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THE PREPARATION OF SOME LOWER HOMOLOGS OF LINEAR METHYLPOLYSILANES

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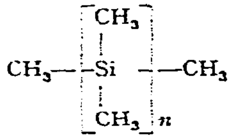
In a recent article Wilson and Smith[1] have reported the preparation of octamethyltrisilane and decamethyltetrasilane. We are now reporting some results of our own studies in the field of organopolysilanes.

Although the chemistry of organosilicon compounds has been the subject of considerable study, comparatively little is known about the organopolysilanes. Examples of methylpolysilanes of definite structure with the general formula (I) have been limited to hexamethyldisilane (I, $n = 2$) and only recently have the two next higher members, mentioned above, *i.e.*, octamethyltri- and decamethyltetrasilane been synthesized.



$$CH_3-\left[\begin{array}{c}CH_3\\ |\\ -Si-\\ |\\ CH_3\end{array}\right]_n-CH_3$$

(I)

We have prepared a homologous series of compounds of the formula (I) with $n = 2$–7, and have determined some of their physical properties.

The synthesis of these compounds has been accomplished by sodium condensation of appropriate chlorosilanes. Initially, we used methods involving the stepwise lengthening of the silylene chain and once the physical constants for individual compounds had been determined, we turned to a more direct method, *i.e.*, one starting with trimethylchlorosilane–dimethyldichlorosilane mixtures.

The results of the stepwise syntheses are summarized below.

$$2Me_3SiCl \xrightarrow{Na} \underset{(II)}{Me_3SiSiMe_3} \tag{1}$$

$$(II) \xrightarrow[2.\ NH_4Cl]{1.\ H_2SO_4} Me_3SiSiMe_2Cl + CH_4 \tag{2}$$

$$(II) \xrightarrow[2.\ NH_4Cl]{1.\ H_2SO_4} ClMe_2SiSiMe_2Cl + 2CH_4 \tag{3}$$

$$Me_3SiCl + Me_3SiSiMe_2Cl \xrightarrow{Na} \underset{(III)}{Me[SiMe_2]_3Me} + (II) \tag{4}$$

$$\text{(III)} \xrightarrow[2.\ NH_4Cl]{1.\ H_2SO_4} ClMe_2SiSiMe_2SiMe_2Cl \quad (5)$$

(IV)

$$2Me_3SiSiMe_2Cl \xrightarrow{Na} Me[SiMe_2]_4Me \quad (6)$$

(V)

$$2Me_3SiCl + \text{(IV)} \xrightarrow{Na} Me[SiMe_2]_5Me + \text{(II)} \quad (7)$$

(VI)

$$2Me_3SiSiMe_2Cl + Me_2SiCl_2 \xrightarrow{Na} \text{(V)} + \text{(VI)} \quad (8)$$

$$2Me_3SiSiMe_2Cl + ClMe_2SiSiMe_2Cl \xrightarrow{Na} Me[SiMe_2]_6Me + \text{(V)} \quad (9)$$

(VII)

$$2Me_3SiSiMe_2Cl + \text{(IV)} \xrightarrow{Na} Me[SiMe_2]_7Me + \text{(V)} \quad (10)$$

(VIII)

All these condensation reactions with metallic sodium were catalyzed by ethyl acetate.

Reactions (1), (4) and (7), in which trimethylchlorosilane was used, were carried out in a 500-ml stainless-steel autoclave. Reaction (1) represents the synthesis of hexamethyldisilane. Reactions (4) and (7), which describe the synthesis of octamethyltrisilane and dodecamethylpentasilane, respectively, were performed with a large excess of trimethylchlorosilane over stoichiometric quantities, in order to suppress self-coupling of the α,ω-dichloropolysilanes. Accordingly, in both cases large amounts of hexamethyldisilane (II) were also formed.

Reactions (6), (8), (9) and (10) were carried out in boiling toluene solutions. In the latter three reactions a large excess of chloropentamethyldisilane was used and, therefore, decamethyltetrasilane (V) was formed in large quantities, along with the pentasilane (VI), hexasilane (VII) or heptasilane (VIII).

Reactions (2) and (3) are related to the unambiguous synthesis of chloropentamethyl- and 1,2-dichlorotetramethyldisilane, respectively, and have already been reported[2]. As has been noted previously, the demethylation of hexamethyldisilane with concd. sulfuric acid proceeds in two distinct stages. If the reaction mixture is treated with ammonium chloride after only one molar equivalent of methane has been evolved, chloropentamethyldisilane is obtained (reaction 2). After evolution of two equivalents of methane, 1,2-dichlorotetramethyldisilane is obtained (reaction 3).

Reaction (5) represents the preparation of 1,3-dichlorohexamethyltrisilane (IV), analogous to reaction (3). In good contrast to the demethylation of hexamethyldisilane with sulfuric acid, that of octamethyltrisilane proceeded continuously until the main evolution of gas came to end (within a 5-h period or so at the reaction temperature of 35–37°). The assignment of structure (IV), and not its isomeric one, $Me_3SiSiMeClSiMe_2Cl$, to the obtained dichlorohexamethyltrisilane is tentative, but good evidence for the proposed structure (IV) is afforded by the fact that the dodecamethylpentasilane (VI) prepared from the dichlorotrisilane (IV) as one of the components of starting materials (reaction 7) was completely identical with the dodecamethylpentasilane prepared from dimethyldichlorosilane and chloropentamethyldisilane (reaction 8).

The yields of 1,3-dichlorohexamethyltrisilane (IV) in several runs fluctuated over the range of 32–45%. These relatively low yields are explained by the following facts. First, some cleavage of silicon–silicon bond took place during the reaction of compound (III) with sulfuric acid. Second, the action of ammonium chloride on the demethylation product was incomplete. In fact, 1,2-dichlorotetramethyldisilane was obtained in relatively large amounts in all runs and hexamethyltrisilanylene sulfate, $(\text{-Me}_2\text{SiSiMe}_2\text{SiMe}_2\text{OSO}_3\text{-})_n$, was isolated, in needle-like crystals, from the distillation residue.

The preparation of methylpolysilanes by the sodium condensation of trimethylchlorosilane and dimethyldichlorosilane was carried out in the presence of a small amount of ethyl acetate at 230–250° in a stainless-steel autoclave. Experiments at two different molar ratios of trimethylchlorosilane to dimethyldichlorosilane (3:1 and 2:1) were made. Discrete members, up to the heptasilane, of a homologous series of linear methylpolysilanes have easily been isolated by fractional distillation. No cyclic polysilane like $[\text{Me}_2\text{Si}]_6$ reported by Burkhard[3] was obtained. Relative yields of the individual compounds varied over a certain range with a change in the molar ratio of the two chlorosilanes employed.

EXPERIMENTAL

All temperatures reported here are uncorrected. Trimethylchlorosilane and dimethyldichlorosilane were supplied by the Tokyo-Shibaura Elec. Co., Ltd.

The silicon analyses were made in essentially the same manner as reported previously[2], but slight modification was necessary. In a 2 × 30 cm hard glass tube there was placed 5 to 6 ml of concd. sulfuric acid and *ca.* 0.5 ml of bromine. The tube was externally cooled by means of a dry ice-acetone bath. To the mixture was added a weighed sample (0.4 to 0.5 g) in a gelatin capsule and then the tube was sealed. Subsequent procedures were the same as reported previously.

Molecular weights were determined by the cryoscopic method in benzene.

(1) *Hexamethyldisilane (II)*

In a 500-ml stainless-steel autoclave there was placed 216 g (2 moles) of trimethylchlorosilane, 46 g (2 g-atoms) of sodium and 5 ml of ethyl acetate. The autoclave was electrically heated to 200–230° and shaken for a 45-h period. After cooling, the contents of the autoclave were taken out on a large Buchner funnel with aid of dry benzene and filtered under reduced pressure. The salt was washed with several 50-ml portions of dry benzene. The filtrate and washings were combined and submitted to fractional distillation through a modified Stedman column rated at about 20 theoretical plates to give (a) recovered trimethylchlorosilane, b.p. 57–58°, 51 g, and (b) crude hexamethyldisilane, slightly contaminated by hexamethyldisiloxane, b.p. 103–115°, 47 g. The residue weighed 22 g. Fraction (b) was treated with cold sulfuric acid so as to completely remove the siloxane, washed to neutral, dried over calcium chloride, and then fractionated to give highly pure hexamethyldisilane, 44 g, b.p. 112–113°, m.p. 13–13.5°, n_D^{20} 1.4230, d_4^{20} 0.7266. The yield was 43% on the basis of unrecovered trimethylchlorosilane. The reported[1] values are: b.p. 112.6–112.8°/750, m.p. 13°, n_D^{20} 1.4229, d_4^{20} 0.7257. Yields of some thirty runs conducted in essentially the same manner as above fluctuated over the range of 40–60%. In the absence of ethyl acetate yields were extremely poor; frequently, most of the sodium employed was recovered intact. In general, higher yields were obtained when a total volume of the reaction mixture was not very large in relation to the capacity of the autoclave. *Chloropentamethyldisilane* and *1,2-dichlorotetramethyldisilane* were prepared from hexamethyldisilane following the techniques previously reported[2].

(2) *Octamethyltrisilane (III)*

In the same autoclave as above 30 g (0.18 mole) of chloropentamethyldisilane, 200 g (1.85 moles) of trimethylchlorosilane and 46 g (2 g-atoms) of sodium were allowed to react in the presence of 5 ml of ethyl acetate at 200–230° for a 45-h period. After a similar treatment to that described in the preceding paragraph, there were obtained, by fractional distillation through 1.0 × 30 cm Stedman column, (a) 36 g of recovered trimethylchlorosilane, b.p. 57–58°; (b) 45 g of hexamethyldisilane, b.p. 112°, 41% yield on the basis of unrecovered trimethylchlorosilane; and (c) 27 g of octamethyltrisilane, b.p. 175–176°, 72% yield on the basis of chloropentamethyldisilane used. Fraction (c) was treated with cold sulfuric acid, washed to neutral, dried, and then redistilled to give 23 g of a highly pure product, b.p. 175–176°, m.p. —52°, n_D^{20} 1.4610 d_4^{20} 0.7757. (literature[1]: b.p. 112–112.5°/106, n_D^{20} 1.4612, d_4^{20} 0.7763).

(Found: C, 46.69; H, 11.72; Si, 41.00; mol. wt., 194. $C_8H_{24}Si_3$ calcd.: C, 46.97; H, 11.82; Si, 41.20%; mol. wt., 205.)

The yields of octamethyltrisilane in dozens of runs were 70–75%.

(3) *1,3-Dichlorohexamethyltrisilane (IV)*

In a similar apparatus to that described previously[2] for the preparation of chloropentamethyl- and 1,2-dichlorotetramethyldisilanes, a mixture of 94 g (0.46 mole) of octamethyltrisilane (III) and 480 g of concd. sulfuric acid was stirred vigorously at 35–37°. After a 5-h period 20.0 l of gas was evolved and further evolution of gas (0.7 l) occurred on additional 3-h stirring. To the resultant sulfuric acid solution there was added, in portions, 89 g (1.7 mole) of dry ammonium chloride with stirring and cooling. Separation of the organic layer (115 g) was followed by simple distillation (initially, at atmospheric pressure; later, at reduced pressure). There were obtained 98 g of a distillate and 16 g of a crystalline residue. Redistillation of the distillate through a 1.0 × 30 cm Stedman column gave: (a) trimethylchlorosilane, 10 g; (b) 1,2-dichlorotetramethyldisilane, b.p. 148–150°, n_D^{20} 1.4548, (reported[2] values: b.p. 148°, n_D^{20} 1.4545), % Cl 37.79 (calcd. 37.87), 24 g; and (c) 1,3-dichlorohexamethyltrisilane, b.p. 82–83°/11, n_D^{20} 1.4852, d_4^{20} 0.9865, MR_D 71.33 (calcd. 71.29), 45 g (40% yield).

(Found: Cl, 28.70. $C_6H_{18}Cl_2Si_3$ calcd.: Cl, 28.90%.)

The crystalline residue in the simple-distillation flask was recrystallized from a mixture of 25 ml of benzene and 75 ml of petroleum ether to give 8 g of white needle-like crystals of *hexamethyltrisilanylene sulfate*, $(-Me_2SiSiMe_2SiMe_2OSO_3-)_n$, m.p. 82–83°. It is very sensitive to moisture. (Found: Si, 30.89; neut. eq. 135. $C_6H_{18}O_4SSi_3$ calcd.: Si, 31.15%; neut. eq., 135.3.)

(4) *Decamethyltetrasilane (V)*

In a 300-ml three-necked flask equipped with a motor-driven stirrer, reflux condenser and thermometer there was placed 44 g (0.26 mole) of chloropentamethyldisilane and

15 g (0.65 g-atom) of sodium. The mixture was heated to 110° and vigorously stirred. After a 1-h period it became viscous, when 150 ml of dry toluene was added, and the reaction was continued for an additional 5 h at the refluxing temperature of toluene. The contents of the flask were filtered; the salt was washed with several small portions of dry toluene; and from the combined filtrate and washings toluene was removed by distillation. The residual oil was treated with cold sulfuric acid to eliminate any siloxane impurity, and then washed to neutral, dried over calcium chloride and finally submitted to fractional distillation through a 1.0 × 30 cm Stedman column to give 19 g (50% yield) of decamethyltetrasilane (V), b.p. 109°/15, m.p. –12°, n_D^{20} 1.4878, d_4^{20} 0.8073 (literature[1]: b.p. 112–113°/16, m.p. —14.5°, n_D^{20} 1.4877, d_4^{20} 0.8066). (Found: C, 46.69; H, 11.72; Si, 42.36; mol. wt., 271. $C_{10}H_{30}Si_4$ calcd.: C, 45.72; H, 11.51; Si, 42.77%; mol. wt., 263.)

Nineteen grams of a siloxane mixture were obtained on pouring the sulfuric layer, which had been separated from the tetrasilane, into water.

(5) *Dodecamethylpentasilane (VI)*

(*a*) *From chloropentamethyldisilane and dimethyldichlorosilane.* In a 500-ml three-necked flask equipped with a stirrer, reflux condenser and dropping funnel, a sodium (20 g, 0.87 g-atom) dispersion in toluene (300 ml) was prepared in a nitrogen atmosphere. To this there was added differentially a mixture of 83 g (0.5 mole) of chloropentamethyldisilane and 20 g (0.16 mole) of dimethyldichlorosilane at about 100° over a 6-h period. After completion of the addition, the mixture was heated to reflux with stirring for an additional 12 h. At this point a further 10 g (0.44 g-atom) of sodium was added, because the characteristic odor of chlorosilanes still remained. Heating and stirring was continued for an additional 24 h. Subsequently the mixture was worked up as described for the trisilane (III). Fractionation gave: (a) decamethyltetrasilane (V), 25 g (38% yield), b.p. 102–103°/13, n_D^{20} 1.4871; and (b) dodecamethylpentasilane (VI), 7 g (9% yield), b.p. 135–136°/13, m.p. –34°, n_D^{20} 1.5060, d_4^{20} 0.8329, n_D^{30} 1.5009, d_4^{30} 0.8235. The residue weighed 12 g. (Found: C, 44.90; H, 11.34; Si, 43.74; mol. wt., 328. $C_{12}H_{36}Si_5$ calcd.: C, 44.92; H, 11.31; Si, 43.76%; mol. wt., 321.)

(*b*) *From 1,3-dichlorohexamethyltrisilane and trimethylchlorosilane.* In the same autoclave as described above 26 g (0.11 mole) of 1,3-dichlorohexamethyltrisilane, 205 g (1.9 moles) of trimethylchlorosilane and 46 g (2 g-atoms) of sodium were allowed to react in the presence of 5 ml of ethyl acetate at 200–230° for a 45-h period. Afterwards, the reaction mixture was worked up by the technique described for the trisilane (III). Fractionation gave: (a) 30 g of recovered trimethylchlorosilane; (b) 40 g of slightly impure hexamethyldisilane, b.p. 110–113°; and 7 g of dodecamethylpentasilane, b.p. 131°/8, n_D^{20} 1.5060, yield 20%.

(6) *Tetradecamethylhexasilane (VII)*

A sodium dispersion was prepared from 29 g (1.2 g-atoms) of sodium and 120 ml of dry toluene. To this was added dropwise, over a 2.5-h period, a mixture of 19 g (0.1 mole) of 1,2-dichlorotetramethyldisilane and 83 g (0.5 mole) of chloropentamethyldisilane at the refluxing temperature of toluene. The reaction was continued for an additional 28 h. After a work-up as described above, the product was simple-distilled under reduced pressure (15 mm) to give 43 g of oil boiling at 50–175° and 10 g of residue. Redistillation through a 1.0 × 30 cm Stedman column gave: (a) decamethyltetrasilane (V), 20 g

(29% yield), b.p. 101°/12; and (b) tetradecamethylhexasilane (VII), 6 g (19 %), b.p. 165°/10, m.p. 28–29°, n_D^{30} 1.5139, d_4^{30} 0.8401. (Found: C, 44.39; H, 11.07; Si, 44.46; mol. wt., 368. $C_{14}H_{42}Si_6$ calcd.: C, 44.36; H, 11.17; Si, 44.46 %; mol. wt., 379.)

(7) *Hexadecamethylheptasilane (VIII)*

To a stirred sodium dispersion prepared from 45 g (1.9 g-atoms) of sodium and 400 ml of dry toluene was added dropwise over a 5-h period a mixture of 36 g (0.15 mole) of 1,3-dichlorohexamethyltrisilane and 166 g (1.0 mole) of chloropentamethyldisilane at the reflux temperature of toluene. The reaction was continued for an additional 36 h. After working up as described for the trisilane (III), 126 g of a toluene-free oil boiling up to 235°/26 was obtained by distillation. The residue weighed 15 g. The distillate was treated with cold concd. sulfuric acid, washed to neutral, dried over calcium chloride and then fractionated through a 1.0 × 30 cm Stedman column to give: (a) decamethyltetrasilane (V), 69 g (53% yield), b.p. 96°/8; and (b) hexadecamethylheptasilane (VIII), 11 g (17% yield), b.p. 194°/16, m.p. 19–20°, n_D^{30} 1.5264, d_4^{30} 0.8492. (Found: C, 44.51; H, 10.99; Si, 44.57; mol. wt., 432. $C_{15}H_{48}Si_7$ calcd.: C, 43.95; H, 11.07; Si, 44.97 %; mol. wt., 438.)

(8) *Preparation from trimethylchlorosilane and dimethyldichlorosilane*

(*a*) *Reaction of Me_3SiCl and Me_2SiCl_2 in 3:1 molar ratio.* In the same autoclave as above there was placed 160 g (1.48 moles) of trimethylchlorosilane, 60 g (0.47 mole) of dimethyldichlorosilane, 56 g (2.2 g-atoms) of sodium and 5 ml of ethyl acetate. The mixture was heated, with shaking, to 230–250° for a 50-h period. The contents of the autoclave were filtered and washed with dry benzene. Five runs were carried out under the same conditions. All the filtrates and benzene-washings were combined and fractionally distilled through a Stedman column rated at about 30 theoretical plates to give the following fractions: (a) recovered trimethylchlorosilane, b.p. 57–58°, 69 g; (b) hexamethyldisilane (II), b.p. 111–113°, 155 g; (c) intermediate fraction, b.p. 114–156°, 21 g; (d) octamethyltrisilane (III), b.p. 78–80°/35, 38 g; (e) intermediate fraction, b.p. 81–124°/35, 21 g; (f) decamethyltetrasilane (V), b.p. 125–129°/35, 25 g; (g) intermediate fraction, b.p. 130–165°/35, 22 g; (h) dodecamethylpentasilane (VI), b.p. 166–168°/35, 16 g; (i) intermediate fraction, boiling up to 116°/1, 13 g; (j) tetradecamethylhexasilane (VII), b.p. 117–119°/1, 10 g; (k) intermediate fraction, b.p. 119-125°/1, 3 g; and (l) hexadecamethylheptasilane (VIII), b.p. 153–155°/1, 6 g. Residue weighed 21 g. Fractions (b), (d), (f) and (h) were treated with cold sulfuric acid, washed to neutral, dried and redistilled through a 1.0 × 30 cm Stedman column to give, respectively, (II), b.p. 112–113°, n_D^{25} 1.4200, 142 g; (III), b.p. 176–177°, n_D^{25} 1.4572, 31 g; (V), b.p. 121°/35, n_D^{30} 1.4810, 19 g; and (VI), b.p. 162–163°/33, n_D^{30} 1.5010, 12 g. Fractions (j) and (l) had n_D^{30} 1.5141 and 1.5235, respectively. No further purification of these two was attempted.

(*b*) *Reaction of Me_3SiCl and Me_2SiCl_2 in 2:1 molar ratio.* In the manner as described in (a), 140 g (1.3 moles) of trimethylchlorosilane, 80 g (0.62 mole) of dimethyldichlorosilane and 60 g (2.6 g-atoms) of sodium were allowed to react in the presence of 5 ml of ethyl acetate at 250° for a 50-h period. Products from five runs were combined and fractionated to give 56 g of recovered trimethylchlorosilane, 78 g of hexamethyldisilane and residue. The residue was flash-distilled under vacuum to give 273 g of distillate and 50 g of higher-boiling residue. The distillate was treated with cold sulfuric acid to remove siloxane compounds and then fractionally distilled through a 1.0 × 30 cm Stedman column to give: (a) octamethyltrisilane (III), b.p. 176–177°, n_D^{20} 1.4615, 37 g; (b) decamethyltetrasilane (V), b.p. 127–128°/35, n_D^{20} 1.4880, 20 g; (c) dodecamethylpentasilane (VI), b.p. 117–118°/5, n_D^{30} 1.5001, 19 g; (d) tetradecamethylhexasilane (VII), b.p. 150–151°/7, n_D^{30} 1.5145, 12 g; and (e) slightly impure hexadecamethylheptasilane (VIII), b.p. 177–180°/7, n_D^{30} 1.5200, 7.5 g. Residue, 15 g. One hundred grams of siloxane mixture was obtained from the sulfuric acid washings.

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SUMMARY

Six lower homologs of linear methylpolysilanes of the formula $Me[Me_2Si]_nMe$ (I) have been prepared by sodium condensation of appropriate methylchlorosilanes. Two methods were employed for the preparations; one involved the stepwise lengthening of the silylene chain, and the other comprised the condensation of trimethylchlorosilane with dimethyldichlorosilane.

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