PREPARATION OF SOME DERIVATIVES OF DISILANE, TRISILANE AND TETRASILANE

MAKOTO KUMADA, MITSUO ISHIKAWA AND SAJIRO MAEDA
Department of Synthetic Chemistry, Kyoto University, Kyoto (Japan)

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INTRODUCTION

During the course of other work it became necessary to prepare a number of methyl derivatives of disilane, trisilane and tetrasilane containing the silicon–hydrogen bond. We report here the synthesis of some of these and related compounds. After our investigation had been completed, Wiberg *et al.*[1] have briefly described a few similar compounds prepared by a method different from ours.

PREPARATIVE METHODS

Formulas and some physical properties for the hydrides prepared in this study are given in Table 1, and those for intermediate compounds in Table 2.

All of these hydrides except 1,1,2-trimethyldisilane (III) were prepared from the corresponding halides (mostly chlorides) by reduction with lithium aluminum hydride. Compound (III) was prepared from the corresponding ethoxide, because the latter can easily be prepared in a pure state as reported previously[2,3]. 1,2-Dimethyldisilane (IV) was also obtained from the ethoxide as well as from the chloride[2,3]. The three halides, chloropentamethyldisilane[2], 1,2-difluorotetramethyldisilane[2] and 1,3-dichlorohexamethyltrisilane*, which were employed for the synthesis of pentamethyldisilane (I), 1,1,2,2-tetramethyldisilane (II) and 1,1,2,2,3,3-hexamethyltrisilane (VII), respectively, were made available as reported previously. 1,1,2,2-Tetrachlorodimethyldisilane as a starting material for hydride (IV) was obtained in a reasonably pure state from the "disilane fraction[2]", from which 1,1,2-trichlorotrimethyldisilane, another main component of the fraction, had previously been removed through photochemical chlorination. The faster chlorination of 1,1,2-trichlorotrimethyldisilane relative to that of 1,1,2,2-tetrachlorodimethyldisilane is the basis of a method for purification of the latter compound. Other chlorides, 1-chloroheptamethyltrisilane (XIV), 2-chloroheptamethyltrisilane (XV) and 1,4-dichlorooctamethyltetrasilane (XVI) used for the synthesis of 1,1,2,2,3,3,3-heptamethyltrisilane (V), 1,1,1,2,3,3,3-heptamethyltrisilane (VI) and 1,1,2,2,3,3,4,4-octamethyltetrasilane (VIII), respectively, were prepared by cleavage reaction of the corresponding phenyl-substituted methylpolysilanes by hydrogen chloride in the presence of anhydrous

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* Previously[4], we assigned the 1,3-dichloro structure to the dichlorohexamethyltrisilane on the basis of the observation that the dodecamethylpentasilane prepared from it was of linear structure. Unequivocal evidence for the proposed structure has now been afforded from the NMR spectra of this compound and the corresponding hydride (VII). See EXPERIMENTAL.

TABLE 1

PHYSICAL PROPERTIES OF METHYLPOLYSILANES WITH Si–H BONDS

No.	Formula	B.P. °C/mm	n_D^{20}	d_4^{20}
(I)	$H(CH_3)_2SiSi(CH_3)_3$	97	1.4300	0.7331
(II)	$H(CH_3)_2SiSi(CH_3)_2H^a$	86–87	1.4290	0.7202
(III)	$H_2(CH_3)SiSi(CH_3)_2H$	68–69	1.4296	0.7101
(IV)	$H_2(CH_3)SiSi(CH_3)H_2$	49	1.4331	0.7008
(V)	$H(CH_3)_2SiSi(CH_3)_2Si(CH_3)_3$	61/22	1.4637	0.7729
(VI)	$(CH_3)_3SiSi(CH_3)HSi(CH_3)_3$	59/21	1.4616	0.7710
(VII)	$H(CH_3)_2SiSi(CH_3)_2Si(CH_3)_2H^a$	54/22	1.4658	0.7716
(VIII)	$H(CH_3)_2Si[Si(CH_3)_2]_2Si(CH_3)_2H$	74/19	1.4922	0.8056

[a] These compounds have recently been obtained also by Wiberg *et al.*[1] through different reactions.

TABLE 2

PHYSICAL PROPERTIES OF SOME NEW ORGANOPOLYSILANES AS INTERMEDIATES FOR PREPARATION OF HYDRIDES

No.	Formula	B.P. °C/mm	n_D^{20}	d_4^{20}
(IX)	$C_6H_5(CH_3)_2SiSi(CH_3)_2OC_2H_5$	121/20	1.5030	0.9199
(X)	$C_6H_5(CH_3)_2SiSi(CH_3)_2Cl$	119/20	1.5225	0.9845
(XI)	$C_6H_5(CH_3)_2SiSi(CH_3)_2Si(CH_3)_3$	142/23	1.5204	0.8769
(XII)	$(CH_3)_3SiSi(CH_3)(C_6H_5)Si(CH_3)_3$	133/19	1.5236	0.8683
(XIII)	$C_6H_5(CH_3)_2Si[Si(CH_3)_2]_2Si(CH_3)_2C_6H_5$	59.5–60.0[a]		
(XIV)	$Cl(CH_3)_2SiSi(CH_3)_2Si(CH_3)_3$	84/21	1.4734	0.8802
(XV)	$(CH_3)_3SiSi(CH_3)(Cl)Si(CH_3)_3$	80.5/20	1.4727	0.8766
(XVI)	$Cl(CH_3)_2Si[Si(CH_3)_2]_2Si(CH_3)_2Cl$	98/5	1.5060	0.9736

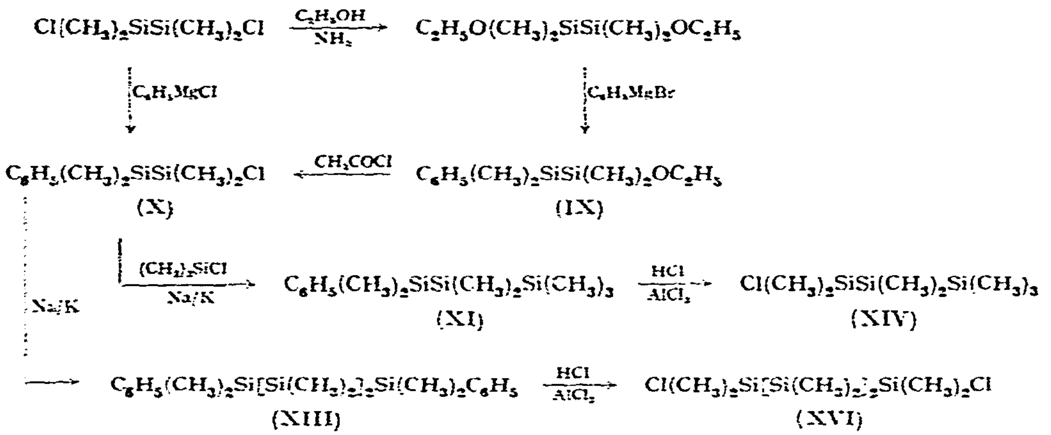
[a] Melting point.

aluminum chloride. It has been established that the chlorodephenylation reaction affords a very convenient method generally applicable to the preparation of methylchloropolysilanes, except in those instances where a silicon atom in the phenylmethylpolysilane bears more than one phenyl group.

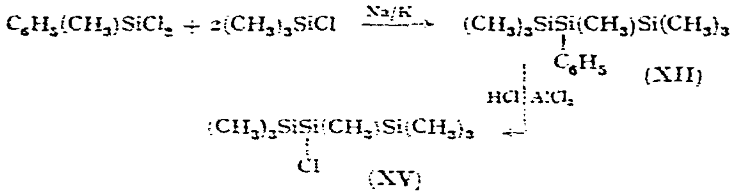
1-Phenylheptamethyltrisilane (XI), 2-phenylheptamethyltrisilane (XII) and 1,4-diphenyloctamethyltetrasilane (XIII) were synthesized by condensation of the appropriate chlorosilanes with sodium–potassium alloy. 1-Chloro-2-phenyltetramethyldisilane (X), an intermediate for compounds (XI) and (XIII), was first prepared in three steps from 1,2-dichlorotetramethyldisilane (namely, ethanolysis to 1,2-diethoxytetramethyldisilane, partial phenylation to 1-ethoxy-2-phenyltetramethyldisilane and ethoxyl-chlorine exchange with acetyl chloride) because we feared that the desired product would not be obtained in high yield by direct partial phenylation because of complexities associated with the partial alkylation of chlorosilanes with organomagnesium bromides. Later, however, we found that the direct partial phenylation of the 1,2-dichlorodisilane with phenylmagnesium chloride in tetrahydrofuran took place very satisfactorily to give compound (X) in much higher overall yield.

Reaction Charts 1 and 2 show the reactions employed for synthesis of chlorides (XIV) and (XVI), and (XV), respectively.

REACTION CHART 1



REACTION CHART 2



EXPERIMENTAL

Boiling points reported here are uncorrected. All procedures using sodium–potassium alloy and also lithium aluminum hydride were performed in an oxygen-free, dry nitrogen atmosphere.

Chloropentamethyldisilane, 1,2-difluorotetramethyldisilane and 1,3-dichlorohexamethyltrisilane were prepared from hexamethyldisilane or octamethyltrisilane by demethylation with concentrated sulfuric acid, followed by treatment with ammonium chloride or fluoride, as reported previously[2,3]. Unequivocal evidence for structure of 1,3-dichlorohexamethyltrisilane has been afforded by its NMR spectrum. Only two signals were obtained: one at 0.25 ppm in δ value, assignable to the internal $-Si(CH_3)_2-$ and the other at 0.53 ppm, assignable to the two identical terminal $Cl(CH_3)_2Si-$ groups.

(1) *1-Ethoxy-2-phenyltetramethyldisilane (IX)*

To a stirred and externally cooled ether solution containing 0.45 mole of phenylmagnesium bromide was added over a 5-min period 90 g (0.43 mole) of 1,2-diethoxytetramethyldisilane[3] (which was easily obtained from ethanolysis of 1,2-dichlorotetramethyldisilane) dissolved in 100 ml of ether. After stirring for an additional 15 min in the cold, the reaction mixture was heated to reflux over a 15-h period. The organic layer was separated from the magnesium salt and distilled to give 70 g (66 % yield) of compound (IX). (Found: C, 60.15; H, 9.57; Si, 23.56. $C_{12}H_{22}OSi_2$ calcd.: C, 60.39; H, 9.30; Si, 23.55 %.)

(2) *1-Chloro-2-phenyltetramethyldisilane* (*X*)

(*a*) *Reaction of* (*IX*) *with acetyl chloride.* A mixture of 65 g (0.27 mole) of compound (IX) with 320 g (4.2 mole) of acetyl chloride was heated to reflux over a 7-h period. Fractional distillation gave 56 g (89 % yield) of compound (X). (Found: Cl, 15.48. $C_{10}H_{17}ClSi_2$ calcd.: Cl, 15.49 %.)

(*b*) *Partial phenylation of 1,2-dichlorotetramethyldisilane with phenylmagnesium chloride.* To 96 g (0.5 mole) of 1,2-dichlorotetramethyldisilane was added a tetrahydrofuran solution containing about 0.5 mole of phenylmagnesium chloride with stirring and external cooling. The mixture was heated to reflux for 4 h, and then the solvent was distilled off. The product was extracted with dry ether from the residual mass and submitted to fractional distillation to give 82 g (70 % yield) of compound (X), b.p. 103° at 9 mm, n_D^{20} 1.5230, d_4^{20} 0.9853. (Found: Cl, 15.30. $C_{10}H_{17}ClSi_2$ calcd.: Cl, 15.49 %.)

(3) *1-Phenylheptamethyltrisilane* (*XI*)

An alloy was prepared from 90 g (2.3 g-atom) of potassium and 10 g (0.43 g-atom) of sodium in 400 ml of xylene. To the stirred mixture was added dropwise a solution of 52 g (0.23 mole) of compound (X) and 216 g (2 mole) of $(CH_3)_3SiCl$ in 200 ml of xylene at 80° over a 3-h period. After addition was completed the reaction mixture was heated at 110–130° with continuous stirring for an additional 15 h. The organic layer was decanted and the salt was washed with five portions of petroleum ether. They were combined and fractionally distilled to give 78 g of hexamethyldisilane and 30 g (48 % yield) of 1-phenylheptamethyltrisilane. (Found: C, 59.05; H, 10.55; Si, 30.89. $C_{13}H_{26}Si_3$ calcd.: C, 58.56; H, 9.83; Si, 31.61 %.) Residue, 21 g.

(4) *2-Phenylheptamethyltrisilane* (*XII*)

To an alloy prepared from 100 g (2.6 g-atoms) of potassium and 10 g (0.4 g-atom) of sodium in 400 ml of xylene was added a mixture of 51 g (0.27 mole) of $C_6H_5(CH_3)SiCl_2$ with 216 g (2 moles) of $(CH_3)_3SiCl$ in 200 ml of xylene. After 20-h reaction at 110–130°, the mixture was decomposed by adding 400 ml of an ethanol–acetic acid mixture (1:1) and then water. The organic layer was separated, washed, dried and fractionally distilled to give 69 g of hexamethyldisilane and 23 g (32 % yield) of compound (XII). (Found: C, 58.55; H, 10.25; Si, 31.80. $C_{13}H_{26}Si_3$ calcd.: C, 58.56; H, 9.83; Si, 31.61 %.)

(5) *1,4-Diphenyloctamethyltetrasilane* (*XIII*)

Compound (X), 83 g (0.36 mole), was allowed to react with a dispersed alloy, prepared from 1.5 g (0.065 g-atom) of sodium and 14.5 g (0.37 g-atom) of potassium in 150 ml of xylene, at 80° over a 23-h period. At this point the reaction mixture was worked up in a similar manner to that described above. Distillation gave 39 g (56 % yield) of a substance which boiled at about 195° under 3 mm and solidified in the condenser.

Recrystallizations twice from 95 % aqueous ethanol gave white needle-like crystals. (Found: C, 62.17; H, 8.71; Si, 29.28. $C_{20}H_{34}Si_4$ calcd.: C, 62.07; H, 8.86; Si, 29.05 %.)

(6) *1-Chloroheptamethyltrisilane* (*XIV*)

In a 1-l three-necked flask, provided with an air-tight stirrer, a gas-inlet tube the stem of which extended into the liquid nearly to the bottom of the flask, and a reflux condenser was placed a mixture of 27 g (0.1 mole) of compound (XI), 2 g of anhydrous aluminum chloride and 500 ml of chloroform. Into the stirred mixture was passed gradually dry hydrogen chloride at room temperature over a 16-h period. At this point the contents of the flask were flash-distilled (initially at ordinary pressure, later *in vacuo*). Fractional distillation of the distillate gave 12 g (53 % yield) of compound (XIV). (Found: Cl, 15.70. $C_7H_{21}ClSi_3$ calcd.: Cl, 15.76 %.)

(7) *2-Chloroheptamethyltrisilane* (*XV*)

This compound was prepared from compound (XII) is essentially the same manner as above in 76 % yield. (Found: Cl, 15.66. $C_7H_{21}ClSi_3$: calcd.: Cl, 15.76 %.)

(8) *1,4-Dichlorooctamethyltetrasilane* (*XVI*)

In quite a similar manner to that described above this compound was obtained from compound (XIII) in 76 % yield. (Found: Cl, 23.18. $C_8H_{24}Cl_2Si_4$ calcd.: Cl, 23.36 %.)

(9) *Pentamethyldisilane* (*I*)

To a stirred suspension of 3.5 g (0.09 mole) of lithium aluminum hydride in 150 ml of dry ether was added dropwise 28 g (0.17 mole) of chloropentamethyldisilane dissolved in 50 ml of ether. During the addition, gentle reflux of ether was observed to take place. The reaction mixture was then heated to reflux for 12 h to complete the reaction. The contents of the flask were placed in a Soxhlet apparatus in which the product was separated from inorganic salt. The ether extract thus obtained was fractionally distilled to give 21 g (94 % yield) of the hydride (I). (Found: C, 45.80; H, 12.51; Si, 42.28. $C_5H_{16}Si_2$ calcd.: C, 45.37; H, 12.19; Si, 42.45 %.)

(10) *1,1,2,2-Tetramethyldisilane* (*II*)

To 6 g (0.16 mole) of lithium aluminum hydride in 200 ml of di-*n*-butyl ether was added differentially at room temperature 31 g (0.2 mole) of 1,2-difluorotetramethyldisilane over a 30-min period. The reaction took place so vigorously that it was necessary to cool intermittently the flask with ice water. After addition was completed, the mixture was heated to 100–120° for 4 h and then submitted to distillation under reduced pressure. Redistillation of the distillate gave 20 g (85 % yield) of compound (II). (Found: C, 41.07; H, 11.86; Si, 47.16. $C_4H_{14}Si_2$ calcd.: C, 40.60; H, 11.92; Si, 47.48 %.)

(11) *1,1,2-Trimethyldisilane* (*III*)

This hydride was prepared in essentially the same manner as compound (II) except that 40 g (0.17 mole) of 1,1,2-triethoxytrimethyldisilane[2,3] was allowed to react with 12 g (0.32 mole) of lithium aluminum hydride in 200 ml of di-*n*-butyl ether at 110–120° over a 15-h period. Fractionation gave 9 g (51 % yield) of compound (III). (Found: Si, 53.55. $C_3H_{12}Si_2$ calcd.: Si, 53.86 %.)

(12) *1,2-Dimethyldisilane (IV)*

(*a*) *From the chloride.* To 16 g (0.42 mole) of lithium aluminum hydride suspended in 250 ml of di-*n*-butyl ether was added 50 g (0.22 mole) of 1,1,2,2-tetrachlorodimethyldisilane [which was obtained by fractional distillation from the "disilane fraction[2]", and had b.p. 157–158°, chlorine contant 62.19 (calcd. 62.28 %)]. After 5-h reaction under reflux the mixture was fractionally distilled to give 9 g (47 % yield) of 1,2-dimethyldisilane (found: Si, 62.40. $C_2H_{10}Si_2$ calcd.: Si, 62.23 %) along with 10 g of unidentified substance which boiled below room temperature.

(*b*) *From the ethoxide.* The procedure was the same as that for hydride (III) except that 35 g (0.13 mole) of 1,1,2,2-tetraethoxydimethyldisilane[2,3] was allowed to react with 8 g (0.21 mole) of lithium aluminum hydride in 250 ml of di-*n*-butyl ether over a 10-h period. Fractionation gave 4 g (35 % yield) of the hydride (IV).

(13) *1,1,2,2,3,3,3-Heptamethyltrisilane (V)*

In accordance with the procedure for preparation of compound (I), 10 g (0.04 mole) of $Cl(CH_3)_2SiSi(CH_3)_2Si(CH_3)_3$ and 1.5 g (0.04 mole) of $LiAlH_4$ were allowed to react in ether solution over a 15-h period. The product weighed 5.5 g (72 % yield). (Found: C, 44.32; H, 12.02; Si, 44.02. $C_7H_{22}Si_3$ calcd.: C, 44.13; H, 11.64; Si, 44.23 %.)

(14) *1,1,1,2,3,3,3-Heptamethyltrisilane (VI)*

The reaction of 26 g (0.12 mole) of $(CH_3)_3SiSi(CH_3)(Cl)Si(CH_3)_3$ with 14 g (0.11 mole) of $LiAlH_4$ in 150 ml of ether gave 16 g (70 % yield) of the product. (Found: C, 44.36; H, 11.61; Si, 44.09. $C_7H_{22}Si_3$ calcd.: C, 44.13; H, 11.64; Si, 44.23 %.)

(15) *1,1,2,2,3,3-Hexamethyltrisilane (VII)*

This compound was obtained from the reaction of 20 g (0.08 mole) of $Cl(CH_3)_2SiSi(CH_3)_2Si(CH_3)_2Cl$ with 5 g (0.13 mole) of $LiAlH_4$ in 120 ml of ether, in 54 % yield (7.5 g). (Found: C, 40.43; H, 11.56; Si, 47.52. $C_6H_{20}Si_3$ calcd.: C, 40.83; H, 11.42; Si, 47.75 %.) The NMR spectrum of this hydride is reproduced in Fig. 1. Both the septet (a) and doublet (b) signals at 3.73 and 0.17 in δ value, respectively, are assignable to each of the two identical terminal $H(CH_3)_2Si-$ structures, and the singlet peak (c) at 0.17 is assignable to the internal $-(CH_3)_2Si-$ structure. The areas of (a), (b) and (c) are approximately in the ratio 1:6:3, as expected.

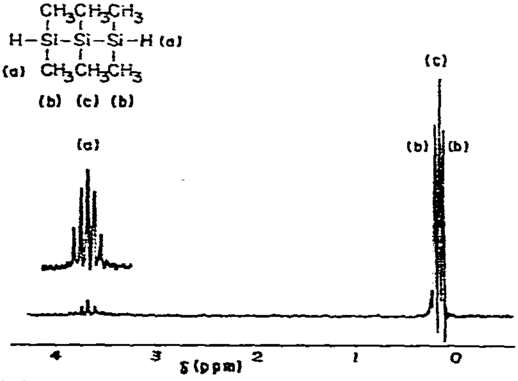


Fig. 1. NMR spectrum of 1,1,2,2,3,3-hexamethyltrisilane (VII).

(16) *1,1,2,2,3,3,4,4-Octamethyltetrasilane* (*VIII*)

In accordance with the procedure for preparation of (I), this hydride was obtained in 72% yield from the reaction of 1,4-dichlorooctamethyltetrasilane (14 g, 0.04 mole) with $LiAlH_4$ (3.5 g, 0.092 mole) in 150 ml of ether. (Found: Si, 47.90. $C_8H_{26}Si_4$ calcd.: Si, 47.88%.)

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SUMMARY

Eight methyl derivatives of disilane, trisilane and tetrasilane, containing the silicon-hydrogen bond, have been prepared from the reaction of appropriate halogen- or ethoxyl-substituted polysilanes with lithium aluminum hydride. Preparation of several new organopolysilanes as intermediates for synthesis of these hydrides is also described.

REFERENCES

1 E. Wiberg, O. Stecher, H. J. Andrascheck, L. Kreuzbichler and E. Staude, *Angew. Chem.*, 75 (1963) 516.
2 M. Kumada, M. Yamaguchi, Y. Yamamoto, J. Nakajima and K. Shiina, *J. Org. Chem.*, 21 (1956) 1264.
3 M. Kumada, M. Ishikawa and B. Murai, *Kogyo Kagaku Zasshi*, 66 (1963) 637.
4 M. Kumada and M. Ishikawa, *J. Organometal. Chem.*, 1 (1963) 153.