with 7 g of greasy residue. Recrystallization of the crystals from acetone gave 6.5 g (67% yield) of dodecamethylcyclohexasilane (VIII), the identity of which was established by comparison of its IR spectrum with that of an authentic sample and by its m.p. 256-257° (reported value:[23] 255-257°) as well as by analysis (Found: C, 41.44; H, 10.38. $C_{12}H_{36}Si_6$ calcd.: C, 41.30; H, 10.40%).

Action of triphenylsilyllithium on (II) and (IV). Under essentially the same conditions as above, from sulfate (II) were produced dodecamethylcyclohexasilane (VIII) in 39% yield, hexaphenyldisilane in 76.5% yield, and unidentified compounds containing silicon-phenyl and silicon-hydrogen bonds. Also, reaction of sulfate (IV) with triphenylsilyllithium gave the cyclohexasilane (VIII) in 14.2% yield and hexaphenyldisilane in 27.8% yield. In this case, 1,1,1,6,6,6-hexaphenyloctamethylhexasilane, $Ph_3Si(SiMe_2)_4SiPh_3$, m.p. 189-190° (reported value:[21] 180-182°), also was isolated in 6% yield (Found: C, 70.49; H, 7.31. $C_{44}H_{54}Si_6$ calcd.: C, 70.33; H, 7.24%).

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