of the methyl groups themselves. The phenyl substituted polysiloxane again reacted much more readily when the catalyst was basic than when it was acidic.

Good yields of 1,5-di-*n*-octoxyhexamethyltrisiloxane were obtained if the reactions were stopped when about one-third of the total theoretically possible water had been collected. The catalyst was washed out, and the partially alcoholyzed product isolated by vacuum distillation. A continuation of the reaction beyond this point, of course, results in further stepwise alcoholysis, but the subsequent products can not readily be separated from one another.

Isolation of products. The course of the reaction was frequently checked by isolating the products formed. The usual procedure was to strip the xylene and excess *n*-octyl alcohol at about 50 mm. pressure from the water-washed reaction mixture. The residue was distilled at 0.5–1.0 mm. pressure. Midcuts of flats were analyzed. Individual compounds so obtained are listed in Table I. An exception to this procedure was in the base-catalyzed reaction of triphenylsilanol with *n*-octyl alcohol. Here the product, hexaphenyldisiloxane, crystallized from the cooled reaction mixture in a relatively pure state.

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[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, SCIENTIFIC LABORATORY OF THE FORD MOTOR CO.]

Preparation of Decamethyltetrasilane and Its Lower Homologs

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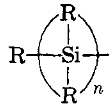
The preparations of three new organosilicon compounds—octamethyltrisilane, decamethyltetrasilane, and a hexamethyl dichlorotrisilane—are reported, together with an improved method for preparing hexamethyldisilane.

Despite the phenomenal growth of organosilicon chemistry within the past twenty years, surprisingly few examples of organo-substituted silicon catenations are known. The examples are limited to a series of disilanes (I, $n = 2$) in which the R groups are aryl or alkyl groups (C_1–C_5)[1–4]; octaphenyltrisilane[5]; the controversial octaphenyltetrasilanes described by Kipping[6] and a possible decaphenyltetrasilane[5]; a cyclic dodecamethylcyclohexasilane[7] and higher molecular weight polydimethylsilanes of indefinite structure.[7–9] Lack of equivalent methods for propagating silicon chains compared with carbon chains coupled with the weaker bond energy (45 kcal./mole)[10] for the silicon-silicon linkage compared with that (80 kcal./mole)[10] for the carbon-carbon linkage probably accounts for the paucity of examples of polysilanes.



$$R\!-\!\left(\begin{array}{c}R\\|\\Si\\|\\R\end{array}\right)_{n}\!-\!R$$

I

Our purpose was the preparation of discrete members of a homologous series of polysilanes with the simplest alkyl group (methyl) in order to fill some of the gaps and determine some of their physical properties. At this time we are able to report the successful syntheses of the tri- and tetrasilanes, hexamethyldichlorotrisilane, and an improved laboratory synthesis of hexamethyldisilane (the key starting material for the preparation of the higher homologs).

Since relatively large quantities of hexamethyldisilane were required for subsequent syntheses, an improved and more convenient method for preparing this intermediate over those described in the literature[3,11–13] was required. After investigating several procedures, the coupling of trimethylchlorosilane with sodium-potassium alloy was found to be very satisfactory and preferred over coupling with metallic sodium. The sequence of reactions for preparing the series of polysilanes reported here is summarized in the following equations:

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(1) F. S. Kipping, *J. Chem. Soc.*, **119**, 647 (1921).

(2) H. Gilman and T. C. Wu, *J. Am. Chem. Soc.*, **75**, 3762 (1953).

(3) M. G. Voronkov and Y. I. Khudobin, *Zhur. Obshcheĭ Khim.*, **26**, 584 (1956); *Chem. Abstr.*, **50**, 13729 (1956).

(4) H. Gilman, R. K. Ingham, and A. G. Smith, *J. Org. Chem.*, **18**, 1743 (1953).

(5) H. Gilman, T. C. Wu, H. A. Hartzfeld, G. A. Guter, A. G. Smith, J. J. Goodman, and S. H. Eidt, *J. Am. Chem. Soc.*, **74**, 561 (1952).

(6) F. S. Kipping and J. E. Sands, *J. Chem. Soc.*, **119**, 839, 848 (1921); F. S. Kipping, *J. Chem. Soc.*, **123**, 2590, 2598 (1923); **125**, 2291 (1924).

(7) C. A. Burkhard, U. S. Patent **2,554,976** (1951); *J. Am. Chem. Soc.*, **71**, 963 (1949).

(8) M. Schmeisser and M. Schwarzman, *Z. Naturforsch.*, **11b**, 278 (1956); *Chem. Abstr.*, **50**, 12715 (1956).

(9) M. J. Hunter, U. S. Patent **2,554,193** (1951).

(10) K. S. Pitzer, *J. Am. Chem. Soc.*, **70**, 2140 (1948).

(11) W. C. Schumb and C. M. Saffer, Jr., *J. Am. Chem. Soc.*, **61**, 363 (1939).

(12) L. O. Brockway and N. R. Davidson, *J. Am. Chem. Soc.*, **63**, 3287 (1941).

(13) M. Kumada, M. Yamaguchi, Y. Yamamoto, J. Nakajima, and K. Shiina, *J. Org. Chem.*, **21**, 1264 (1956).

$$(CH_3)_3SiCl\ (II) \xrightarrow{a} (CH_3)_3SiSi(CH_3)_3\ (III)$$

$$(III) \xrightarrow{b} (CH_3)_3SiSi(CH_3)_2Cl\ (IV) + CH_4$$

$$(II) + (IV) \xrightarrow{a} (CH_3)_3SiSi(CH_3)_2Si(CH_3)_3\ (V)$$

$$(IV) \xrightarrow{a} (CH_3)_3Si[Si(CH_3)_2]_2Si(CH_3)_3\ (VI)$$

$$(V) \xrightarrow{b} (IV) + (CH_3)_6Si_3Cl_2 + CH_4$$

a. Na-K alloy
b. 1. concd. H_2SO_4. 2. NH_4Cl

We also desired to establish whether or not the demethylation of methylated polysilanes by sulfuric acid occurred specifically at the α- and ω-silicon atoms—with hexamethyldisilane only one isomer is possible. Octamethyltrisilane theoretically could give two isomers. The tetrasilane, VI, offered the possibility of investigating the demethylation reaction, since VI can also be prepared by the coupling of heptamethylchlorotrisilane and trimethylchlorosilane. Unfortunately, the reaction of sulfuric acid and ammonium chloride with octamethyltrisilane did not yield the anticipated chloro intermediate, but instead resulted in some cleavage of the silicon-silicon bonds (evidenced by an 18% yield of IV), a 26% yield of a dichloro compound of undetermined substitution (hexamethyldichlorotrisilane), and recovery of unchanged octamethyltrisilane (45%).

The physical properties of polysilanes III, V, and VI are summarized in Table I.

TABLE I

PHYSICAL PROPERTIES OF METHYLPOLYSILANES

Silane	M.P.	B.P.	n_D^{20}	d_4^{20}
III	13	112.6–112.8/750	1.4229	0.7257
V	−48	112.0–112.5/106	1.4612	0.7763
VI	−14.5	112–113/16	1.4877	0.8066

EXPERIMENTAL

All reactions reported here were conducted under a nitrogen atmosphere in conventional all-glass equipment. The trimethylchlorosilane (Dow-Corning) was redistilled prior to use and all solvents were dried over calcium hydride.

Hexamethyldisilane. Several procedures for coupling trimethylchlorosilane, including different alkali metals and their alloys, quantities and types of solvents, stirring rates, and temperatures were investigated and the following procedure consistently resulted in yields of 70% or better:

Sodium-potassium alloy was prepared *in situ* in a 2-l. flask from 18.2 g. (0.79 g.-atom) of sodium and 125.8 g. (3.22 g.-atoms) of potassium and covered with 100 ml. of xylene. While the alloy was stirred slowly, 429 g. (3.95 moles) of trimethylchlorosilane was added dropwise. An immediate and vigorous exothermic reaction ensued, accompanied by the formation of the characteristic purple color. As the reaction proceeded, dilution with more solvent (*ca.* 400 ml.) was necessary to facilitate stirring, and the addition of the silane required 2 hr. After an additional 2-hr. reflux period, the mixture was diluted with 500 ml. of xylene, the reflux condenser replaced by a distilling head, and the mixture distilled until the vapor temperature reached 130°. The cooled slurry was filtered (under nitrogen) through a 2″ × 36″ glass tube (constricted at one end and plugged with glass wool). The precipitate was washed several times with fresh xylene and the washings combined with the original filtrate. Distillation yielded 219.6 g. (76%) of hexamethyldisilane, b.p. 112–113°. Refractionation through a 4-ft. column, packed with glass helices, yielded 197 g. (69%) of hexamethyldisilane, b.p. 112.6–112.8° (750 mm.), m.p. 13°, n_D^{20} 1.4229, d_4^{20} 0.7257, M_R (calcd.) 51.07, M_R (found) 51.33. Gas chromatography indicated impurities to be less than one part per thousand parts, and the infrared absorption spectrum exhibited only a trace of siloxane. The reported[15] values are: b.p. 112°, m.p. 11°, n_D^{20} 1.4228 and d_4^{20} 0.7265.

Pentamethylchlorodisilane. The directions of Kumada and coworkers[13] were followed for this preparation. In larger runs, a creased flask gave more efficient mixing of the reactants. The yields of pentamethylchlorodisilane were 62–66%.

Octamethyltrisilane. Sodium-potassium alloy, prepared from 9.0 g. (0.39 g.-atom) of sodium and 87 g. (2.2 g.-atoms) of potassium was covered with 100 ml. of benzene and a mixture of 196 g. (1.8 moles) of trimethylchlorosilane, 100 g. (0.6 mole) of pentamethylchlorodisilane, and 160 ml. of benzene added (over a 2-hr. period) to the alloy. An additional 200 ml. of benzene was added to facilitate stirring, and the mixture was finally diluted with 600 ml. of benzene and refluxed for 9 hr. The work-up procedure described for hexamethyldisilane was followed. Fractionation yielded 25.7 g. (13% recovery) of trimethylchlorosilane, 18.2 g. (13.8%) of hexamethyldisilane, 7.3 g. (7.3% recovery) of pentamethylchlorodisilane, and 84.6 g. (69%) of crude octamethyltrisilane (b.p. 175–176°/750 mm.) and 7.9 g. of higher-boiling (220–228°) liquid—probably crude decamethyltetrasilane. The crude octamethyltrisilane was contaminated with a siloxane (infrared absorption spectrum) which was removed by washing a pentane solution of the product with cold concentrated sulfuric acid. The pentane solution was then filtered through a sodium bicarbonate and sodium sulfate mixture to remove water and acid. Refractionation yielded 66.9 g. (53%) of octamethyltrisilane, b.p. 112.0–112.5° (106 mm.), m.p. −48°, n_D^{20} 1.4612, d_4^{20} 0.7763, M_R (calcd.) 71.86, M_R (found) 72.33.

Anal. Calcd. for $C_8H_{24}Si_3$: C, 46.97; H, 11.83; Si, 41.20. Found: C, 47.10, 47.11; H, 10.95, 11.19; Si, 41.73, 41.84.

Decamethyltetrasilane. A solution of 116.3 g. (0.69 mole) of pentamethylchlorodisilane in 150 ml. of benzene was added (over a 90-min. period) to sodium-potassium alloy [4.0 g. (0.17 g.-atom) of sodium and 30.3 g. (0.77 g.-atom) of potassium] in 100 ml. of benzene. In this instance external heating was necessary to maintain the reaction, and refluxing was continued for 11 days. Periodic titrations for unchanged pentamethylchlorodisilane indicated that the amount of unchanged chlorosilane decreased from 0.35 mole after 2 days to 0.085 mole after 11 days. Using the preceding work-up procedure, 52.4 g. (54%) of crude decamethyltetrasilane was obtained. Contaminating siloxane was removed by the technique described for the trisilane. Careful refractionation yielded 24.6 g. (27%) of decamethyltetrasilane, b.p. 112–113° (16 mm.), m.p. −14.5°, n_D^{20} 1.4877, d_4^{20} 0.8066, M_R (calcd.) 92.65, M_R (found) 93.79, mol. wt. (calcd.) 262.7, mol. wt. (found) 258.8 (cryoscopic in benzene).

Anal. Calcd. for $C_{10}H_{30}Si_4$: C, 45.72; H, 11.51; Si, 42.77. Found: C, 45.81, 46.09; H, 11.29, 11.43; Si, 42.43, 42.68.

Heptamethylchlorotrisilane (*attempted*). A mixture of 60 g. (0.29 mole) of octamethyltrisilane and 170 g. (1.73 moles) of concd. sulfuric acid was rapidly stirred at 30° in a creased flask. The theoretical quantity of methane (7.2 l.) was liberated after 6 hr. The mixture was cooled in an ice bath and 23.3 g. (0.44 mole) of ammonium chloride was added over a 30-min. period. The mixture was diluted with hexane and the organic layer separated. Fractional distillation yielded 8.5 g. (18%) of pentamethylchlorodisilane, 25.3 g. (45%) of unchanged octamethyltrisilane, and 26.2 g. (26%) of a clear liquid, b.p. 103-106° (36 mm.). The titratable halogen in this latter fraction indicated it to be hexamethyldichlorotrisilane (% chlorine 28.9; found 27.8). None of the expected heptamethylchlorotrisilane was isolated.

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[CONTRIBUTION FROM THE STERLING-WINTHROP RESEARCH INSTITUTE]

Mercuration of Some Derivatives of 1,2,3,6-Tetrahydropyridazine

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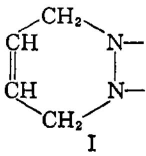
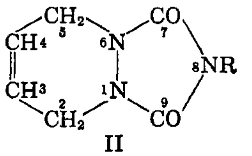
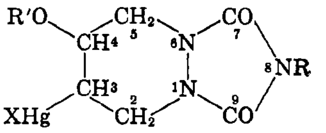
The preparation of some mercurated 1,6,8-triazabicyclo[4.3.0]nonanes (III), 1,6-diazabicyclo[4.4.0]decanes (VIII), and a mercurated hexahydropyridazine is described. The structure of III (X = OH, R = H, R′ = CH_3) is discussed.

The formation of 1,2-dicarbamyl-1,2,3,6-tetrahydropyridazine (I) and its pyrolytic conversion to 1,6,8-triazabicyclo[4.3.0]-3-nonene-7,9-dione (II, R = H) have been reported.[1] Also, the preparation of a series of highly active diuretic agents of general formula III from II has been described, but without comment.[2] Some of the phenomena noted in the production of these mercurated compounds appear worth reporting.


I


II


III

The conditions for alkoxymercuration of II were standard—*i.e.*, mixing a hot alcoholic solution of II with a hot alcoholic solution of mercuric acetate followed by addition of a few drops of concentrated nitric acid as a catalyst. In the mercuration reaction involving II where R was H, if the reaction mixture were allowed to cool before addition of the nitric acid catalyst, an intermediate separated which contained loosely bound mercury[3] and gave analytical values corresponding to the simple salt II where R was $HgOCOCH_3$. Addition of nitric acid to a methanolic suspension of this salt resulted in its rapid dissolution and formation of the 3-mercurated derivative discussed below.

Compound II with R other than H regularly furnished compound III with X = $OCOCH_3$.[2] These products showed no tendency toward hydrolysis in the presence of water to give a hydroxymercuri derivative. In the reaction above involving II where R was H (the solvent was methanol), the product invariably had the composition $C_7H_{11}HgN_3O_4$,[2] which corresponded to III with X = OH, R = H, and R′ = CH_3 or to a hydrated inner salt form, either monomeric or polymeric.

This product was amorphous, extremely insoluble in water, soluble in dilute sodium hydroxide solution, and recoverable unchanged by addition of carbon dioxide to this alkaline solution. In spite of its amorphous character the product invariably held one molecule of loosely bound water.[4]

Occasionally, when an alkaline solution of this mercury compound had stood for fifteen to thirty minutes, the development of cloudiness and subsequent precipitation of a crystalline solid was observed. The formation of this crystalline product was more rapid and complete in dilute ammonium hydroxide. The infrared spectra of the amorphous and crystalline materials were quite similar and the analytical values on the crystalline material (including water determination) indicated no change in chemical composition. Indeed, when the amorphous material was triturated in warm water with seeds of the crystalline material, it slowly crystallized and its infrared spectrum was then identical with that of material which had crystallized from alkaline solution.

This mercurated product showed $\epsilon_{223\,m\mu(sh)}^{C_2H_5OH}$ 6700 which suggested an enolized form of the imide group. The unmercurated starting material II (R = H) showed $\epsilon_{219\,m\mu(sh)}^{C_2H_5OH}$ 5600. Addition of sodium hydroxide to these samples produced shifts to ϵ_{227} mμ (sh) 6200 and ϵ_{223} mμ (sh) 5000 respectively. The general enolized character of the urazole ring system seems probable, *cf.*, structure IV.

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[1] W. T. Hunter, U. S. Pat. 2,813,867, Nov. 19, 1957; R. L. Clarke, U. S. Pat. 2,813,866, Nov. 19, 1957.

[2] R. L. Clarke and F. W. Gubitz, U. S. Pat. 2,813,865, Nov. 19, 1957.

[3] Addition of dilute sodium hydroxide to an aqueous suspension of this material produced a precipitate of mercuric oxide whereas compounds of type III did not.

[4] The normal Karl-Fischer procedure for determination of water in this material gave anomalous results, but when the sample was shaken with methanol for 3 hr., the insoluble material removed by filtration, and the water which had been absorbed by the methanol was titrated, the presence of one equivalent of water could be demonstrated.