

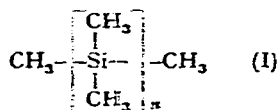
THE PREPARATION OF SEVERAL PERMETHYLATED LINEAR POLY-SILANES. FROM OCTASILANE TO DODECASILANE

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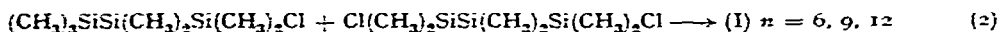
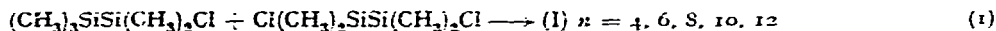
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Recently we have reported the preparation of six lower members of a homologous series of permethylated linear polysilanes with the formula (I), from hexamethyldisilane to hexadecamethylheptasilane, by the sodium condensation with appropriate chlorosilanes¹. The trisilane and tetrasilane derivatives have been prepared also by Wilson and Smith² and by Stolberg³, using sodium-potassium alloy.



As an extension of the previous work, we have now prepared an additional five higher homologs with the general formula described above: octadecamethyloctasilane (I, $n = 8$), eicosamethylnonasilane (I, $n = 9$), docosamethyldecasilane (I, $n = 10$), tetracosamethylundecasilane (I, $n = 11$) and hexacosamethyldodecasilane (I, $n = 12$). These compounds were synthesized by treating appropriate methylchlorosilanes with sodium-potassium alloy in a benzene-ligroin (b.p. 100–120°) or benzene-*n*-heptane mixture. In order to facilitate the separation of products by fractional distillation, the two chlorosilanes were so chosen that the polysilanes to be produced would differ by two or three silicon atoms from each other. Thus, the octasilane, decasilane and dodecasilane were obtained, along with the previously reported tetrasilane and hexasilane, from the reaction involving chloropentamethyldisilane and 1,2-dichlorotetramethyldisilane (eqn. 1); the nonasilane was obtained together with the hexasilane and dodecasilane from the reaction involving 1-chloroheptamethyltrisilane and 1,3-dichlorohexamethyltrisilane (eqn. 2); and the undecasilane was produced along with the pentasilane and octasilane from the reaction of chlorotrimethylsilane with 1,3-dichlorohexamethyltrisilane (eqn. 3).



These five new permethylated linear polysilanes are all white crystalline substances. The boiling and melting points, and analytical data of them are listed in Table I.

TABLE I

PHYSICAL CONSTANTS AND ANALYTICAL DATA FOR PERMETHYLATED LINEAR POLYSILANES

Compound	B.p. °C/mm	M.p. °C	% C Found (Calcd.)	% H Found (Calcd.)	% Si Found (Calcd.)	Mol. wt. Found (Calcd.)
$[\text{Si}(\text{CH}_3)_2]_3\text{CH}_3$	198/4	63	43.56 (43.65)	10.97 (10.99)	45.44 (45.37)	499 (495)
$[\text{Si}(\text{CH}_3)_2]_9\text{CH}_3$	231/4	90.5	43.51 (43.42)	10.86 (10.91)	45.20 (45.76)	578 (553)
$[\text{Si}(\text{CH}_3)_2]_{10}\text{CH}_3$	245/4	115	43.47 (43.20)	11.09 (10.88)	45.59 (45.92)	612 (612)
$[\text{Si}(\text{CH}_3)_2]_{11}\text{CH}_3$	257/3	130	43.34 (43.04)	10.89 (10.84)	46.09 (46.12)	644 (670)
$[\text{Si}(\text{CH}_3)_2]_{12}\text{CH}_3$	280/4	153	43.08 (42.90)	10.75 (10.80)	46.51 (46.30)	706 (728)

The melting points of the permethylated linear polysilanes (I) are plotted against the number of silicon atoms in Fig. 1. It is seen that the alternating effect of odd and even numbered structures on the melting point exists up to the octasilane, but, afterwards, the melting points display a regular progression as the molecular weight increases.

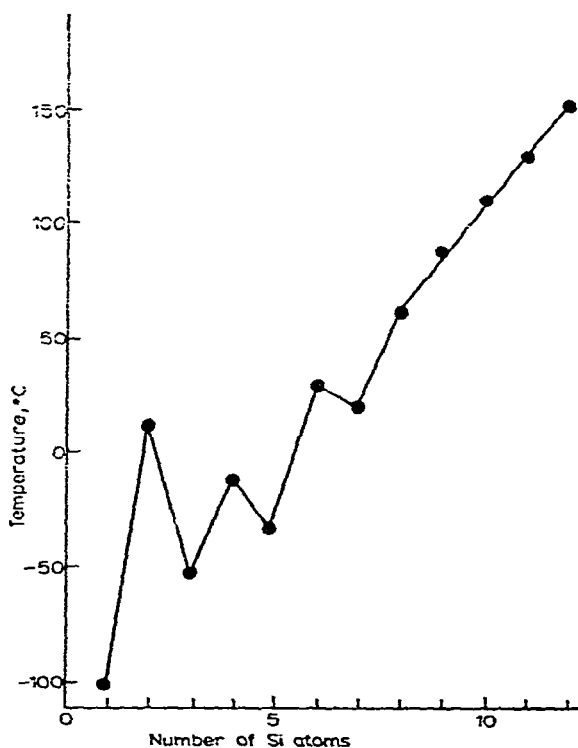


Fig. 1. Plots of melting points of permethylated linear polysilanes against number of silicon atoms.

Further studies of the permethylated linear polysilanes along various lines, including chemical reactions and physical chemistry, are in progress.

EXPERIMENTAL

All temperatures reported here are uncorrected. Molecular weights were determined by the cryoscopic method in benzene.

Chloropentamethyldisilane¹, 1,2-dichlorotetramethyldisilane¹, 1-chloroheptamethyltrisilane⁵, 1,3-dichlorohexamethyltrisilane^{1,5} were prepared as reported previously.

Octadecamethyloctasilane ($I, n = 8$), *docosamethyldecasilane* ($I, n = 10$) and *hexacosamethyldodecasilane* ($I, n = 12$)

An alloy was prepared from 7 g (0.3 g-atom) of sodium and 64.5 g (1.65 g-atom) of potassium in 260 ml of ligroin (boiling range 100–120°). To the stirred mixture was added dropwise a mixture of 100 g (0.6 mole) of chloropentamethyldisilane and 113 g (0.6 mole) of 1,2-dichlorotetramethyldisilane diluted with 300 ml of benzene under gentle reflux. After addition was completed, the reaction mixture was kept under reflux over a period of 40 h with stirring. At this point it was then decomposed by adding successively 200 ml of an ethanol-acetic acid mixture (1:1), 300 ml of 70% aqueous ethanol and water. The organic layer was separated from the water layer and an insoluble substance (4 g), washed, dried and distilled. The solvent-free reaction product (120 g) thus obtained was dissolved in petroleum ether and treated with concentrated sulfuric acid in the cold to remove any silicon-functional substances. The petroleum ether layer was separated, washed to neutral and fractionally distilled under reduced pressure in a column packed with glass helices rated at about 20 theoretical plates to give: (1) decamethyltetrasilane ($I, n = 4$), b.p. 79–80°/4 mm, 19 g; (2) tetradecamethylhexasilane ($I, n = 6$), b.p. 141–142°/4 mm, crystals, 11 g; (3) octadecamethyloctasilane ($I, n = 8$), b.p. 198–200°/4 mm, crystals, 6.5 g; (4) docosamethyldecasilane ($I, n = 10$), b.p. 245°/4 mm, crystals, 5 g; and (5) hexacosamethyldodecasilane ($I, n = 12$), b.p. 280°/4 mm, crystals, 3 g. Several recrystallizations of fractions (2), (3), (4) and (5) from ethanol gave, respectively, 7 g of the hexasilane, m.p. 29°; 4 g of the octasilane, m.p. 63°; 2.5 g of the decasilane, m.p. 115°; and 1.1 g of the dodecasilane, m.p. 153°.

To the sulfuric acid layer which had been separated from the petroleum layer was added 70 g of ammonium hydrogen fluoride in the cold to give 47 g of an organic layer. The latter was fractionally distilled to give the following three fluorosilanes: 9 g of 1,2-difluorotetramethyldisilane, b.p. 93°, n_D^{20} 1.3852 (lit.⁴ b.p. 92–93°, n_D^{20} 1.3837) (Found: F, 24.51. $C_4H_{12}F_2Si_2$ calcd.: F, 24.63%); 4 g of fluoropentamethyldisilane, b.p. 100°, n_D^{20} 1.4029 (lit.⁴ b.p. 102°, n_D^{20} 1.4031) (Found: F, 12.70. $C_5H_{15}FSi_2$ calcd.: F, 12.64%) and 5 g of 1,4-difluorooctamethyltetrasilane, b.p. 86°/14 mm, n_D^{20} 1.4621, d_4^{20} 0.9168, MR_D 81.16 (ca. cd.: 81.45). (Found: F, 14.15. $C_8H_{24}F_2Si_4$ calcd.: F, 14.04%.)

Eicosamethylnonasilane ($I, n = 9$)

To a stirred alloy prepared from 2.3 g (0.1 g-atom) of sodium and 22.4 g (0.57 g-atom) of potassium in 150 ml of ligroin was added a mixture of 1-chloroheptamethyltrisilane (70 g, 0.31 mole) and 1,3-dichlorohexamethyltrisilane (38 g, 0.16 mole) in

benzene (300 ml) under gentle reflux. The reaction mixture was then worked up in essentially the same manner as described above. There were obtained crude crystals of (1) 20 g of tetradecamethylhexasilane (I, $n = 6$), b.p. $138-139^{\circ}/4$ mm, (2) 10 g of eicosamethylnonasilane (I, $n = 9$), b.p. $231^{\circ}/4$ mm, and (3) 5.5 g of hexacosamethyldodecasilane (I, $n = 12$), b.p. $282^{\circ}/4$ mm. Repeated recrystallizations of fractions (1), (2) and (3) mostly from ethanol gave, respectively, pure samples of the hexasilane (m.p. 29° , 12.6 g), nonasilane (m.p. 90.5° , 4.7 g) and dodecasilane (m.p. 153° , 1.4 g).

Tetracosamethylundecasilane (I, $n = 11$)

A mixture of 48.7 g (0.45 mole) of chlorotrimethylsilane, 110 g (0.45 mole) of 1,3-dichlorohexamethyltrisilane in 300 ml of dry benzene was added to a stirred alloy of sodium (5.1 g, 0.22 g-atom) and potassium (49.1 g, 1.26 g-atom) in 150 ml of *n*-heptane. The reaction mixture was then worked up as above. Fractional distillation of the product after treatment with sulfuric acid gave the following three fractions as identified substances: (1) 26 g of dodecamethylpentasilane (I, $n = 5$), b.p. $111^{\circ}/3$ mm, n_D^{20} 1.5061, d_4^{20} 0.8296 (lit.¹ b.p. $131^{\circ}/8$ mm, n_D^{20} 1.5060, d_4^{20} 0.8329); (2) 9 g of crystalline octadecamethyloctasilane (I, $n = 8$), b.p. $194-198^{\circ}/3$ mm; and (3) 6 g of crystalline tetracosamethylundecasilane (I, $n = 11$), b.p. $257^{\circ}/3$ mm. Several recrystallizations from ethanol of fractions (2) and (3) gave, respectively, pure samples of the octasilane (m.p. $62.5-63^{\circ}$, 4.5 g) and the undecasilane (m.p. 130° , 1.0 g).

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SUMMARY

Five new permethylated linear polysilanes of the formula $\text{CH}_3[\text{Si}(\text{CH}_3)_2]_n\text{CH}_3$, where n is equal to 8, 9, 10, 11 and 12, have been prepared from the co-condensation of appropriate chlorosilanes using sodium-potassium alloy as condensing agent in a benzene-ligroin or benzene-*n*-heptane mixture. These compounds are all white crystalline substances. The melting points display a regular progression as the number of silicon atoms increases, in good contrast with those of the lower homologs of this series of compounds for which the melting points of odd and even numbered structures alternate.

REFERENCES

- 1 M. KUMADA AND M. ISHIKAWA, *J. Organometal. Chem.*, **1** (1963) 153.
- 2 G. R. WILSON AND A. G. SMITH, *J. Org. Chem.*, **26** (1961) 557.
- 3 U. G. STOLBERG, *Angew. Chem.*, **74** (1964) 696.
- 4 M. KUMADA, M. YAMAGUCHI, Y. YAMAMOTO, J. NAKAJIMA AND K. SHIINA, *J. Org. Chem.*, **21** (1956) 1264.
- 5 M. KUMADA, M. ISHIKAWA AND S. MAEDA, *J. Organometal. Chem.*, **2** (1964) 478.