INTRAMOLECULAR REARRANGEMENT, WITH SULFURIC ACID, OF ISOPROPENYL DERIVATIVES OF DISILANE AND TRISILANE

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INTRODUCTION

It has been reported by Sommer and Evans[1] that isopropenyltrimethylsilane undergoes an intramolecular rearrangement with concentrated sulfuric acid through an α-carbonium ion intermediate to produce a *tert*-butylsilane derivative: they obtained, on hydrolysis of the reaction mixture, crystals of *tert*-butyldimethylsilanol hemihydrate.

Previous studies from this Laboratory have demonstrated that (chloromethyl)-pentamethyldisilane undergoes intramolecular rearrangement to disilylmethane derivatives with an electrophilic reagent (aluminum chloride)[2] and also with a nucleophilic one (sodium ethoxide in ethyl alcohol)[3]. The phenomenon of intramolecular rearrangement of silyl from silicon to carbon in organodisilanes has also been observed with hexamethyldisilane, which readily undergoes rearrangement at 600° to give trimethyl(dimethylsilylmethyl)silane[4].

As an extension of the previous work we have now carried out the synthesis of isopropenylpentamethyldisilane (I), 1,2-diisopropenyltetramethyldisilane (II) and 1,3-diisopropenylhexamethyltrisilane (III), and their reactions with concentrated sulfuric acid.

RESULTS AND DISCUSSION

All compounds reported here are listed with some of their physical constants in Table 1.

Synthesis

Compound (I), (II) and (III) were prepared by the reactions of isopropenylmagnesium bromide with chloropentamethyldisilane, 1,2-dichlorotetramethyldisilane and 1,3-dichlorohexamethyltrisilane, respectively, in tetrahydrofuran. Yields were higher than 80% in all cases.

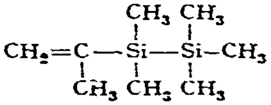
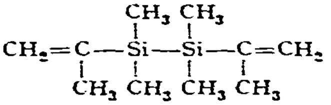
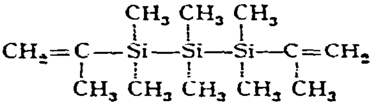
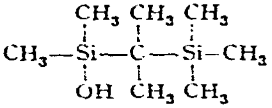
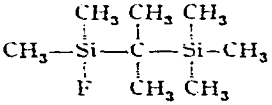
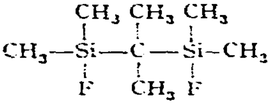
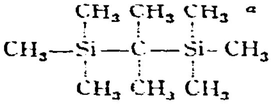
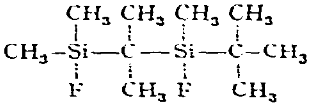
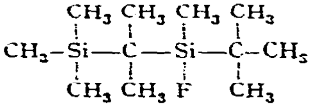
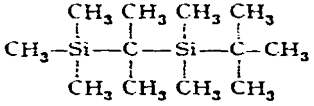
$$Cl(CH_3)_2SiSi(CH_3)_3 \xrightarrow{CH_2=C(CH_3)MgBr} CH_2=C(CH_3)(CH_3)_2SiSi(CH_3)_3 \quad (I)$$

$$Cl(CH_3)_2SiSi(CH_3)_2Cl \xrightarrow{2CH_2=C(CH_3)MgBr} CH_2=C(CH_3)(CH_3)_2SiSi(CH_3)_2C(CH_3)=CH_2 \quad (II)$$

$$Cl(CH_3)_2SiSi(CH_3)_2Si(CH_3)_2Cl \xrightarrow{2CH_2=C(CH_3)MgBr} CH_2=C(CH_3)(CH_3)_2SiSi(CH_3)_2Si(CH_3)_2C(CH_3)=CH_2 \quad (III)$$

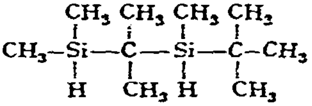
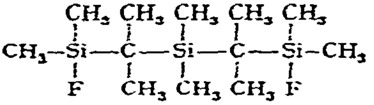
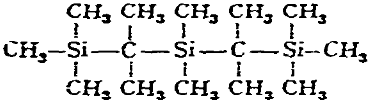
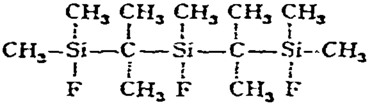
TABLE 1

SOME PHYSICAL CONSTANTS FOR ISOPROPENYL DERIVATIVES OF DISILANE AND TRISILANE, AND THEIR REARRANGEMENT PRODUCTS

No.	*Compound*	*B.p.* °*C/mm*	n_D^{20}	d_4^{20}
(I)	 $CH_2{=}C(CH_3){-}Si(CH_3)_2{-}Si(CH_3)_3$	152	1.4517	0.7720
(II)	 $CH_2{=}C(CH_3){-}Si(CH_3)_2{-}Si(CH_3)_2{-}C(CH_3){=}CH_2$	97–98/32	1.4750	0.8081
(III)	 $CH_2{=}C(CH_3){-}Si(CH_3)_2{-}Si(CH_3)_2{-}Si(CH_3)_2{-}C(CH_3){=}CH_2$	110/15	1.4983	0.8340
(IV)	 $CH_3{-}Si(CH_3)(OH){-}C(CH_3)_2{-}Si(CH_3)_2{-}CH_3$	90/23	1.4598	0.8896
(V)	 $CH_3{-}Si(CH_3)(F){-}C(CH_3)_2{-}Si(CH_3)_2{-}CH_3$	160	1.4256	0.8690
(VI)	 $CH_3{-}Si(CH_3)(F){-}C(CH_3)_2{-}Si(CH_3)(F){-}CH_3$	151	1.4080	0.9421
(VII)	 $CH_3{-}Si(CH_3)_2{-}C(CH_3)_2{-}Si(CH_3)_2{-}CH_3$ [a]	178	1.4459	0.8004
(VIII)	 $CH_3{-}Si(CH_3)(F){-}C(CH_3)_2{-}Si(CH_3)(F){-}C(CH_3)_2{-}CH_3$	99/30	1.4340	0.9476
(IX)	 $CH_3{-}Si(CH_3)_2{-}C(CH_3)_2{-}Si(CH_3)(F){-}C(CH_3)_2{-}CH_3$	91/13	1.4507	0.8836
(X)	 $CH_3{-}Si(CH_3)_2{-}C(CH_3)_2{-}Si(CH_3)_2{-}C(CH_3)_2{-}CH_3$	118/21	1.4722	0.8412

(continued on page 138)

TABLE I *(continued)*

No.	*Compound*	*B.p. °C/mm*	n_D^{20}	d_4^{20}
(XI)	 $CH_3-\underset{H}{\overset{CH_3}{Si}}-\underset{CH_3}{\overset{CH_3}{C}}-\underset{H}{\overset{CH_3}{Si}}-\underset{CH_3}{\overset{CH_3}{C}}-CH_3$	100/32	1.4610	0.8120
(XII)	 $CH_3-\underset{F}{\overset{CH_3}{Si}}-\underset{CH_3}{\overset{CH_3}{C}}-\underset{CH_3}{\overset{CH_3}{Si}}-\underset{CH_3}{\overset{CH_3}{C}}-\underset{F}{\overset{CH_3}{Si}}-CH_3$	125/13	1.4593	0.9713
(XIII)	 $CH_3-\underset{CH_3}{\overset{CH_3}{Si}}-\underset{CH_3}{\overset{CH_3}{C}}-\underset{CH_3}{\overset{CH_3}{Si}}-\underset{CH_3}{\overset{CH_3}{C}}-\underset{CH_3}{\overset{CH_3}{Si}}-CH_3$	149/13	1.4870	0.8733
(XIV)	 $CH_3-\underset{F}{\overset{CH_3}{Si}}-\underset{CH_3}{\overset{CH_3}{C}}-\underset{F}{\overset{CH_3}{Si}}-\underset{CH_3}{\overset{CH_3}{C}}-\underset{F}{\overset{CH_3}{Si}}-CH_3$	115.5/13	1.4410	1.0179

[a] Reported also by Fritz and Grobe[6].

Reaction of (I)

Compound (I) was found to react with concentrated sulfuric acid in the cold to give the expected rearrangement products with the $SiC(CH_3)_2Si$ grouping. Thus, hydrolysis of the reaction mixture gave 2,3,3,4,4-pentamethyl-2-hydroxy-2,4-disilapentane (IV) as a viscous oil with a camphor-like odor in 68 % yield, while treatment with ammonium hydrogen fluoride yielded 2,3,3,4,4-pentamethyl-2-fluoro-2,4-disilapentane (V) along with 2,3,3,4-tetramethyl-2,4-difluoro-2,4-disilapentane (VI). None of these rearrangement products react with bromine, even on slight warming, thus indicating complete disappearance of the silicon–silicon linkage and carbon–carbon double bond present in the starting compound.

$$(I) + H_2SO_4 \longrightarrow [(HSO_4)(CH_3)_2SiC(CH_3)_2Si(CH_3)_3]$$

$$\xrightarrow{H_2O} HO(CH_3)_2SiC(CH_3)_2Si(CH_3)_3 \quad (IV)$$

$$\xrightarrow{NH_4F\cdot HF} \underset{(V)}{F(CH_3)_2SiC(CH_3)_2Si(CH_3)_3} + \underset{(VI)}{F(CH_3)_2SiC(CH_3)_2Si(CH_3)_2F}$$

The relative yields of (V) and (VI) depended upon the reaction temperature and the quantity of concentrated sulfuric acid; at a lower temperature and with a smaller quantity of the acid, (V) was obtained in a higher yield. Undoubtedly the formation of (VI) is the result of a well-known demethylation reaction of trimethylsilyl compounds with concentrated sulfuric acid[5].

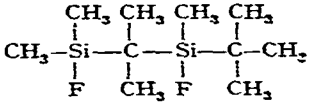
A mixture of compound (V) and (VI) was treated with methylmagnesium bromide to give 2,2,3,3,4,4-hexamethyl-2,4-disilapentane (VII).

$$(V) + (VI) \xrightarrow{CH_3MgBr} (CH_3)_3SiC(CH_3)_2Si(CH_3)_3 \quad (VII)$$

After this investigation had been completed, compound (VII) was reported by Fritz and Grobe[6], who obtained it as one of the reaction products of $Cl_3SiCCl_2SiCl_3$ with methyllithium and with methylmagnesium chloride.

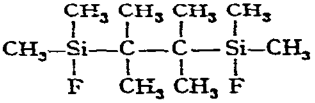
Reaction of (II)

The reaction of compound (II) with concentrated sulfuric acid followed by treatment with ammonium hydrogen fluoride gave, on fractional distillation, two compounds: (VI) in 22 % yield and 2,3,3,4,5,5-hexamethyl-2,4-difluoro-2,4-disilahexane (VIII) in 55.7 % yield.



$$CH_3-\underset{F}{\overset{CH_3}{Si}}-\underset{CH_3}{\overset{CH_3}{C}}-\underset{F}{\overset{CH_3}{Si}}-\underset{CH_3}{\overset{CH_3}{C}}-CH_3$$

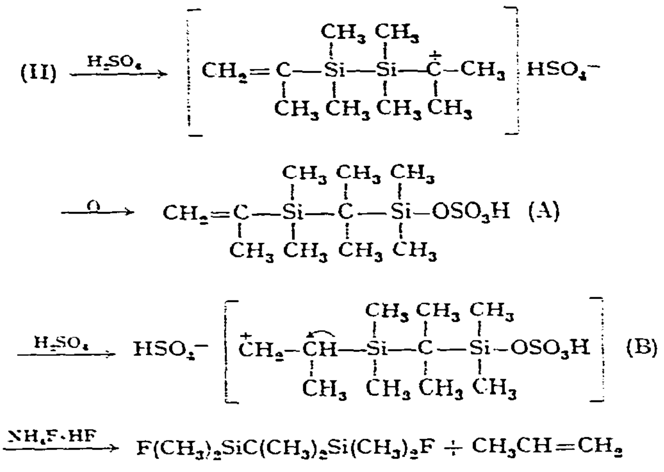
(VIII)



$$CH_3-\underset{F}{\overset{CH_3}{Si}}-\underset{CH_3}{\overset{CH_3}{C}}-\underset{CH_3}{\overset{CH_3}{C}}-\underset{F}{\overset{CH_3}{Si}}-CH_3$$

(VIIIa)

Compound (VI) is a product resulting from a single intramolecular rearrangement followed by cleavage, probably through a β-carbonium ion intermediate (B), of an isopropenyl group from silicon.



$$(II)\xrightarrow{H_2SO_4}\left[CH_2=\underset{CH_3}{C}-\underset{CH_3}{\overset{CH_3}{Si}}-\underset{CH_3}{\overset{CH_3}{Si}}-\underset{CH_3}{\overset{+}{C}}-CH_3\right]HSO_4^-$$

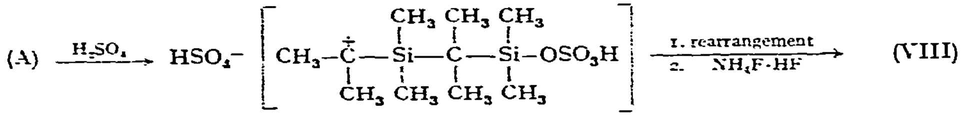
$$\xrightarrow{O} CH_2=\underset{CH_3}{C}-\underset{CH_3}{\overset{CH_3}{Si}}-\underset{CH_3}{\overset{CH_3}{C}}-\underset{CH_3}{\overset{CH_3}{Si}}-OSO_3H \quad (A)$$

$$(A)\xrightarrow{H_2SO_4} HSO_4^-\left[\overset{+}{C}H_2-\underset{CH_3}{CH}-\underset{CH_3}{\overset{CH_3}{Si}}-\underset{CH_3}{\overset{CH_3}{C}}-\underset{CH_3}{\overset{CH_3}{Si}}-OSO_3H\right] \quad (B)$$

$$\xrightarrow{NH_4F\cdot HF} F(CH_3)_2SiC(CH_3)_2Si(CH_3)_2F + CH_3CH=CH_2$$

(VI)

Compound (VIII) is one of the two possible isomers which should result from an α-carbonium ion intermediate (C). Another possible isomer corresponds to structure (VIIIa).



$$(A)\xrightarrow{H_2SO_4} HSO_4^-\left[CH_3-\underset{CH_3}{\overset{+}{C}}-\underset{CH_3}{\overset{CH_3}{Si}}-\underset{CH_3}{\overset{CH_3}{C}}-\underset{CH_3}{\overset{CH_3}{Si}}-OSO_3H\right]\xrightarrow[2.\ NH_4F\cdot HF]{1.\ \text{rearrangement}} (VIII)$$

(C)

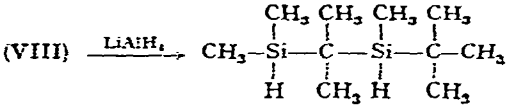
Good evidence for the proposed structure (VIII), but not (VIIIa), is afforded by the following facts. Only one of the two fluorine atoms in the molecule could be replaced by a methyl group with relative ease through the Grignard reagent, and the product, 2,2,3,3,4,5,5-heptamethyl-4-fluoro-2,4-disilahexane, (IX), was found to be fairly stable to hydrolysis. It was necessary to heat the reaction mixture at 100° for a 30-h period in order to effect further methylation of (IX) to give 2,2,3,3,4,4,5,5-octamethyl-2,4-disilahexane, (X).

$$\text{(VIII)} \xrightarrow{CH_3MgBr} (CH_3)_3SiC(CH_3)_2SiF(CH_3)C(CH_3)_3 \quad \text{(IX)}$$

$$\text{(IX)} \xrightarrow{CH_3MgBr} (CH_3)_3SiC(CH_3)_2Si(CH_3)_2C(CH_3)_3 \quad \text{(X)}$$

These findings indicate the presence of one sterically hindered silicon–fluorine bond.

An unequivocal answer to the structure problem was available from a study of the proton nuclear magnetic resonance spectra of the difluoride (VIII) and the dihydride 2,3,3,4,5,5-hexamethyl-2,4-disilahexane (XI), which was obtained in 95% yield from compound (VIII) by reduction with lithium aluminum hydride.



$$\text{(VIII)} \xrightarrow{LiAlH_4} CH_3-\underset{H}{\overset{CH_3}{Si}}-\underset{CH_3}{\overset{CH_3}{C}}-\underset{H}{\overset{CH_3}{Si}}-\underset{CH_3}{\overset{CH_3}{C}}-CH_3$$

(XI)

In Fig. 1 is reproduced the NMR spectrum of compound (VIII). The two doublet peaks (a) at 0.23 and (b) at 0.19 in δ value, each with the coupling constant of 7.5 cps, are assignable to $F(CH_3)_2Si-$ and $F(CH_3)Si\!<$ structure, respectively. The signal (c) at 1.02 is assignable to $(CH_3)_3C-$, and (d) at 1.16 is to $(CH_3)_2C\!<$ structure. The areas of (a) + (b), (c) and (d) are approximately in the ratio 3:3:2, as expected.

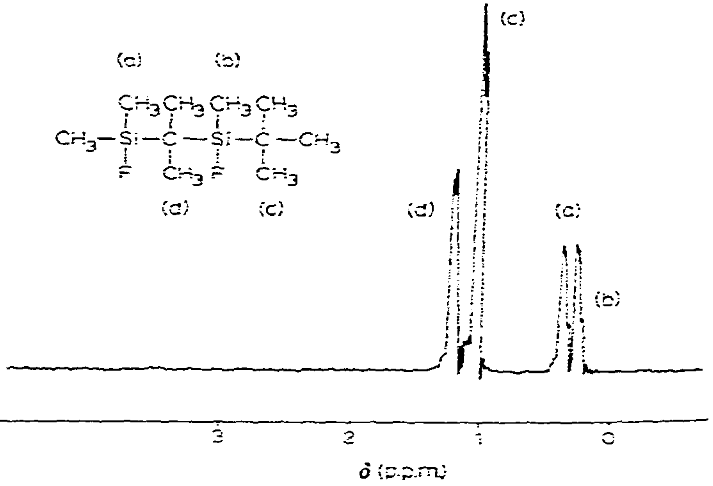


Fig. 1. The NMR spectrum of 2,3,3,4,5,5-hexamethyl-2,4-difluoro-2,4-disilahexane (VIII).

The NMR spectrum of the dihydride (XI) shown in Fig. 2 is compatible with the structure presented, *i.e.*, the terminal silane hydrogen (a) splits into a septuplet ($\delta = 3.89$, $J = 3.5$ cps) by six methyl hydrogens (b) and the internal silane hydrogen (d) splits into a quadruplet ($\delta = 3.53$) by three methyl hydrogens (e). The peak (f) at

1.03 is again assignable to $(CH_3)_3C-$ and the peak (c) at 1.14 is to $(CH_3)_2C\!<$ structure. The areas of (a), (d), (b) + (e), (c) and (f) are approximately in the ratio 1:1:9:6:9, as expected.

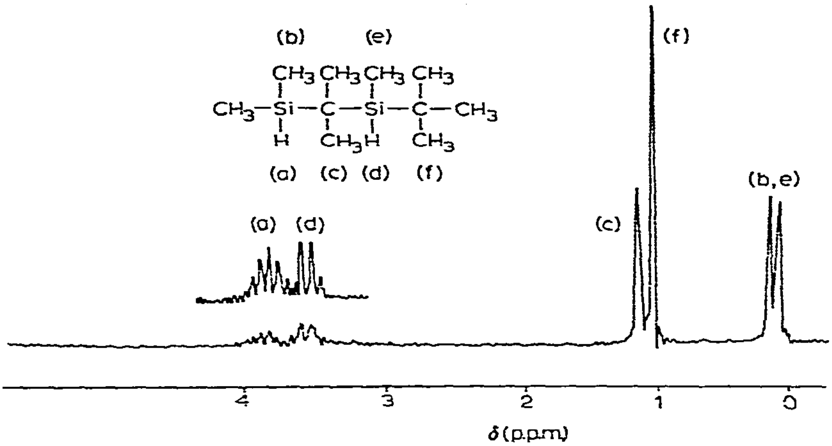
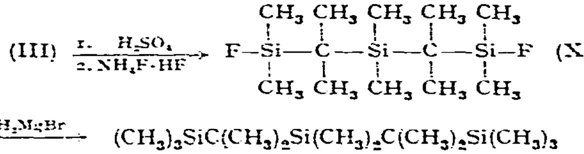


Fig. 2. The NMR spectrum of 2,3,3,4,5,5-hexamethyl-2,4-disilahexane (XI).

Reaction of (III)

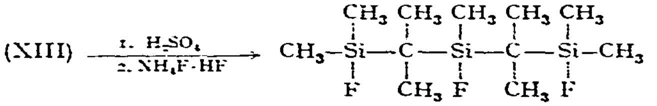
It was found that compound (III) also readily undergoes the intramolecular rearrangement with concentrated sulfuric acid in the cold to give, after treatment of the resulting solution with ammonium hydrogen fluoride, the expected product 2,3,3,4,4,5,5,6-octamethyl-2,6-difluoro-2,4,6-trisilaheptane (XII) in 80% yield. Compound (XII) was converted, by the Grignard reaction, into 2,2,3,3,4,4,5,5,6,6-decamethyl-2,4,6-trisilaheptane (XIII) in 66% yield



$$\text{(III)} \xrightarrow[\text{2. }NH_4F\cdot HF]{\text{1. }H_2SO_4} F-Si(CH_3)_2-C(CH_3)_2-Si(CH_3)_2-C(CH_3)_2-Si(CH_3)_2-F \quad \text{(XII)}$$

$$\xrightarrow{CH_3MgBr} (CH_3)_3SiC(CH_3)_2Si(CH_3)_2C(CH_3)_2Si(CH_3)_3 \quad \text{(XIII)}$$

Demethylation of compound (XIII) at 40°, followed by treatment with ammonium hydrogen fluoride, gave 2,3,3,4,5,5,6-heptamethyl-2,4,6-trifluoro-2,4,6-trisilaheptane (XIV) in 83.5% yield.



$$\text{(XIII)} \xrightarrow[\text{2. }NH_4F\cdot HF]{\text{1. }H_2SO_4} CH_3-SiF(CH_3)-C(CH_3)_2-SiF(CH_3)-C(CH_3)_2-SiF(CH_3)-CH_3 \quad \text{(XIV)}$$

It is noteworthy that the internal silicon–fluorine bond in (XIV) is too sterically hindered to undergo hydrolysis under relatively mild conditions. Thus, only two of the three fluorine atoms in the molecule could be back-titrated with 0.1 *N* aqueous solution of sodium hydroxide at room temperature, and all the three fluorine atoms could be quantitatively displaced by OH groups only after a sample was heated at about 50° for several hours in aqueous ethanol containing sodium hydroxide.

EXPERIMENTAL

Boiling points are uncorrected. NMR spectra were obtained in carbon tetrachloride solutions containing cyclohexane (Varian A-60, 60 Mc/sec). Chemical shifts are expressed in δ value in ppm from internal tetramethylsilane. To obtain δ value we have taken 1.43 ppm as signal difference between cyclohexane and tetramethylsilane.

Chloropentamethyldisilane[7], 1,2-dichlorotetramethyldisilane[7] and 1,3-dichlorohexamethyltrisilane[8] were prepared as reported previously. Isopropenyl bromide was made by the method of Braude and Evans[9].

Synthesis of isopropenylpentamethyldisilane (I), 1,2-diisopropenyltetramethyldisilane (II) and 1,3-diisopropenylhexamethyltrisilane (III)

These compounds were prepared in essentially the same manner, from the corresponding chlorosilanes and isopropenylmagnesium bromide. Yields and analytical data for silicon content were as follows:

Compound	*Yield %*	*Si found*	*Si calcd.*
(I) $C_8H_{20}Si_2$	81.5	32.18	32.58
(II) $C_{10}H_{22}Si_2$	80.5	28.20	28.31
(III) $C_{12}H_{28}Si_3$	85.5	32.83	32.84

The following detailed description of the synthesis of compound (III) is representative of the method used. A solution of isopropenylmagnesium bromide in tetrahydrofuran was prepared in a 500-ml three-necked flask in the usual manner from 75 g (0.62 mole) of isopropenyl bromide, 14.8 g (0.62 g-atom) of magnesium turnings in 150 ml of dry tetrahydrofuran. To the stirred solution was added 58 g (0.23 mole) of 1,3-dichlorohexamethyltrisilane with cooling. After completion of addition, the reaction mixture was heated at 50–55° over a 20-h period. Then, the mixture was hydrolyzed with an aqueous solution of ammonium chloride and the organic layer was separated. The aqueous layer was shaken with two 50-ml portions of ether, and the ether extracts were combined with the above organic layer. It was washed and dried. After evaporation of the solvent, the residual liquid was fractionally distilled in a 1.0 × 40 cm Stedman column to give 52 g (85.5 % yield) of 1,3-diisopropenylhexamethyltrisilane, b.p. 110° at 15 mm.

Intramolecular rearrangement of (I)

(*a*) *Isolation of the product as 2,3,3,4,4-pentamethyl-2-hydroxy-2,4-disilapentane (IV).* To 100 g of concd. sulfuric acid stirred and cooled to *ca.* —8° was added gradually 20 g (0.116 mole) of compound (I) over a 30-min period. A slightly colored, homogeneous solution resulted. After stirring for an additional 4 h at room temperature, the reaction mixture was poured onto 400 g of ice water over a 1-h period. The organic layer was separated and the water layer was extracted with petroleum ether (b.p. 43–50°). These were combined, washed with sodium bicarbonate solution and dried over potassium carbonate. After removing the solvent the residue was fractionally distilled to give 15 g (68 % yield) of 2,3,3,4,4-pentamethyl-2-hydroxy-2,4-disilapentane, b.p. 90° at 23 mm. It is a colorless, viscous oil having a camphor-like odor characteristic of trialkylsilanols. (Found: Si, 29.45. $C_8H_{22}OSi_2$ calcd.: Si, 29.50 %.)

An infrared spectrum of this compound exhibited the O–H absorption band. The high purity of the compound is shown by the fact that a weighed sample gave the theoretical volume of hydrogen on slight warming with sodium in dry xylene. A sample did not react with bromine at room temperature.

(*b*) *Isolation of the products as 2,3,3,4,4-pentamethyl-2-fluoro-2,4-disilapentane (V) and 2,3,3,4-tetramethyl-2,4-difluoro-2,4-disilapentane (VI).* To 180 g of concd. sulfuric acid, stirred and cooled to 0°, was added dropwise 20 g (0.12 mole) of (I). After stirring for 4 h, 13 g (0.23 mole) of dry pulverized ammonium hydrogen fluoride was added, and stirring was continued for an additional 2 h. The organic layer which resulted on standing, was separated and fractionated through a 1.0 × 40 cm Stedman column to give the following two fractions: (1) slightly impure 2,3,3,4-tetramethyl-2,4-difluoro-2,4-disilapentane (VI), b.p. 151°, 6.5 g (28.5% yield) (Found: F, 19.15. $C_7H_{18}F_2Si_2$ calcd.: F, 19.38%.) and (2) 2,3,3,4,4-pentamethyl-2-fluoro-2,4-disilapentane (V), b.p. 160°, 7 g (31% yield). (Found: F, 9.98. $C_8H_{21}FSi_2$ calcd.: F, 9.93%.)

In a second run the above experiment was repeated, but 26 g (0.15 mole) of (I) was allowed to react with 130 g of concd. sulfuric acid at —15° and then to the mixture was added 18 g (0.32 mole) of ammonium hydrogen fluoride. Fractionation of the organic layer gave 3 g (10% yield) of (VI) and 24 g (83% yield) of (V).

2,2,3,3,4,4-Hexamethyl-2,4-disilapentane (VII)

To a solution of methylmagnesium bromide prepared from 13 g (0.54 g-atom) of magnesium and methyl bromide in 200 ml of ether was added 35 g of a mixture of compounds (V) and (VI), containing 11.5% of fluorine. When the addition was complete the reaction mixture was heated to reflux for a 10-h period, and then worked up in the usual way. Fractional distillation yielded 28 g of 2,2,3,3,4,4-hexamethyl-2,4-disilapentane (VII), b.p. 79° at 31 mm, 178° at 760 mm (lit.[6], b.p. 183°, $n_D^{21.4}$ 1.4439). (Found: Si, 29.78. $C_9H_{24}Si_2$ calcd.: Si, 29.81%.)

Intramolecular rearrangement of 1,2-diisopropenyltetramethyldisilane (II)

To 140 g of concd. sulfuric acid stirred and cooled to —10° was added gradually 30 g (0.15 mole) of (II) over a 1.5-h period. A deep-yellow, homogeneous solution resulted. After an additional 2-h stirring at 0°, 27 g (0.48 mole) of ammonium hydrogen fluoride was added with stirring and cooling. The resulting organic layer was separated and the sulfuric layer was extracted with petroleum ether (b.p. 43–50°). These were combined and submitted to fractional distillation to give two fractions as follows: (1) 6.5 g (22% yield) of compound (VI) in a reasonably pure state, b.p. 57° at 33 mm. (Found: F, 19.36. $C_7H_{18}F_2Si_2$ calcd.: F, 19.38%.) and (2) 20 g (55.7% yield) of 2,3,3,4,5,5-hexamethyl-2,4-difluoro-2,4-disilahexane (VIII), b.p. 99° at 30 mm. (Found: F, 16.07. $C_{10}H_{24}F_2Si_2$ calcd.: F, 15.93%.)

2,2,3,3,4,5,5-Heptamethyl-4-fluoro-2,4-disilahexane (IX)

To 0.46 mole of methylmagnesium bromide was added 36 g (0.15 mole) of compound (VIII). The reaction mixture was allowed to stand overnight and after removing ether, it was heated at 60–70° for a period of 20 h. Fractional distillation gave 31 g (87% yield) of gas-chromatographically pure compound (IX). A weighed sample was shaken with 30 ml of ethanol and 25 ml of 0.1N sodium hydroxyde for a period of 30 min at room temperature and then titrated with 0.1N hydrochloric acid. The content of fluorine thus obtained was only 4.59 %, whereas $C_{11}H_{27}FSi_2$ requires 8.10 % F. A good analytical result (% F, 7.91) was obtained when a similar mixture to that above was heated to 40–50° for 30 min, allowed to stand for 1 h and then titrated with 0.1N HCl.

2,2,3,3,4,4,5,5-Octamethyl-2,4-disilahexane (X)

To a Grignard reagent prepared from 3 g (0.13 g-atom) of magnesium and 15 g of methyl bromide was added 20 g (0.085 mole) of compound (IX). The ether was distilled off and the residual mass was heated at 100° over a period of 30 h. The mixture was hydrolyzed and then worked up as usual to give 8 g of a forerun boiling over the range of 104–118° at 21 mm and 8 g (41 % yield) of a pure sample of compound (X). (Found: C, 62.33; H, 13.26; Si, 24.89. $C_{12}H_{30}Si_2$ calcd.: C, 62.51; H, 13.12; Si, 24.37 %.) The forerun was shown by gas-chromatographic analysis to consist of 27 % of unchanged (IX), 49 % of compound (X) and 24 % of an unidentified substance.

2,3,3,4,5,5-Hexamethyl-2,4-disilahexane (XI)

To a mixture of 1.9 g (0.05 mole) of lithium aluminum hydride with 100 ml of ether was added a solution of 12 g (0.05 mole) of compound (VIII) in 20 ml of ether with stirring at room temperature. After addition was completed, the mixture was heated to reflux over a period of 10 h. The product was separated by Soxhlet extraction and then fractional distillation under nitrogen atmosphere to give 9.5 g (94 % yield) of compound (XI), b.p. 100° at 32 mm. (Found: C, 59.51; H, 12.95. $C_{10}H_{26}Si_2$ calcd.: C, 59.31; H, 12.94 %.)

Intramolecular rearrangement of (III)

In essentially the same manner as that described in the rearrangement of compound (I), 38 g (0.15 mole) of (III) was allowed to react with 140 g of concd. sulfuric acid and the reaction mixture was then treated with 20 g (0.35 mole) of ammonium hydrogen fluoride. Fractional distillation of the resulting organic layer gave 35 g (80 % yield) of compound (XII), b.p. 125° at 13 mm. (Found: C, 48.46; H, 10.24; F, 12.87; Si, 28.39. $C_{12}H_{30}F_2Si_3$ calcd.: C, 48.59; H, 10.19; F, 12.81; Si, 28.41 %.)

A sample of this compound did not react with bromine on warming. Both silicon–fluorine bonds of this compound were quantitatively hydrolyzed by 0.1 N aqueous solution of sodium hydroxide in the cold.

2,2,3,3,4,4,5,5,6,6-Decamethyl-2,4,6-trisilaheptane (XIII)

To an ether solution containing 0.3 mole of methylmagnesium bromide there was added 30 g (0.1 mole) of (XII) dissolved in 30 ml of dry ether. The reaction mixture was heated to reflux for a 15-h period, and then hydrolyzed with dilute hydrochloric acid. After a work-up in the usual manner, fractionation gave 27 g of a liquid, boiling over the range of 115–126° at 6 mm. This product was found to contain a trace of fluorine still bonded to silicon, but no hydroxyl groups were detected (from the infra-red spectrum) in spite of the subjection to acidic hydrolysis. Therefore, the distillate was again treated with 0.2 mole of methylmagnesium bromide. The reaction mixture was heated to 80–90° with stirring for a 40-h period after removing most of the solvent. After a work-up in the usual way, fractional distillation gave 19 g (66 %

yield) of (XIII), b.p. 149° at 13 mm. (Found: C, 58.65; H, 12.47; Si, 29.12. $C_{14}H_{36}Si_3$ calcd.: C, 58.24; H, 12.57; Si, 29.19%.)

2,3,3,4,5,5,6-Heptamethyl-2,4,6-trifluoro-2,4,6-trisilaheptane (XIV)

In a similar apparatus to that described previously for the preparation of fluoropentamethyldisilane from hexamethyldisilane[7], a mixture of 17.5 g (0.06 mole) of compound (XIII) with 100 g of concentrated sulfuric acid was stirred vigorously at 40°. After 3.9 l (theory 4.2 l) of methane was evolved, no further evolution of gas was observed on additional stirring. To the resulting sulfuric acid solution was added, in portions, 11 g (0.2 mole) of dry ammonium hydrogen fluoride with stirring and cooling. Separation of the organic layer was followed by fractional distillation to give 15.5 g (85.4% yield) of (XIV), b.p. 115.5° at 13 mm.

It was analyzed for fluorine by the usual back-titration method after hydrolysis with a 0.1 N aqueous solution of sodium hydroxide at room temperature. The observed percentage of fluorine (12.51) was in good agreement with the calculated value (12.64), assuming that only two fluorine atoms were hydrolyzed. It was then found that all the three fluorines could quantitatively be replaced when a sample was heated to 50° for a 5-h period in an ethanolic solution of sodium hydroxide. (Found: C, 44.48; H, 9.16; F, 18.27; Si, 27.96. $C_{11}H_{27}F_3Si_3$ calcd.: C, 43.95; H, 9.05; F, 18.96; Si, 28.03%.)

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SUMMARY

Isopropenylpentamethyldisilane, 1,2-diisopropenyltetramethyldisilane and 1,3-diisopropenylhexamethyltrisilane were prepared by the reaction of isopropenylmagnesium bromide with the corresponding chlorosilanes. It was found that all these compounds readily undergo intramolecular rearrangement with concentrated sulfuric acid in the cold to give, after treatment with ammonium hydrogen fluoride, fluorosilanes with the $SiC(CH_3)_2Si$ grouping as a framework of the molecule in good yields. An unambiguous evidence for structure of the rearrangement product of 1,2-diisopropenyltetramethyldisilane was afforded by the NMR spectra of this product and the dihydride derived from it.

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