[CONTRIBUTION FROM THE WHITMORE LABORATORY, THE PENNSYLVANIA STATE COLLEGE]

Aliphatic Organo-functional Siloxanes[1]

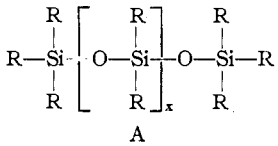
BY L. H. SOMMER, R. P. PIOCH, N. S. MARANS, G. M. GOLDBERG, J. ROCKETT AND J. KERLIN

RECEIVED JANUARY 16, 1953

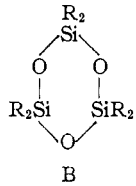
The synthesis of seven aliphatic organosiloxanes which contain functional groups linked to carbon is described. The key reaction for their preparation involves cleavage of one methyl group from trimethylsilyl, Me_3Si, by concd. sulfuric acid.

Introduction

The important and unusual properties, both physical and chemical, of aliphatic organosilicon compounds which set them sharply apart from ordinary organic monomers and polymers are largely found in the organosiloxanes and derive from the unique architecture of these substances which comprises a basic framework of alternate silicon and oxygen atoms with organic groups linked to silicon. Typical examples of these structures are the linear organosiloxanes A and the cyclic structure B.[2]



A



B

Thus, the polymethylpolysiloxanes (R = Me) have received extensive study and currently enjoy a wide variety of applications in the form of oils, greases, resins and elastomers.[2]

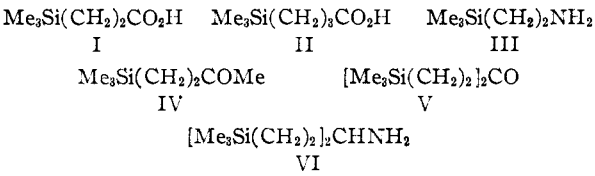
In our view, one of the remaining largely unexplored directions in which aliphatic organosiloxane chemistry may be expanded lies in the elaboration and study of structures having functional groups linked to carbon. Incorporation of functions such as ketone, carboxylate, amino, etc., leads to the possibility of preparing new type organosiloxanes whose properties may prove to be of interest from both theoretical and practical standpoints.

At present, a beginning has already been made in the above direction. Thus chloromethylmethylpolysiloxanes,[3] acetoxymethyl- and hydroxymethyldisiloxanes[4] and aminomethylsiloxanes[5] have been prepared.

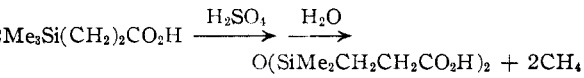
However, in the chloromethylmethylpolysiloxane series it has been found that chloromethyl groups are readily cleaved from silicon by bases. Thus, even so weak a base as alcoholic ammonia gives this change.[3a] Further, the acetoxymethyldisiloxanes readily give scission of the acetoxymethyl groups as methyl acetate with aqueous alkali, and *sym*-bis-(hydroxymethyl)-tetramethyldisiloxane is unstable even at room temperature, being converted to a polymer of unknown composition on standing.[4] Thus, of the aliphatic organo-functional siloxanes already reported only the aminomethylsiloxanes appear to hold promise of being reasonably resistant to carbon–silicon cleavage.

The above facts, taken together with previous work in this Laboratory on organo-functional monomers[6] enabled us to anticipate with some degree of assurance that certain organo-functional siloxanes would prove to be reasonably stable toward cleavage of the organic functional group from silicon. However, a good general method for the synthesis of these substances was lacking until it was found that concentrated sulfuric acid gives selective cleavage of one methyl group from trimethylsilyl in certain organosilicon structures.[7] In the present paper this simple reaction has been used for the preparation of seven aliphatic organo-functional siloxanes.

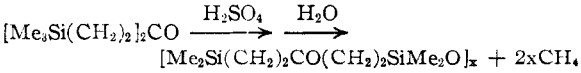
Monomers.—The present investigation deals with six organo-functional silanes which are here termed "monomers" from the fact that these substances (I–VI) may be converted by the sulfuric



acid cleavage of one methyl group from trimethylsilyl to dimers in the case of the mono-silicon compounds (I–IV), *e.g.*, for I



and to polymers in the case of the di-silicon compounds, *e.g.*, for V



Monomers I, III and IV have been prepared previously and the present syntheses of II, V and VI were unexceptional and need no comment here. It is, however, of some interest to note that all six may be prepared from chloromethyltrimethylsilane as a starting material by multi-step procedures.

Organo-functional Siloxanes.—The new organo-functional siloxanes are listed in Table I. The synthesis of VII–X involved simply the use of I–IV in the sulfuric acid reaction. In the case of VIII

(1) Paper 33 in a series on organosilicon chemistry; for 32 see P. D. George, L. H. Sommer and F. C. Whitmore, THIS JOURNAL, **75**, 1585 (1953).

(2) A review of the rapidly expanding organosiloxane field would be out of place in the present article. For an excellent treatment 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) (a) R. H. Krieble and J. R. Elliott, THIS JOURNAL, **67**, 1810 (1945); (b) J. L. Speier, *ibid.*, **71**, 273 (1949).

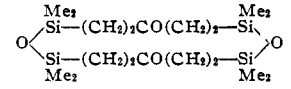
(4) J. L. Speier, B. F. Daubert and R. R. McGregor, *ibid.*, **71**, 1474 (1949).

(5) J. E. Noll, J. L. Speier and B. F. Daubert, *ibid.*, **73**, 3867 (1952).

(6) For a summary see L. H. Sommer and N. S. Marans, *ibid.*, **72**, 1935 (1950).

(7) L. H. Sommer, N. S. Marans, G. M. Goldberg, J. Rockett and R. P. Pioch, *ibid.*, **73**, 882 (1951).

TABLE I

	Compound	Yield, %	B.p. °C.	Mm.	M.p., °C.	$n^{20}D$	d^{20}	MR_D Found	MR_D Calcd.	Element	Analyses Found	Calcd.
VII	$O(SiMe_2CH_2CH_2CO_2H)_2$	95			53–54					Si	20.02	20.16
										N.e.	140	139
VIII	$O(SiMe_2CH_2CH_2CH_2CO_2H)_2$	82			49–49.5					Si	18.5	18.3
										N.e.	154.0	153.2
IX	$O(SiMe_2CH_2CH_2NH_2)_2$	76	115	13		1.4473	0.9075	64.89	65.12	Si	24.9	25.4
	Dihydrochloride	85			267–268					Cl	24.3	24.2
X	$O(SiMe_2CH_2CH_2COMe)_2$	62	142	6		1.4390				Si	20.60	20.46
										M.w.	283	274
XI		23			129–130					Si	26.6	25.9
										M.w.	425	432
XII	$Me_3SiOSiCH_2CH_2COCH_2CH_2SiOSiMe_3$ (Me, Me)	41	95	2		1.4262	0.8857	108.7	109.6	Si	29.6	29.6
XIII	$Me_3SiOSiCH_2CH_2CH(NH_2)CH_2CH_2SiOSiMe_3$ (Me, Me)	49	98	2		1.4282	0.8654	112.8	113.0	Si	29.9	29.6

it was found that the reaction could best be performed at ice-temperature in order that cleavage of the carboxyalkyl group, as butyric acid, be kept to a minimum, *ca.* 10%. Higher temperatures gave increasing amounts of this side-reaction up to 20%.

Reaction of V with concentrated sulfuric acid followed by pouring on ice gave a viscous polymer. In an effort to isolate a polysiloxanepolyketone of relatively simple structure which could be purified and studied as an individual substance, use was made of the known property of organosiloxanes to undergo rearrangement of their siloxane bonds with the production of more volatile substances from the application of high temperatures.[8] Thermal rearrangement of the polymer at 370–385° (3.5 mm.) gave a distillate comprising a mixture of solid XI and liquid polymer. Compound XI is a crystalline solid and contains a 16-membered ring.

Since the utility of organo-functional siloxanes for the synthesis of new type organosiloxanes would be greatly enhanced if the former would undergo copolymerization with other simple organosiloxanes, the liquid polymer obtained in addition to XI in the thermal rearrangement was subjected to equilibration with excess hexamethyldisiloxane using concentrated sulfuric acid as the reagent. The latter is known to bring about the conversion of cyclic organosiloxanes to linear polymers in the presence of a source of trimethylsiloxy groups such as hexamethyldisiloxane.[9] This procedure readily gave XII.

Finally, compound XIII was prepared by equilibration of the polysiloxanepolyamine from VI with hexamethyldisiloxane using potassium hydroxide as the catalyst in an isopropyl alcohol–water solvent.[10]

Experimental

Synthesis of the Monomers

Compounds I,[11] III[12] and IV[13] were previously prepared and hence require no experimental details.

Compound II was easily synthesized by treatment of γ-bromopropyltrimethylsilane[14] with magnesium to give the Grignard reagent followed by carbonation with Dry Ice. Compound II, γ-trimethylsilylbutyric acid, b.p. 118° (10 mm.), $n^{20}D$ 1.4324, was obtained in 74% yield.[15]

Anal. Calcd. for $C_7H_{16}SiO_2$: Si, 17.5; neut. equiv., 160.3. Found: Si, 17.4; neut. equiv., 161.6.

Compound V, 2,2,8,8-tetramethyl-2,8-disila-5-nonanone, was prepared from ethyl β-trimethylsilylpropionate[13] in two steps. Claisen condensation of the ester to the β-ketoester was best effected by the use of diisopropylaminomagnesium bromide as the condensing agent[16] in ethyl ether as the solvent. Ethyl α-(β-trimethylsilylpropionyl)-β-trimethylsilylpropionate, b.p. 141° (8 mm.), $n^{20}D$ 1.4472, d^{20} 0.9196, was obtained in 81% yield.

Anal. Calcd. for $C_{14}H_{30}Si_2O_3$: Si, 18.6; MR_D, 87.98. Found: Si, 19.1; MR_D, 87.74.

Hydrolysis and decarboxylation of the β-ketoester was achieved by heating to reflux (four hours) 33 g., 0.108 mole, of the β-ketoester with a solution of 14 cc. of concd. sulfuric acid, 9 cc. of water and 73 cc. of glacial acetic acid. Compound V, b.p. 103° (7 mm.), $n^{20}D$ 1.4414, d^{20} 0.8424, was obtained in 80% yield.

Anal. Calcd. for $C_{11}H_{26}Si_2O$: Si, 24.4; MR_D, 72.32. Found: Si, 24.2; MR_D, 72.20.

Compound VI, 2,2,8,8-tetramethyl-2,8-disila-5-aminononane, was prepared in two steps from compound V. The following were heated on the steam-bath for two hours: compound V, 0.583 mole; $NH_2OH{\cdot}HCl$, 0.641 mole; abs. ethanol, 250 cc.; dry pyridine, 225 cc. Evaporation of the solvents gave a crystalline residue which was washed with water, filtered and dried in a vacuum. Recrystallization from methanol gave 122.5 g. of pure ketoxime, m.p. 76–76.5°, an 86% yield.

Anal. Calcd. for $C_{11}Si_2H_{27}ON$: Si, 22.86. Found: Si, 22.9.

Reduction of the ketoxime with lithium aluminum hydride in dry ether gave compound VI, b.p. 115° (15 mm.), $n^{20}D$ 1.4438, d^{20} 0.8123, in 44% yield.

Anal. Calcd. for $C_{11}Si_2H_{29}N$: Si, 24.41; MR_D, 75.79. Found: Si, 24.9; MR_D, 76.61.

Synthesis of Organo-functional Siloxanes

4,4,6,6-Tetramethyl-4,6-disila-5-oxa-nonanedioic Acid (VII).—Into a 500-cc., 3-necked, round-bottomed flask fitted with a dropping funnel, a mercury-sealed stirrer and a reflux condenser there was placed 400 cc., 8 moles, of concd. sulfuric acid. To the cooled acid (10°) there was added, with stirring during 1.5 hours, 294 g., 2.0 moles, of compound I. Evolution of methane (identified by infrared absorption spectrum) was so vigorous as to cause extensive frothing of the reaction mixture. The β-trimethylsilylpropionic acid dissolves in the concd. sulfuric acid as rapidly as it is added. Reaction was completed by warming on the steam-bath for one hour. In a smaller run, measurement of the evolved methane gave a volume corresponding to 99% of the theoretical. The reaction mixture was cooled and poured onto cracked ice giving immediate formation of a

(8) D. W. Scott, THIS JOURNAL, **68**, 356 (1946).

(9) W. I. Patnode and D. F. Wilcock, *ibid.*, **68**, 361 (1946).

(10) M. J. Hunter, E. L. Warrick, J. F. Hyde and C. C. Currie, *ibid.*, **68**, 2284 (1946).

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

(12) L. H. Sommer and J. Rockett, *ibid.*, **73**, 5130 (1951).

(13) L. H. Sommer and N. S. Marans, *ibid.*, **72**, 1935 (1950).

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

(15) This compound was first prepared in this Laboratory by R. E. Van Strien.

(16) F. C. Frostick and C. R. Hauser, THIS JOURNAL, **71**, 1350 (1949).

white solid. The solid was filtered and dried under an infrared lamp. Recrystallization from hexane gave 265 g. of pure VII.

5,5,7,7-Tetramethyl-5,7-disila-6-oxa-undecanedioic Acid (VIII).—After two exploratory runs which gave low yields, below 50%, of the desired product, the following procedure was found to be satisfactory. Compound II, 5.23 g., 0.0326 mole, was placed in a 200-cc., three-necked round-bottomed flask, equipped with a dropping funnel, mercury-sealed stirrer and reflux condenser. Sulfuric acid, 20 cc., was placed in the funnel, the reaction flask immersed in an ice-bath, and then the concd. sulfuric acid was added slowly with stirring to II. After eight hours, the ice-bath was removed and the flask allowed to come to room temperature. The evolved methane corresponded to 95% of the theoretical amount.

The homogeneous solution of the reaction product was poured onto ice and the resulting mixture stirred and allowed to come to room temperature. A white solid separated and was filtered, washed and dried. An additional 0.5 g. was obtained by extracting the aqueous filtrate with ether. Recrystallization from heptane gave 4.10 g. of pure VII.

Formation of *n*-butyric acid in the above experiment was indicated by the characteristic odor of this substance. In a subsequent experiment during which the reactants were heated at 60° for five hours, *n*-butyric acid was isolated in 21% yield and identified by the *p*-phenylphenacyl derivative, m.p. 82°, lit. 82°.

1,7-Diamino-3,3,5,5-tetramethyl-3,5-disila-4-oxaheptane (IX).—In a 500-cc. round-bottomed flask was placed 15.4 g., 0.1 mole, of β-trimethylsilylethylamine hydrochloride.[12] The flask was fitted with a reflux condenser and 100 cc. of concentrated sulfuric acid was added to the amine hydrochloride. Gaseous hydrogen chloride was evolved along with methane as the salt gradually dissolved in the acid. The reaction mixture was then heated on the steam-bath for about one hour until methane evolution was complete. The product was then poured onto cracked ice and the resulting solution made strongly basic with sodium hydroxide solution. Steam distillation followed by acidification with concd. hydrochloric acid and evaporation of the solvent gave the dihydrochloride which was purified by recrystallization from alcohol–acetone.

To a solution of 24.2 g., 0.0826 mole, of the dihydrochloride in 50 cc. of dry methanol was added a solution of 11.3 g. of potassium hydroxide dissolved in 100 cc. of dry methanol. Filtration of the potassium chloride was followed by removal of methanol by distillation. Ether extraction of the resulting product followed by fractional distillation gave pure IX.

5,5,7,7-Tetramethyl-5,7-disila-6-oxa-2,10-undecanedione (X).—The reaction of 4-trimethylsilyl-2-butanone (IV) with concd. sulfuric acid was carried out in a manner similar to that employed for the synthesis of VII.

1,1,3,3,9,9,11,11-Octamethyl-1,3,9,11-tetrasila-2,10-dioxa-6,14-cyclohexadecanedione (XI).—In a 1-liter, 3-necked, round-bottomed flask fitted with a mercury-sealed stirrer, a dropping funnel and a condenser there was placed 475 g., 4.8 moles, of concd. sulfuric acid. There was then added to the water-cooled acid (18°), over a period of 2.5 hours, 138 g., 0.60 mole, of the ketone (V). The homogeneous reaction mixture was stirred an additional hour at room temperature and then one-half hour at 85° until evolution of methane ceased. The mixture was cooled and was then poured onto 1.5 kg. of ice. The viscous organic layer which separated was extracted three times with 400-cc. portions of ether, and the ether extract was washed with water, 10% $NaHCO_3$, and then water again and finally was dried over anhydrous sodium sulfate. The ether was rapidly distilled and the viscous material which remained, 134 g., was transferred to a Claisen flask and thermally rearranged at a pressure of 3–5 mm. The vapor temperature varied from 230–250° and the flask temperature from 370–385°. Thus there was obtained 112.5 g. of distillate which consisted of a mixture of solid and liquid. The solid was filtered and recrystallized from 95% ethanol to give 30.1 g. of XI.

2,2,4,4,10,10,12,12-Octamethyl-2,4,10,12-tetrasila-3,11-dioxa-7-tridecaneone (XII).—In a 1-liter, 3-necked, round-bottomed flask fitted with a mercury-sealed stirrer and a condenser and connected to a Gilman sulfuric acid trap there were placed 487 g., 3.0 moles, of hexamethyldisiloxane, 35 cc. of concd. sulfuric acid and 58.5 g. of the liquid polymer obtained as a by-product in the synthesis of XI. The mixture was stirred at room temperature for four hours, 100 cc. of water was added, and then the contents stirred for an additional ten minutes. The aqueous layer, 135 cc., was then separated and the organic layer washed twice with 100-cc. portions of water and then dried over anhydrous potassium carbonate. The excess hexamethyldisiloxane was distilled at atmospheric pressure and then fractional distillation under vacuum gave XII.

2,2,4,4,10,10,12,12-Octamethyl-2,4,10,12-tetrasila-3,11-dioxa-7-aminotridecane (XIII).—In a 200-cc. 3-necked, round-bottomed flask fitted with a mercury-sealed stirrer, a condenser and a dropping funnel there was placed 68 cc., 1.2 moles, of concd. sulfuric acid. Compound VI, 40 g., 0.174 mole, was added to the acid during two hours with stirring and cooling in an ice–water bath. Methane evolution occurred throughout the addition of the amine. The reaction mixture was then stirred at room temperature during the next 24 hours and finally heated at 85° for one-half hour. The reaction mixture was then poured onto cracked ice and a viscous liquid separated. This mixture was then made strongly alkaline with potassium hydroxide solution and extracted with four 250-cc. portions of ether. The ether extracts were combined and dried over a mixture of sodium sulfate and potassium carbonate. The ether was distilled and there remained 39 g. of a very viscous and sticky polymeric material. This material was then placed in a one-liter, 3-necked, round-bottomed flask fitted with a thermometer, a condenser and a mercury-sealed stirrer. To the polysiloxanepolyamine were added 200 cc. of isopropyl alcohol, a solution of 40 g. of KOH in 35 cc. of water, and 310 g., 2 moles, of hexamethyldisiloxane. The mixture was stirred at 78° during the next 22 hours. Then the mixture was cooled, washed three times with 150-cc. portions of saturated ammonium chloride solution and dried over anhydrous potassium carbonate. The excess hexamethyldisiloxane and remaining isopropyl alcohol were distilled at atmospheric pressure and then fractionation of the residual material under vacuum gave XIII.

STATE COLLEGE, PENNSYLVANIA