THE PRESENT STATE OF ORGANOSILICON CHEMISTRY[1]

C. A. BURKHARD AND E. G. ROCHOW

Research Laboratory, General Electric Company, Schenectady, New York

AND

H. S. BOOTH AND J. HARTT[2]

Morley Chemical Laboratory, Western Reserve University, Cleveland, Ohio

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CONTENTS

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[1] When the first two authors, who were at work on a review on this subject, learned that the latter two were also writing a review on the same subject based on a thesis submitted by James Hartt in 1941 in partial fulfillment of the requirements for a degree of Master of Arts in Western Reserve University, they suggested that efforts be combined. The last three authors gratefully acknowledge the heavy burden carried by the first named author in integrating this information. E. G. R., H. S. B., J. H.

McBee "Keysort" punch cards were used in the assembly of this paper.

[2] Present address: Nyotex Chemicals, Inc., Houston, Texas.

I. Introduction

Nature provides no ready source of organosilicon compounds,[3] for while silicon is abundant in the earth, it occurs in the highly oxidized form. If organosilicon compounds have any utility, then, it could not have been apparent to the pioneer investigators; only curiosity could have led them to find out how to make such compounds and then to study their behavior. For this reason organosilicon chemistry was and is purely a product of laboratory research. Progress in the field has followed closely the improvements in methods of synthesis, and has moved ahead in several well-defined surges originating in the development of new methods. Now that the commercial manufacture and application of organosilicon materials (49, 290) have brought wider interest in the field and have encouraged many new investigations, it has seemed appropriate to review the present state of our knowledge of organosilicon compounds.

As seen by the authors, the chief function of such a review paper at this time is to assemble a complete bibliography and to comment upon the individual publications to an extent that will make the list more valuable and more usable to the research chemist. The bibliography at the end of this paper is believed to be complete to June 3, 1946, insofar as the facilities at the disposal of the authors made that possible. In the preparation of the bibliography it has seemed advisable to define organosilicon compounds as those in which there is at least one carbon–silicon bond (306), i.e., those in which one or more carbon atoms are linked directly to silicon atoms. The articles have been selected in accordance with this definition; hence articles on the organic esters of orthosilicic acid or any other class of compounds in which organic groups are linked through some third element to silicon atoms have not been included.

A further aim of the authors has been to collect data on the physical constants of all the known organosilicon compounds, so that the data would be available for ready reference. Tables of these compounds and their physical properties therefore also appear at appropriate places in the paper, and it is believed that these are complete through the publication date.

With the tables and bibliography appearing in this form there is much less need for detailed abstracting of the separate publications, and therefore it has been the intention of the authors to discuss classes of compounds and types of reaction rather than to paraphrase the findings of the individual investigators.

Other reviews of the literature have been presented by Kipping (168), Krause and von Grosse (196), Bygdén (41), and Dolgov (65).

II. Nomenclature

The early practice of naming organosilicon compounds after their organic analogs was soon found to be cumbersome and ambiguous (306); nevertheless some of the oldest terms have persisted up to the present time. Every investigator in the field has felt the need for a satisfactory and accepted terminology to

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[3] The presence of silicon dioxide in the ash obtained by burning straw or feathers indicates the presence of soluble or dispersed compounds of silicon in the living tissue, but the state of combination has not been clearly defined and it seems unlikely that organosilicon compounds (with the definition used herein) are present (68).

simplify the problem of identifying compounds, but conflicting views have long prevented the adoption of one scheme. The first consistent system of nomenclature was devised by Kipping (147, 155, 158), who based the names of all his compounds on the name *silicane* for the parent substance SiH_4. The Kipping system was unambiguous, but its use often resulted in unpronounceable names of fifteen or more syllables. It is not surprising, then, to find the more recent trend toward the shorter names based upon the system devised by Stock (342, 344) for naming the normal hydrides of silicon (306). According to this system the parent substance SiH_4 is called *silane,* a hydroxy derivative is called *silanol,* a compound with alternate silicon and oxygen atoms is a *siloxane,* etc. The organic compounds are then named as derivatives of the hydrides. The matter is no longer one for controversy, because it has been resolved by a committee on nomenclature of the American Chemical Society, and the recommendations of that committee are followed in this paper (50). The committee has established the root name of *silane* for SiH_4, and the names of the simpler types of compounds become *siloxane, silazane, cyclosiloxane, cyclosilazane, silanol,* etc. Groups are named as derivatives of the hydride groups such as silyl ($H_3Si—$), silylene ($H_2Si=$), disilanyl ($H_3Si—SiH_2—$), siloxy ($H_3SiO—$), etc. It is hoped that all authors in the field will adopt and encourage the American Chemical Society system, so that in the future those who abstract articles or assemble bibliographies will find their tasks less difficult.

III. METHODS FOR THE SYNTHESIS OF ORGANOSILICON COMPOUNDS

As was pointed out in the introduction, investigations of organosilicon compounds have followed quite closely patterns set by the available methods of synthesis. It seems appropriate to consider these individual methods before going on to a discussion of the various classes of compounds. It will then be seen that the separate compounds fall into groups or classes for which general methods of preparation may be given.

A. SYNTHESIS OF ORGANOSILANES AND ORGANOCHLOROSILANES

We may classify the available methods of synthesis as either substitution methods or direct methods (290a). In the substitution methods some reactive covalent compound of silicon (such as a halide or ester) is employed as a starting material, and the desired organic groups are attached to the central silicon atom by a reaction which involves substitution for the halogen or ester groups. In the direct method, crystalline or elementary silicon is caused to react directly with a hydrocarbon halide to produce a mixture of organosilicon halides. The substitution methods have been in use a great deal longer than the direct method, but both find their spheres of application in the plant as well as in the laboratory.

Most of the substitution methods involve the reaction of an active organometallic compound with a silicon halide or ester, and therefore require the preliminary preparation of that active compound. Thus the method of Friedel and Crafts (81, 85) involves the reaction of zinc alkyls or aryls with silicon tetrachloride or with ethyl orthosilicate according to the metathesis:

$$2ZnR_2 + SiX_4 = SiR_4 + 2ZnX_2$$

The substitution is stepwise and hence may be used for the attachment of one to four organic groups, depending upon the molar proportions and the reaction conditions used. Such reactions are carried out in sealed tubes at a temperature of 150–200°C. or more, so that the quantity which can be prepared in one operation is necessarily limited. Moreover, the preparation of the necessary zinc alkyls is in itself an arduous task, and these highly poisonous metal alkyls are unpleasant substances to handle in the laboratory. Nevertheless the reaction still finds application in some exceptional circumstances.

In 1884 Pape (258) introduced a variation in which a mixture of propyl iodide, metallic zinc, and silicon tetrachloride was heated in a sealed tube instead of preparing the zinc alkyl separately, but this method has not been widely used.

Another variation which was used a great deal by Ladenburg eliminated the sealed tube by the use of metallic sodium along with the zinc alkyl (203):

$$2Na + Zn(C_2H_5)_2 + Si(OC_2H_5)_4 = (C_2H_5)_2Si(OC_2H_5)_2 + 2NaOC_2H_5 + Zn$$

In an elaboration of the mechanism for this reaction, Ladenburg was able to show that the alkyl groups which were attached directly to silicon were derived from the zinc alkyl rather than by reduction of the ester groups on the silicon; therefore it seems probable that the real alkylating agent was a sodium alkyl derived from reaction of the metallic sodium in the zinc alkyl. The higher reactivity of the sodium alkyl makes unnecessary the higher temperatures for which a sealed tube is required.

Alkylation of chlorosilanes in the gas phase rather than in solvents or in sealed tubes was accomplished by Stock (347) in his investigation on the silicon hydrides. He found that the vapor of dimethylzinc would react with the gaseous chlorosilanes at moderate temperatures to deposit zinc chloride and accomplish a stepwise substitution of methyl for chlorine on the silicon. A different kind of vapor-phase alkylation (116) involves passing the mixed vapors of a silicon halide and alkyl halide over a finely divided reactive metal and abstracting the chlorine as metal chloride, yielding a mixture of organosilanes. In this latter method it is possible that an alkyl of the reactive metal is formed first and that this alkyl then reacts at once with the silicon tetrachloride, but it is not necessary that this intermediate reaction be assumed.

The second method to come into general use in the period following 1884 involved the condensation of silicon tetrachloride and an alkyl or aryl chloride with metallic sodium (258). This reaction usually is carried out in dry ether as a solvent, and it is customary to add a little ethyl acetate as catalyst (178). With an excess of the alkyl or aryl chloride, tetrasubstitution takes place:

$$SiCl_4 + 4RCl + 8Na = SiR_4 + 8NaCl$$

The reaction is highly exothermic, the liberated energy being sufficient to break silicon–silicon bonds (318). For this reason the method cannot be used for preparing organic derivatives of disilanes or siloxanes, nor can it be used satisfactorily for preparing mono- and di-substituted chlorosilanes. In order properly to control the substitution reaction it is necessary that the heat of the sodium reaction be dissipated in some way. One way of accomplishing this is to carry out the synthesis in two stages (320). For example, metallic sodium reacts with monochlorobenzene in dry ether to produce reactive phenylsodium, and then the solution or suspension of phenylsodium is introduced in proper proportion into a solution of silicon tetrachloride. The second reaction then can be controlled to give satisfactory yields of the intermediate substitution products like dichlorodiphenylsilane. Carried out in this way, the sodium condensation method is about as convenient as the Grignard method.

The application of the Grignard reagent to organosilicon chemistry was first accomplished independently by Kipping (146) and Dilthey (63), but Kipping made by far the most extended use of the method. As ordinarily carried out, the Grignard reagent is prepared in a normal manner and then added to a stirred solution of silicon tetrachloride in ether. Should the Grignard reagent have a very low reactivity, however, it may be separated from the ether in which it was prepared and heated with the silicon tetrachloride in a sealed tube, or in a high-boiling solvent (52, 319). Several simplifications have been suggested, among them the introduction of a mixture of silicon tetrachloride and alkyl chloride to a suspension of magnesium turnings in ether, or the addition of magnesium to a solution of the mixed halides. The use of alcohol-free and very dry ether as a solvent for the Grignard reaction has been avoided in some cases by carrying out the reaction in an excess of one of the reagents. Thus, monochlorobenzene reacts with magnesium in an excess of the chlorobenzene as solvent (290a), and ethyl orthosilicate serves as solvent for the preparation of a Grignard reagent and for the reaction of that reagent with the ethyl silicate (5, 6, 8, 9, 10). In the latter instance the method becomes a one-stage reaction in which the organic halide, ethyl silicate, and magnesium are heated in a sealed vessel under pressure (234).

Substitution of the chlorine in silicon tetrachloride by Grignard reagents takes place as a series of consecutive competitive reactions, to produce a mixture of products in which the individual compounds are present in proportions depending upon the relative concentrations of the reagents and a relative reactivity of the chlorine atoms on each compound (95b). The mathematical expression for the proportion of products agrees with the experimental yield data only when a high reactivity is assigned to $RSiCl_3$. It seems that the chlorine atoms attached to silicon are not uniformly reactive nor reactive in proportion to their number, but rather achieve a characteristic reactivity which is dependent upon the symmetry of the molecule and the kind of substituents already present.

Another substitution method which is related to the Grignard synthesis makes use of the reaction between alkyls of lithium and a chlorosilane (76, 102a). The lithium alkyl is prepared and handled much like a Grignard reagent, but is more reactive and so is particularly suited to syntheses in which the Grignard reagent provides only meager yields. There is also a related reaction between lithium alkyls and silicon–hydrogen bonds (103a, 246a). This has been used to prepare butyltriethylsilane from triethylsilane and butyllithium in ether solution:

$$(C_2H_5)_3SiH + n\text{-}C_4H_9Li \rightarrow (C_2H_5)_3(n\text{-}C_4H_9)Si + LiH$$

Ethyl ether seems to be necessary for this reaction, for it is not found to occur in petroleum ether or in tertiary butyl alcohol. Lithium amide and lithium ethoxide react similarly with triethylsilane in ammonia or ethyl alcohol, respectively, but in these syntheses the lithium hydride reacts with the solvent to regenerate the amide or ethoxide and release hydrogen.

A radically different substitution method involves the absorption of ethylene or of other olefinic hydrocarbons in silicon tetrachloride at elevated temperature and under high pressure (325):

$$CH_2{=}CH_2 + SiCl_4 = ClC_2H_4SiCl_3$$

This reaction has been reported to take place at 10–100 atm. and in the presence of molar proportions of a catalyst such as aluminum chloride or oxychlorides of mercury or copper. Substitution of only one chlorine on the silicon is indicated in the only published report (325). The reaction of acetylene with silicon tetrachloride under similar conditions is stated to produce β-chlorovinyltrichlorosilane, and the reaction of carbon monoxide is said to produce trichlorosilylcarbonyl chloride. All of these products have reactive chlorine atoms in the organic portions and therefore should prove to be interesting intermediates for further organosilicon syntheses.

A related reaction is described in which saturated hydrocarbons react with silicon tetrachloride in the vapor phase at a temperature of 450°C. or more to produce a mixture of organosilicon halides (250). In this and the preceding method no reactive metal is used as condensing agent, but the methods still involve substitution of chlorine in the silicon tetrachloride and so may be classed as substitution reactions.

The direct synthesis (289, 290a, 299) brings about simultaneous reaction of organic groups and halogen atoms with elementary silicon to produce organosilicon halides:

$$2RCl + Si = R_2SiCl_2$$

$$4RCl + 2Si = R_3SiCl + RSiCl_3 \text{ etc.}$$

This is a general reaction for alkyl and aryl halides in either the liquid or the vapor phase. However, it is most convenient to use alkyl or aryl chlorides as starting material and to carry out the reaction in the gas phase at a temperature of 200–450°C., depending upon the reactivity of the particular chloride (302). It is apparent that at the higher temperatures which may be required for reaction of the more inert chlorides the organic compounds may suffer considerable pyrolysis, with consequent deposition of carbon in the reactive zone. Such decomposition can be avoided in large part by the use of a metallic (289) or metal oxide (303) catalyst which will reduce the temperature required for effective reaction. Powdered copper is such a catalyst, and has been used satisfactorily in the reaction of methyl chloride with elementary silicon to prepare methylchlorosilanes. The use of copper enables one to reduce the reaction temperature by about 100°C. and so to obtain satisfactory conversion of the methyl chloride without large losses by pyrolysis.

The action of the catalyst in the direct reaction is of interest as well as of economic importance, and therefore has been studied in some detail (118). It appears that the methyl chloride first reacts with finely divided copper to produce cuprous chloride and methylcopper, and that the latter then decomposes quite rapidly into free copper and free methyl groups. The cuprous chloride is readily reduced by silicon at the temperature of the reaction, regenerating free copper and transferring the chlorine to the silicon. The partially chlorinated silicon then is able to take up free methyl groups or more chlorine atoms until it has four substituents, whereupon it becomes sufficiently volatile to leave the reaction zone. This reaction mechanism would add methyl groups and chlorine atoms at random, so that a mixture of all possible methyl- and chlorine-substituted silanes becomes possible. It is found that silicon tetrachloride, tetramethylsilane, and all the intermediate methylchlorosilanes are produced. If the copper catalyst is not sufficiently effective or the temperature rises to too high a value, methyl groups are lost by pyrolysis and the product becomes richer in chlorine. The copper therefore is classed more properly as a chemical reagent than as a physical catalyst, but because of the cyclic reactions it is used over and over without leaving the scene of the reaction. It is interesting to note that in the reaction of chlorobenzene with silicon to form dichlorodiphenylsilane as the principal product, finely divided silver is more effective than copper as a catalyst (302).

Of the five general methods which have been described, the Grignard method seems most universally applicable. Of the others, the sodium condensation method has been used principally to prepare tetrasubstituted silanes, and the direct method has been used principally to prepare dialkyl- or diaryl-substituted dichlorosilanes.

B. SYNTHESIS OF ORGANOFLUOROSILANES

1. By the Grignard reaction

The reaction of the Grignard reagent with silicon tetrafluoride is carried out in the same manner as with the other silicon halides, but with considerably different results. No mono- or di-substituted products have been reported, the main product in all cases being R_3SiF with smaller amounts of the SiR_4 compound (100, 135, 247, 248).

When silicon tetrafluoride was passed into ethyl-, propyl-, butyl-, or amylmagnesium chloride, the reaction was complete in an hour, yielding mostly the trialkylfluorosilanes (100). With the ethylmagnesium bromide, some tetraethylsilane was formed.

While (248) it is reported that tetraphenylsilane cannot be prepared from silicon tetrafluoride even with excess of the Grignard reagent, others have usually obtained some tetrasubstituted product.

Good yields of tribenzylfluorosilane with some tetrabenzylsilane using silicon tetrafluoride at room temperature have been reported (247). The silicon tetrafluoride (333) has also been introduced into the reaction in the form of sodium fluosilicate, and it has been found that there is no appreciable formation of tetrabenzylsilane until a temperature of 160–170°C. has been reached. By using five times the theoretical amount of sodium fluosilicate, the yield was increased from 20 per cent fo 54 per cent (334).

2. From silicones

Triethylfluorosilane (77) has been prepared by treating a mixture of hexaethyldisiloxane ($(C_2H_5)_6Si_2O$) and concentrated sulfuric acid with sodium or ammonium fluoride. After standing for some hours the mixture was extracted with petroleum ether, from which it was separated by distillation. Yields were reported to be quantitative.

Diethyldifluorosilane (73) has been made by gently warming a solution of diethyl silicone dissolved in concentrated sulfuric acid to which calcium fluoride had been added, whereupon a reaction set in forming a layer of a clear liquid on the surface, which on distillation proved to be diethyldifluorosilane.

Ethyltrifluorosilane (73) has been prepared by distilling a mixture of ethylsilanetriol, calcium fluoride, and sulfuric acid.

By bubbling anhydrous hydrogen fluoride through a mixture of a methyl silicone oil, sulfuric acid, 30 per cent fuming sulfuric acid, and Tergitol (wetting agent), and passing the effluent gas through absorbent sodium fluoride pellets to remove excess hydrogen fluoride, a condensate was obtained which upon distillation yielded pure trifluoromethylsilane, difluorodimethylsilane, and fluorotrimethylsilane (24a).

The reaction of anhydrous hydrogen fluoride, or mixtures which yield it, in the presence of a suitable reagent to absorb the water produced by the reaction, upon silicones yields fluorides corresponding to the organochlorosilanes from which the silicone was originally made and appears to be a general reaction.

3. From organochlorosilanes

Various fluorides with or without catalysts react with organochlorosilanes to yield organofluorosilanes.

The fluorides of lead (73), zinc (73, 252a), antimony (24b–24g), and calcium (24d) have been used. Lead fluoride reacts sluggishly and antimony fluoride rapidly, while zinc fluoride is intermediate in speed.

The three methyl- (252a) and ethyl-fluorosilanes (73), trifluorophenylsilane (73), and difluorodiphenylsilane (73) have been prepared by the reaction of zinc fluoride on the corresponding chloride. No evidence of the formation of fluorochlorides was obtained.

Organochlorosilanes are not only solvolyzed by water and liquid ammonia, but also by anhydrous hydrogen fluoride (268). When the alkylchlorosilanes are added to anhydrous hydrogen fluoride, hydrogen chloride is evolved. After standing for some hours, the residual hydrogen fluoride is removed by the addition of anhydrous sodium fluoride, and the alkylfluorosilane is purified by distillation.

C. SYNTHESIS OF ORGANOCHLOROFLUOROSILANES

By the reaction of sublimed antimony trifluoride in the presence of about 5 per cent of antimony pentachloride as a catalyst, chlorine attached to the silicon atom in an organochlorosilane may be replaced with fluorine stepwise (24b). The yields of the chlorofluorides are low compared to the completely fluorinated product. The replacement of one chlorine atom by a fluorine atom not only lowers the boiling point about 35°C., but also lowers the threshold fluorinating temperature to a considerable extent, with the result that the fluorination is greatly accelerated. In the fluorination of an organotrichlorosilane, it is difficult to obtain more than traces of the monochlorodifluoro compound by the usual reaction procedure, but the completely fluorinated product is obtained in abundance (24c, 24d, 24e). The yield of chlorofluorides can be increased by forcing the reaction as rapidly as possible, with no condensation of partially fluorinated products and with rapid removal of all gaseous products (24f, 24g).

Equal amounts of all three fluorination products of trichloromethylsilane have been obtained by passing the vapors of trichloromethylsilane over calcium fluoride powder heated to 200°C. at 700–750 mm. pressure in a rotating copper tube, although the total yield was small (24d).

IV. BEHAVIOR OF CLASSES OF ORGANOSILICON COMPOUNDS

A. NORMAL ALKYLS OF THE TYPE SiR_4, R_3SiSiR_3, ETC.

Compounds of the type SiR_4, in which all of the organic radicals (R) are alkyl or aryl hydrocarbon groups, are the most stable substances known to organosilicon chemistry. Tetraethyl- and tetramethyl-silanes are inert to alkalies and to concentrated sulfuric acid and are affected only by strong oxidizing agents. The thermostability of tetraphenylsilane and its resistance to oxidation have been commented upon at length (196), and it must be conceded that the substance is far more stable toward reagents and toward pyrolysis than are most hydrocarbons. The phenyl groups resist oxidation at the boiling point (*ca.* 450°C.), and pyrolysis of the phenyl groups sets in at some much higher (but as yet undetermined) temperature. It would be a great mistake, however, to conclude that carbon–silicon bonds in general are similarly inert or convey exceptional stability to the rest of the molecule. In molecules with very high organic content the effect of a silicon atom is greatly diluted or is entirely lost. More than this, the introduction of a silicon atom may even introduce a point of molecular instability, as is found in the ready hydrolysis of ethylphenylsilanes (355). A wide variation in chemical behavior therefore is encountered in the normal alkyls and their derivatives.

Alkyls of the type SiR_4 may be prepared by the Wurtz reaction, by the Grignard synthesis, or by the reaction of zinc, lithium, or mercury alkyls with silicon tetrachloride. It has been found that mercury diaryls are more satisfactory for preparing aryl derivatives of silicon than are the corresponding zinc compounds, while the reverse is true for the aliphatic derivatives.

Besides the alkyls in which all four groups are identical there is a long series of related alkyls containing two, three, or four different alkyl or aryl radicals. These are almost always prepared by the successive reaction of different Grignard reagents upon silicon tetrachloride, and they show reactions that are characteristic of all the constituent groups. There appears to be no steric hindrance to the attachment of very large groups; the silicon atom has a sufficiently higher atomic volume than carbon so that four tolyl or naphthyl groups may be attached. The physical constants of these and the other known normal alkyls of the type SiR_4, together with references to the original papers describing their preparation, are given in table 1.[4]

Higher alkyls of the type Si_2R_6, Si_3R_8, etc., are generally more difficult to prepare and are much more reactive than simple alkyls. Attempts to prepare alkyl derivatives of Si_2Cl_6 by sodium condensation with organic chlorides results only in fission of the silicon–silicon bond and formation of the corresponding SiR_4 compounds (318), unless the reaction is carried out in two stages according to the plan previously described (320). The regular two-stage Grignard reaction may successfully be employed. The known alkyl and aryl disilanes, together with their physical constants and references to the original papers, are listed in table 2.

B. THE ALKYLSILANES, R_nSiH_{4-n}

The replacement of hydrogen in a silane by alkyl or aryl groups has not been accomplished except by indirect means. Such hydrogen may easily be replaced with halogen, as in the chlorination of monosilane with hydrogen chloride in the presence of aluminum chloride as a catalyst. The halogen may then in turn be replaced by an organic group by the use of the Grignard reaction or by the reaction of other metal alkyls. In this way Stock (347) prepared methylsilane and dimethylsilane, which are listed with the other alkylsilanes in table 3.

The ready availability of trichlorosilane ($SiHCl_3$) has led to the preparation of alkyl derivatives through the application of Grignard reagents. Triethylsilane has also been obtained as a reduction product in the reaction of ethyl silicate with sodium and ethylzinc (203).

Cyanosilane, SiH_3CN, has been obtained by a related synthesis in which iodosilane is first obtained by the action of hydrogen iodide and aluminum iodide on monosilane, and then is treated with silver cyanide to replace the iodine with the cyanide group (290a, p. 33).

C. ORGANOSILANES WITH SUBSTITUTED ALKYL AND ARYL GROUPS

The organic radical of organosilicon compounds is capable of undergoing many of the reactions that are common to hydrocarbons. In general, the organic group may be halogenated, sulfonated, and nitrated under suitably special conditions. The alkylsilanes and alkylhalogenosilanes may be chlorinated by the reaction of sulfuryl chloride in the presence of benzoyl peroxide (330, 332) or by direct chlorination in the presence of phosphorus pentachloride and ultraviolet radiation (361), or with ultraviolet light alone (198). Chlorine so sub-

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[4] The compounds listed in the tables have been arranged in order of increasing complexity of the organic groups. Where two or more dissimilar organic groups appear in the compound, the groups are written in order of increasing complexity and are listed according to the first group. All fluorosilanes are listed in such order of their organic groups, then all chlorosilanes, etc.

TABLE 1

Tetraalkyl- and tetraaryl-silanes, R_4Si

COMPOUND	MELTING POINT	BOILING POINT	d	n_D	REFERENCES
	°C.	°C.			
$(CH_3)_4Si$		26.5	0.646[a]		(11, 12, 24, 31, 37, 41, 84, 112, 142, 279, 326, 358, 359, 362)
$(CH_3)_3SiC_2H_5$		62	0.6849[a]	1.3820[b]	(37, 41, 362)
$(CH_3)_3Si(n\text{-}C_3H_7)$		90	0.7020[a]	1.3929[b]	(37, 41, 362)
$(CH_3)_3Si(n\text{-}C_4H_9)$		115	0.7181[a]	1.4030[b]	(37, 362)
$(CH_3)_3Si(i\text{-}C_4H_9)$		108	0.7322[c]		(37, 41)
$(CH_3)_3Si(n\text{-}C_5H_{11})$		139	0.7313[a]	1.4096[b]	(362)
$(CH_3)_3Si(i\text{-}C_5H_{11})$		131.5	0.7322[c]		(37, 41)
$(CH_3)_3Si(n\text{-}C_6H_{13})$		163	0.7422[a]	1.4154[b]	(362)
$(CH_3)_3Si(n\text{-}C_7H_{15})$		184	0.7506[a]	1.4201[b]	(362)
$(CH_3)_3Si(n\text{-}C_8H_{17})$		202	0.7581[a]	1.4242[b]	(362)
$(CH_3)_3Si(n\text{-}C_{10}H_{21})$		240	0.7705[a]	1.4310[b]	(362)
$(CH_3)_3Si(n\text{-}C_{12}H_{25})$		273	0.7800[a]	1.4358[b]	(362)
$(CH_3)_3Si(n\text{-}C_{14}H_{29})$		300	0.7911[a]	1.4410[b]	(362)
$(CH_3)_3SiC_6H_5$		171.6	0.873[c]		(38, 41, 66)
$(CH_3)_3SiCH_2C_6H_5$		191	0.872[c]		(38, 41)
$(CH_3)_2Si(C_2H_5)_2$		95.8	0.7214[c]		(37, 41)
$(CH_3)_2Si(C_2H_5)(n\text{-}C_3H_7)$		121	0.7347[c]		(37, 41)
$(CH_3)_2Si(C_2H_5)(i\text{-}C_4H_9)$		138	0.7463[c]		(37, 41)
$(CH_3)_2Si(n\text{-}C_3H_7)_2$		141.5	0.7414[d]		(41)
$(CH_3)_2Si(CH_2)_5$		133.5	0.8039[a]	1.4394[e]	(39 ,41)
$(CH_3)_2Si(C_6H_5)_2$		177 (45 mm.)			(165)
$(CH_3)_2Si(C_2H_5)(C_6H_5)$		198	0.881[c]		(38, 41)
$CH_3Si(C_2H_5)_3$		127	0.7437[a]	1.4160[b]	(87, 362)
$(CH_3)(C_2H_5)(n\text{-}C_3H_7)\text{-}(C_6H_5)Si$		229			(147, 150)
$(CH_3)(C_2H_5)(n\text{-}C_3H_7)\text{-}(C_6H_5CH_2)Si$		250			(147, 149, 151)
$CH_3Si(C_6H_5)_3$	67				(192, 222, 223)
$(C_2H_5)_4Si$		153	0.7662[a]	1.4268[b]	(4, 21, 24, 37, 41, 43, 44, 67, 81, 82, 83, 86, 87, 89, 94, 100, 129, 133, 134, 135, 178, 203, 318, 348, 352, 359, 362)
$(C_2H_5)_3SiCH{=}CH_2$		146			(354)
$(C_2H_5)_3Si(n\text{-}C_3H_7)$		173	0.7724[a]	1.4308[b]	(38, 41, 43, 44, 66, 362)

TABLE 1—*Continued*

COMPOUND	MELTING POINT	BOILING POINT	d	n_D	REFERENCES
	°C.	°C.			
$(C_2H_5)_3Si(n\text{-}C_4H_9)$		192	0.7786[a]	1.4348[b]	(38, 41, 362)
$(C_2H_5)_3Si(i\text{-}C_4H_9)$		187	0.784[c]		(38, 41, 66)
$(C_2H_5)_3Si(n\text{-}C_5H_{11})$		211	0.7835[a]	1.4377[b]	(362)
$(C_2H_5)_3Si(i\text{-}C_5H_{11})$		205	0.785[c]		(38, 41, 66)
$(C_2H_5)_3Si(n\text{-}C_6H_{13})$		230	0.7880[a]	1.4400[b]	(362)
$(C_2H_5)_3Si(n\text{-}C_7H_{15})$		247	0.7907[a]	1.4422[b]	(362)
$(C_2H_5)_3Si(n\text{-}C_8H_{17})$		262	0.7971[a]	1.4438[b]	(362)
$(C_2H_5)_3Si(n\text{-}C_{10}H_{21})$		293	0.8036[a]	1.4472[b]	(362)
$(C_2H_5)_3SiC_6H_5$		239	0.906[f]		(38, 41, 107, 129, 193, 206, 207)
$(C_2H_5)_3SiCH_2C_6H_5$		268			(193)
$p\text{-}(C_2H_5)_3SiC_6H_4C_2H_5$		118 (18 mm.)	0.8950[a]		(106)
$p\text{-}(C_2H_5)_3SiC_6H_4Si(C_2H_5)_3$		196 (16.5 mm.)	0.8967[a]		(106)
$(C_2H_5)_3SiGe(C_6H_5)_3$	93.5				(193)
$(C_2H_5)_2Si(n\text{-}C_3H_7)_2$					(43, 44)
$(C_2H_5)_2Si(CH_2)_5$		184–194			(39, 41)
$(C_2H_5)_2Si(C_6H_5)_2$		297			(129, 173, 206, 207, 208)
$(C_2H_5)_2Si(C_6H_5)(p\text{-}C_6H_4C_2H_5)$		170 (14 mm.)	0.9831[a]		(106)
$C_2H_5Si(n\text{-}C_3H_7)_3$					(43, 44)
$C_2H_5Si(C_6H_5)_3$	76				(222, 223, 333)
$(C_2H_5)(n\text{-}C_3H_7)(i\text{-}C_4H_9)(C_6H_5CH_2)Si$		283			(174)
$(C_2H_5)(n\text{-}C_3H_7)_2(C_6H_5CH_2)Si$		280			(223)
$(C_2H_5)(n\text{-}C_3H_7)(C_6H_5CH_2)_2Si$		264 (90 mm.)			(46)
$(C_2H_5)(C_6H_{11})_2(C_6H_5)Si$	52–3	*ca.* 370			(52, 173)
$(C_2H_5)(n\text{-}C_3H_7)(C_6H_5)(C_6H_5CH_2)Si$		250			(150)
$(n\text{-}C_3H_7)_4Si$		212	0.7883[c]		(43, 44, 257, 258, 319, 348, 359)
$(n\text{-}C_4H_9)_4Si$		157 (22 mm.)	0.8008[a]	1.4465[b]	(104b, 278, 352)
$(n\text{-}C_5H_{11})_4Si$		318	0.8252[j]	1.4510[j]	(318)
$(i\text{-}C_5H_{11})_4Si$		275			(351)
$C_{12}H_{26}Si$		208			(258)
$(C_6H_5)_4Si$	233	428 (*cf.* reference 212b)			(19, 48, 69, 98, 99, 129, 192, 217, 218, 220, 272, 273, 318, 319, 320, 321, 327, 348)

TABLE 1—*Concluded*

COMPOUND	MELTING POINT	BOILING POINT	d	n_D	REFERENCES
	°C.	°C.			
$(C_6H_5CH_2)_4Si$	127.5		1.0776[k]		(218, 247, 272, 333, 334)
$(m\text{-}CH_3C_6H_4)_4Si$	150.8		1.1188[k]		(273, 319)
$(p\text{-}CH_3C_6H_4)_4Si$	228		1.0793		(48, 272, 273, 319)
$(p\text{-}C_6H_5C_6H_4)_4Si$	274				(48, 318)
$(C_4H_3S)_4Si$	135.5				(195)

a, d_4^{20}; b, n_D^{20}; c, d_4^{15}; d, $d_4^{17.6}$; e, $n_D^{20.1}$; f, d_{15}^{15}; g, d_4^{22}; h, n_D^{22}; i, d_4^{32}; j, n_D^{25}; k, d^{20}.

TABLE 2

Organopolysilanes

COMPOUND	MELTING POINT	BOILING POINT	d	n_D	REFERENCES
	°C.	°C.			
$[(CH_3)_3Si]_2$	14.0–14.4	113	0.7230[d]	1.4207[e]	(24, 30, 38, 41)
$[(C_2H_5)_3Si]_2$		252	0.8403[a]		(67, 90, 93, 94, 95, 193)
$[(C_2H_5)(n\text{-}C_3H_7)\text{-}(C_6H_5)Si]_2$		268 (100 mm.)			(161)
$(C_2H_5)_2(C_6H_5)_8Si_4$	253–4				(162)
$[(n\text{-}C_3H_7)_3Si]_2$		114 (3 mm.)	0.8693[b]	1.4740[c]	(319)
$[(C_6H_5)_3Si]_2$	352				(154, 192, 316, 319, 320)
$(C_6H_5)_8Si_4$	>300				(186)
$(C_6H_5)_8Si_4I_2$	>250				(186)
$(C_6H_5)_8Si_4Cl_2$	180				(186)
$(C_6H_5)_8Si_4O$	*ca.* 225				(186)
$(C_6H_5)_8Si_4O_2$	*ca.* 245				(186)
	ca. 222				(186)
$[(C_6H_5CH_2)_3Si]_2$	194				(320)
$[(p\text{-}CH_3C_6H_4)_3Si]_2$	345				(319)
$[(p\text{-}CH_3C_6H_4)_2Si]_4$	310				(341)
	292				(341)
$[(p\text{-}CH_3C_6H_4)_2Si]_4O$	228–9				(341)
$[(p\text{-}CH_3C_6H_4)_2Si]_4I_2$	300 dec.				(341)

a, d_{20}^{20}; b, d_4^{26}; c, n_D^{20}; d, $d_4^{24.4}$; e, $n_D^{24.4}$.

stituted may be replaced by iodine by means of the sodium iodide reagent (361). The (chloromethyl)silanes and siloxanes undergo hydrolytic cleavage in the presence of alkaline catalysts to give halogenomethanes and siloxanes (198, 198a). In contrast to this reaction the carbon-chlorine bond of β-chloroethyltrichlorosilane reacts quantitatively with dilute alkali (332):

$$ClCH_2CH_2SiCl_3 \xrightarrow[H_2O]{OH^-} CH_2{=}CH_2 + Si(OH)_4 + 4Cl^-$$

The beta chlorine can be removed by dehydrohalogenation using dry quinoline without cleavage of the carbon–silicon bond, in this way forming vinyl derivatives (117). A chlorine in the gamma position, while it can not be titrated, undergoes reaction with alcoholic caustic at room temperature, yielding cyclopropane in the case of γ-chloropropyltrichlorosilane (330).

Organosilanes containing halogenated aryl groups may be prepared by direct halogenation (292) or by an indirect synthesis in which a bromohalogenobenzene is allowed to react with magnesium to form the halogenophenylmagnesium bromide, which, in turn, reacts with silicon tetrachloride to form a halogenochlorophenylsilane (35a, 106, 107). The chlorine attached to silicon in these compounds may be replaced by other organic groups by further Grignard synthesis (106, 107). When the halogen that occurs in a halogenophenyltrialkylsilane is bromine it may react with magnesium to give the corresponding Grignard reagent (106, 107). This Grignard reagent is then capable of reaction with aldehydes to give the corresponding alcohols, or with other organometallic compounds to give condensation products.

TABLE 3

Organomonosilanes, R_nSiH_{4-n}

COMPOUND	MELTING POINT	BOILING POINT	d	REFERENCES
	°C.	*°C.*		
CH_3SiH_3	−157	−57	0.62[a]	(347, 366)
$(CH_3)_2SiH_2$	−150	−20	0.68[b]	(347, 366)
$(CH_3)_3SiH$		9		(349)
$(C_2H_5)_3SiH$		107		(203)
$(n\text{-}C_3H_7)_3SiH$		107–1	0.7621[c]	(257, 258)
$(i\text{-}C_4H_9)_3SiH$		205		(351)
$(i\text{-}C_5H_{11})_3SiH$		245		(351)
$(C_6H_5)_3SiH$	202			(192, 208, 281)
$(C_6H_5CH_2)_3SiH$	91			(75, 272)
$(C_6H_{11})_2(C_6H_5)SiH$		182 (4 mm.)		(52)

a, d^{-57}; b, d^{-80}; c, d^{15}_4.

Kipping succeeded in nitrating the phenyl group of a number of organosilicon compounds (170, 173, 178, 356), and found that in general most of the nitration occurred in the meta position. He reduced these nitro compounds to the corresponding amines and formed derivatives of these (171, 173) with acetic acid and acetone. The phenyl and benzyl groups attached to silicon have both been sulfonated with sulfuric acid (41, 42, 46, 47, 148, 149, 150, 151, 152, 153, 154, 161, 174, 179, 215, 216, 222, 223). A list of these compounds, with the references to the original papers, is given in table 4.

D. ALKYL- AND ARYL-HALOGENOSILANES, R_nSiX_{4-n}

The organosilicon halides or alkylhalogenosilanes have been popular as intermediates for the preparation of a great many of the organosilicon compounds,

TABLE 4

Organosilanes with substituted alkyl and aryl groups

COMPOUND	MELTING POINT	BOILING POINT	d	n_D	REFERENCES
	°C.	°C.			
$(CH_3)_3SiCH_2Cl$		97.1	0.8791[a]	1.4180[b]	(361)
$(CH_3)_3SiCH_2I$		139.5	1.4431[a]	1.4917[b]	(361)
$(CH_3)_3SiCH_2HgCl$	75				(361)
$(CH_3)_3SiCHClCH_3$		117.8		1.4242[b]	(332)
$(CH_3)_3SiCH(HgCl)CH_3$	97				(332)
$p\text{-}(CH_3)_3SiCH_2C_6H_4SO_3H$	116				(41, 42)
$p\text{-}(CH_3)_3SiCH_2C_6H_4SO_2Cl$	46				(41, 42)
$p\text{-}(CH_3)_3SiCH_2C_6H_4SO_2Br$	60.5				(41, 42)
$p\text{-}(CH_3)_3SiCH_2C_6H_4SO_2NH_2$	81.5				(41, 42)
$p\text{-}(CH_3)_3SiCH_2C_6H_4SO_2NHCH_3$	77				(41, 42)
$p\text{-}(CH_3)_3SiCH_2C_6H_4SO_2NHC_6H_5$	125				(41, 42, 371)
$p\text{-}(CH_3)_3SiCH_2C_6H_4SO_2N(CH_3)(C_6H_5)$	72				(41, 42)
$p\text{-}(CH_3)_3SiCH_2C_6H_4SO_2NHCH_2C_6H_5$	131				(41, 42)
$p\text{-}(CH_3)_3SiCH_2C_6H_4SO_2NH(o\text{-}C_6H_4CH_3)$	153				(41, 42)
$p\text{-}(CH_3)_3SiCH_2C_6H_4SO_2NH(p\text{-}C_6H_4CH_3)$	98				(41, 42)
$(C_2H_5)_3SiCH_2CH_2Cl$		80 (9 mm.)	0.9158	1.4562	(83, 86, 87, 253, 354)
$(C_2H_5)_3SiCHClCH_3$		72 (9 mm.)	0.9147	1.4538	(354)
$(C_2H_5)_3SiCH_2CHCl_2$		208			(87)
$(C_2H_5)_3SiCH_2CH_2OH$		190			(87, 253)
$(C_2H_5)_3SiCH_2CH_2OCOCH_3$		211			(87, 253)
$p\text{-}(C_2H_5)_3SiC_6H_4Cl$		137 (14.5 mm.)	1.0056[c]	1.5219[d]	(107)
$p\text{-}(C_2H_5)_3SiC_6H_4Br$		149 (14 mm.)	1.1652[a]	1.5332[b]	(107)
$p\text{-}(C_2H_5)_3SiC_6H_4I$		165 (13 mm.)	1.3304[a]	1.5623[b]	(107)
$(C_2H_5)_3SiC_6H_4NO_2$		307			(173)
$p\text{-}(C_2H_5)_3SiC_6H_4Pb(CH_3)$		191 (17 mm.)	1.3997[e]	1.5494[f]	(107)
$p\text{-}(C_2H_5)_3SiC_6H_4Sn(C_2H_5)_3$		214 (18 mm.)	1.1216[g]	1.5276[h]	(107)
$p\text{-}(C_2H_5)_3SiC_6H_4As(C_6H_5)_2$		280 (17 mm.)	1.1661[i]	1.6146[j]	(107)
$[p\text{-}(C_2H_5)_3SiC_6H_4As(C_6H_5)_2]\cdot HgCl_2$	188				(107)
$[p\text{-}(C_2H_5)_3SiC_6H_4As(C_6H_5)_2]\cdot HgBr_2$	181				(107)
$[p\text{-}(C_2H_5)_3SiC_6H_4As(C_6H_5)_2]\cdot HgI_2$	139.5				(107)

TABLE 4—*Concluded*

COMPOUND	FREEZING POINT	BOILING POINT	d	n_D	REFERENCES
	°C.	°C.			
p-$(C_2H_5)_3SiC_6H_4CHOH$-CH_3		174 (14.5 mm.)	0.9596[a]		(106)
p-$(C_2H_5)_3SiC_6H_4CHOH$-CH_2CH_3		185 (16.5 mm.)	0.9575[a]		(106)
p-$(C_2H_5)_3SiC_6H_4CHOH$-$(CH_2)_2CH_3$		200 (21 mm.)	0.9491[a]		(106)
p-$(C_2H_5)_3SiC_6H_4CHOH$-$CH(CH_3)_2$		191 (18 mm.)	0.9512[a]		(106)
$(C_2H_5)_2(C_6H_5)(p$-$BrC_6H_4)Si$		203 (13.7 mm.)	1.2153[a]		(106)
$(C_2H_5)_2Si(m$-$C_6H_4NO_2)_2$	103				(173)
$(C_2H_5)_2Si(m$-$C_6H_4NH_2)_2$	90				(173)
$(C_2H_5)_2Si(m$-C_6H_4NH-$COCH_3)_2$	164				(173)
p-$(n$-$C_3H_7)_3SiC_6H_4Cl$		160 (14 mm.)	0.9708[k]	1.5123[l]	(107)
$(m$-$C_6H_4NO_2)_4Si$	256				(170, 178, 356)
$(m$-$C_6H_4NH_2)_4Si$	380 dec.				(171)
$(m$-$C_6H_4NHCOCH_3)_4Si$	301				(171)
$[m$-$C_6H_4NHCH(CH_3)_2]_4Si$	135				(171)
$C_{12}H_{27}BrSi$		138 (60 mm.)			(258)

a, d_4^{20}; b, n_D^{20}; c, $d_4^{9.6}$; d, $n_2^{9.6}$; e, $d_4^{23.4}$; f, $n_D^{23.4}$; g, $d^{21.2}$; h, $n_D^{21.2}$; i, $d_4^{21.3}$; j, $n_D^{21.3}$; k, d_4^9; l, n_D^9

See also chlorine-substituted organosiloxanes and halogenosilanes in their respective tables.

because the halogen atoms easily undergo replacement reactions as well as hydrolysis and ammonolysis. Synthesis by the stepwise replacement of the halogen atoms in a silicon halide has already been discussed, and also the preparation by the direct reaction of hydrocarbon halides with elementary silicon. The properties of the known compounds and the references to the original papers are listed in table 5. The change of boiling point with consecutive replacement of chlorine atoms in silicon tetrachloride by methyl, ethyl, and propyl groups is shown in figure 1.

1. *Properties of the organochlorosilanes*

The trialkylchlorosilanes, R_3SiCl, are sources of the hexaalkyldisiloxanes and disilazanes through reaction of such chlorides with water or ammonia. Under special conditions the hydrolysis to silanols of the type R_3SiOH has been accomplished without the simultaneous condensation of such silanols to the corresponding disiloxanes (307).

The dialkyldihalogenosilanes are the intermediates from which the linear silicon polymers are made, and therefore have been of particular importance (290a). Their preparation by the direct reaction has already been discussed. Most of the other methods of synthesis may also be applied, with yields that are somewhat higher than would be expected from theory (95b); it appears that the

TABLE 5

Organohalogenosilanes

COMPOUND	MELTING POINT	BOILING POINT	d	n_D	REFERENCES
Fluorosilanes					
	°C.	°C.			
CH_3SiF_3	−72.8	−30.2			(24d, 268)
$(CH_3)_2SiF_2$	−87.5	2.7			(24g, 268)
$(CH_3)_3SiF$	−74.3	16.4			(24g, 252a)
$C_2H_5SiF_3$	−113.3	−4.2			(24b, 73)
$(C_2H_5)_2SiF_2$	−78.7	60.9			(73)
$(C_2H_5)_3SiF$		109	0.8354[a]	1.3900[b]	(77, 78, 100)
n-$C_3H_7SiF_3$		24.9			(24c)
$(n$-$C_3H_7)_3SiF$		175	0.8339[a]	1.4107[b]	(100)
i-$C_3H_7SiF_3$	−127.6	15.7			(24f)
n-$C_4H_9SiF_3$	−96.9	52.4	1.006[c]		(24e, 268)
$(n$-$C_4H_9)_2SiF_2$		154	0.9048[c]		(268)
$(n$-$C_4H_9)_3SiF$		224	0.8372[a]	1.4250[b]	(100, 268)
n-$C_5H_{11}SiF_3$		77	0.9923[c]		(268)
$(n$-$C_5H_{11})_2SiF_2$		193	0.8972[c]		(268)
$(n$-$C_5H_{11})_3SiF$		267	0.8389[a]	1.4305[b]	(100, 268)
$C_6H_5SiF_3$		102	1.201		(73, 268)
$(C_6H_5)_2SiF_2$		247	1.155		(73, 268)
$(C_6H_5)_3SiF$	64	205 (10 mm.)			(248)
$(C_6H_5CH_2)_3SiF$	79	235.5			(247)
CH_3SiF_2Cl	*ca.* −110	*ca.* −0.5			(24d)
CH_3SiFCl_2	−98.7	29.5			(24d)
$(CH_3)_2SiFCl$	−85.1	36.4			(24g)
$C_2H_5SiF_2Cl$	s	27.2			(24b)
$C_2H_5SiFCl_2$	s	62.2			(24b)
n-$C_3H_7SiF_2Cl$	s	55–57 (745 mm.)			(24c)
n-$C_3H_7SiFCl_2$	s	88–89 (745 mm.)			(24c)
i-$C_3H_7SiF_2Cl$	s	48.8			(24f)
i-$C_3H_7SiFCl_2$	s	84.0			(24f)
n-$C_4H_9SiF_2Cl$	s	84.0			(24e)
n-$C_4H_9SiFCl_2$	s	116.1			(24e)
Chlorosilanes					
CH_3SiHCl_2	−93	41	1.105[e]		(313a, 347)
CH_3SiH_2Cl	−134	8			(347, 366)
CH_3SiCl_3	−77.8	65.7			(24d, 32, 101, 293)
$(CH_3)_2SiCl_2$	−76.1	70.0	1.06[d]		(24g, 32, 101, 128, 293)
$(CH_3)_3SiCl$	−57.7	57.3	0.8536[e]		(24g, 102, 214, 237, 293, 349)

TABLE 5—*Continued*

COMPOUND	MELTING POINT	BOILING POINT	d	n_D	REFERENCES
Chlorosilanes—*Continued*					
	°C.	°C			
$(CH_3)_2(CH_2Cl)SiCl$		115			(198)
$(CH_3)(CH_2Cl)_2SiCl$		172			(198)
$(CH_3)_2(CHCl_2)SiCl$		149.5			(198)
$(CH_3)_2SiCl(OC_4H_9(n))$		142			(308)
$(CH_3)(CH_2Cl)SiCl_2$		121.3			(198)
$(CH_3)(CHCl_2)SiCl_2$		107.5 (225 mm.)			(198)
$(CH_3)(CCl_3)SiCl_2$	99	109 (150 mm.)			(198)
$(CH_3)(CH_3CHCl)SiCl_2$		136			(117)
$(CH_3)(CH_2ClCH_2)SiCl_2$		157			(117)
$(CH_3)(CH_2{=}CH)SiCl_2$		93	1.085[f]		(117)
$(CH_3)_2(CH_2{=}CHCH_2)SiCl$		113	0.922[g]		(117)
$(CH_3)(CH_2{=}CHCH_2)SiCl_2$		120	1.057[g]		(117)
$Cl[(CH_3)_2SiO]Si(CH_3)_2Cl$	−37	138	1.038[h]		(266)
$Cl[(CH_3)_2SiO]_2Si(CH_3)_2Cl$	−53	184	1.018[h]		(266)
$Cl[(CH_3)_2SiO]_3Si(CH_3)_2Cl$	−62	222	1.011[h]		(266)
$Cl[(CH_3)_2SiO]_4Si(CH_3)_2Cl$	*ca.* −80	138 (20 mm.)	1.005[h]		(266)
$Cl[(CH_3)_2SiO]_5Si(CH_3)_2Cl$	*ca.* −80	161 (20 mm.)	1.003[h]		(266)
$(CH_3)(C_6H_5)SiCl_2$		82.5 (13 mm.)	1.1876[d]		(128)
$C_2H_5SiCl_3$	−105.6	97.9	1.2388[i]		24b, 41, 91, 149, 203)
$C_2H_5SiCl(OC_2H_6)_2$		151			(203)
$(C_2H_5)_2SiCl_2$	−96.5	129	1.106[j]		(2, 41, 128, 203, 231)
$(C_2H_5)_2SiCl(OC_2H_5)$		147			(199, 203)
$(C_2H_5)_3SiCl$		143.5	0.9249		(78, 200, 203, 231)
$(C_2H_5)(n\text{-}C_3H_7)SiCl_2$		153	1.0420[k]		(37, 41)
$(C_2H_5)(i\text{-}C_4H_9)SiCl_2$		169	1.0235[b]		(37, 41)
$CH_2ClCH_2SiCl_3$		152			(117, 332)
$CH_3CHClSiCl_3$		138			(117, 332)
$(C_2H_5)(n\text{-}C_3H_7)(C_6H_5)SiCl$		178 (100 mm.)			(147, 150, 161)
$(C_2H_5)(n\text{-}C_3H_7)(C_6H_5CH_2)SiCl$		195 (100 mm.)			(146, 147, 151, 161)
$(C_2H_5)(i\text{-}C_4H_9)(C_6H_5CH_2)SiCl$		200 (100 mm.)			(215)

TABLE 5—*Continued*

COMPOUND	MELTING POINT	BOILING POINT	d	n_D	REFERENCES
		Chlorosilanes—*Continued*			
	°C.	°C.			
$(C_2H_5)(C_6H_5)SiCl_2$		230	1.159 [l]		(38, 41, 128, 146, 150)
$(C_2H_5)(C_6H_5)_2SiCl$		207 50 mm.			(147, 222, 223)
$(C_2H_5)(C_6H_5CH_2)SiCl_2$		169 (100 mm.)			(147, 151, 215, 282, 368)
$(C_2H_5)(C_6H_5CH_2)_2SiCl$		246 (100 mm.)			(46, 282)
p-$(C_2H_5)_3SiC_6H_4SiCl_3$		175 (13.5 mm.)			(106)
$CH_2{=}CHSiCl_3$		92	1.264 [e]		(117)
$(CH_2{=}CH)_2SiCl_2$		119	1.088 [e]		(117)
n-$C_3H_7SiCl_3$		122.7	1.1967 [h]		(24c, 41, 246, 249, 330)
$(n$-$C_3H_7)_2SiCl_2$		175	1.035 [l]		(41)
i-$C_3H_7SiCl_3$	−87.7	119.4			(24f)
$C_2H_5CHClSiCl_3$		157			(330)
$CH_3CHClCH_2SiCl_3$		162			(330)
$CH_2ClC_2H_4SiCl_3$		178.5			(330)
$CH_2{=}CHCH_2SiCl_3$		117.5	1.211 [e]		(117)
$(CH_2{=}CHCH_2)HSiCl_2$		97	1.086 [e]		(117)
$(CH_2{=}CHCH_2)_2SiCl_2$		166 (83 mm.)			(117)
n-$C_4H_9SiCl_3$		148.9	1.1623 [m]		(24e, 37, 41)
i-$C_4H_9SiCl_3$		141	1.154 [h]		(37, 41)
i-$C_4H_9SiCl(OCH_3)(OC_2H_5)$		155			(178)
n-$C_5H_{11}SiCl_3$		107 (120 mm.)			(362)
i-$C_5H_{11}SiCl_3$		46 (9 mm.)			(41, 249)
$(CH_2)_5SiCl_2$		170	1.1560 [h]	1.4697 [n]	(39, 41)
n-$C_6H_{13}SiCl_3$		127 (98 mm.)			(362)
$C_6H_{11}SiCl_3$		210			(256)
$(C_6H_{11})_2SiCl_2$		150 (4 mm.)			(256)
$(C_6H_{11})(C_8H_5)SiCl_2$		124 (0.5 mm.)			(51)
$(C_6H_{11})_2(C_6H_5)SiCl$	47	190 (2 mm.)			(51)
n-$C_8H_{17}SiCl_3$		119 (28 mm.)			(362)

TABLE 5—*Continued*

COMPOUND	MELTING POINT	BOILING POINT	d	n_D	REFERENCES
Chlorosilanes—*Continued*					
	°C.	°C.			
n-$C_{10}H_{21}SiCl_3$		183 (84 mm.)			(362)
n-$C_{12}H_{25}SiCl_3$		120 (3 mm.)			(362)
n-$C_{14}H_{29}SiCl_3$		156 (3 mm.)			(362)
$Cl_3SiCH_2SiHCl_2$		52 (10 mm.)			(263)
$(Cl_3Si)_2CH_2$		64 (10 mm.)			(263)
$[Cl_2SiCH_2]_3$	81–82.5	130 (10 mm.)			(263, 264)
$[Cl_2SiCH_2]_n$, $(n>3)$		200 (10 mm.)			(263)
$(Cl_3SiCH_2)_2$	27–9	93 (25 mm.)			(263)
$[(CH_3CO)_2CH]_3SiCl$	96–8 dec.				(305)
$C_6H_5SiCl_3$		201.5	1.3256^m		(41, 204, 207, 245, 250, 289, 302, 320)
$(C_6H_5)_2SiCl_2$		305.2			(128, 159, 180, 289, 302, 321)
$(C_6H_5)_2SiCl(OC_6H_5)$		253 (40 mm.)			(167)
$(C_6H_5)_3SiCl$	88–9	378			(178, 194, 223, 273, 302)
p-$ClC_6H_4SiCl_3$		105 (15 mm.)			(107)
p-$BrC_6H_4SiCl_3$		123 (15 mm.)			(107)
$(p$-$BrC_6H_4)_2SiCl_2$		239 (21 mm.)			(107)
$(C_6H_5)(C_6H_5CH_2)SiCl_2$		318			(224, 286)
$(C_6H_5)(p$-$BrC_6H_4)SiCl_2$		200 (4 mm.)	1.5005^h		(106)
$[Cl(C_6H_5)_2Si]_2O$	38	240 (1 mm.)			(35)
$Cl[(C_6H_5)_2SiO]_2Si(C_6H_5)_2Cl$		300 (1 mm.)			(35)
$C_6H_5CH_2SiCl_3$		216	1.2889^p		(38, 41, 231, 246, 249)
$(C_6H_5CH_2)_2SiCl_2$	50–2	243 (100 mm.)			(231)

TABLE 5—*Concluded*

COMPOUND	MELTING POINT	BOILING POINT	d	n_D	REFERENCES
Chlorosilanes—*Concluded*					
	°C.	°C.			
$(C_6H_5CH_2)_3SiCl$	14				(231, 282)
$C_6H_4CHClSiCl_3$		162 (75 mm.)			(332)
p-$CH_3C_6H_4SiCl_3$		219			(206, 207, 271)
$(p$-$CH_3C_6H_4)_2SiCl_2$		238 (50 mm.)			(271, 341)
$(p$-$CH_3C_6H_4)_3SiCl$	116				(340)
α-$C_{10}H_7SiCl_3$		168 (22 mm.)	1.3760		(249)
$(C_6H_5)_8Si_4Cl_2$	180				(186)
Bromosilanes					
CH_3SiBr_3		133.5			(289)
$(CH_3)_2SiBr_2$		112.3			(289)
$(CH_3)_3SiBr$		80	1.189^h		(101a)
$(C_2H_5)_3SiBr$		66.5 (24 mm.)	1.1766^h		(78, 87, 106 193)
$(n$-$C_3H_7)_3SiBr$		213			(257, 258)
$(i$-$C_4H_9)_3SiBr$		245			(351)
$(i$-$C_5H_{11})_3SiBr$		279			(351)
$(C_6H_5)_2SiBr_2$		180 (12 mm.)			(208, 289)
$(C_6H_5)_3SiBr$	119				(192, 208)
Iodosilanes					
$(C_6H_5)_8Si_4I_2$	>250				(186)
$[(p$-$CH_3C_6H_4)_2Si]_4I_2$	300 dec.				(341)

a, d_4^{25}; b, n_D^{25}; c, $d_4^{26.5}$; d, d_{25}^{25}; e, d_{27}^{27}; f, d_{27}^{25}; g, d_{27}^{27}; h, d_4^{20}; i, $d_4^{19.4}$; j, d^{15}; k, $d_4^{20.7}$; l, d_4^{15}; m, $d_4^{18.8}$; n, $n_D^{20.2}$; p, $d_4^{19.3}$; r, d^0; s, forms glass.

symmetry of the actions of the dihalosilanes decreases their reactivity toward alkylating reagents. Hydrolysis of the dialkyldihalosilanes yields corresponding silanediols of the type $R_2Si(OH)_2$, which can be isolated if the condensation to a siloxane does not proceed rapidly at room temperature. In general, the larger the organic group the slower will be that condensation. Strong acids and alkalies are known to have a marked catalytic effect on the condensation (35, 159).

The alkyltrihalogenosilanes, $RSiX_3$, are by-products of the direct reaction and may be obtained by the substitution of a single chlorine atom in silicon tetrachloride. These substances hydrolyze very readily to form the corresponding silanetriols, $RSi(OH)_3$. These silanetriols condense very readily to highly polymeric or cross-linked products rather than to the so-called "siliconic acids" of the type RSiOOH, as was originally supposed (245).

The formation of alkylhalogenosilanes with unsaturated organic groups requires special methods. Trichlorovinylsilane may be made by the direct reaction of vinyl chloride with silicon (117), but the yields are relatively poor because of the pyrolysis of vinyl chloride at the temperature of the reaction. It is more convenient first to prepare trichloroethylsilane, and then to chlorinate this compound to give trichloro(chloroethyl)silane, followed by dehydrohalogenation to leave trichlorovinylsilane (117). Such removal of hydrogen chloride is aided by the action of a tertiary amine such as quinoline. Of course the absorption of unsaturated hydrocarbons by silicon tetrachloride (325) is particularly suited to the preparation of such unsaturated halogenosilanes (see table 5).

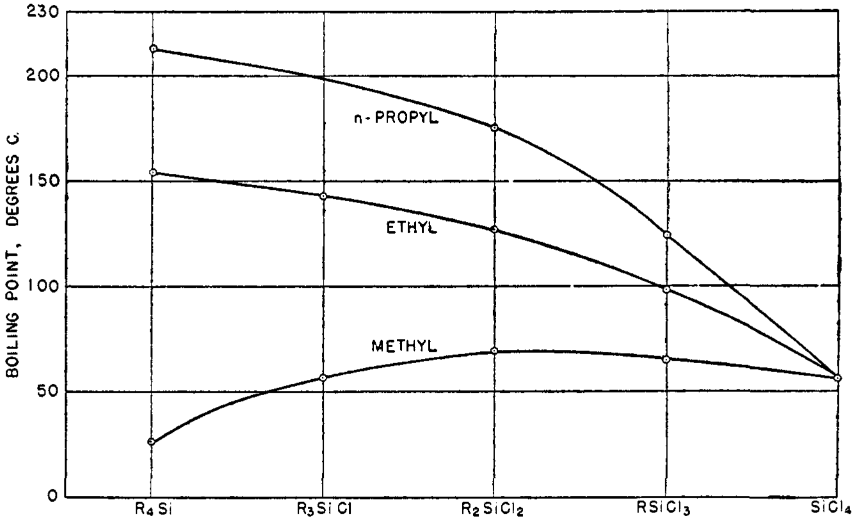


FIG. 1. Change in boiling points with successive replacement of chlorine atoms by alkyl groups.

2. *Properties of the organochlorofluorosilanes*

The physical properties of organochlorofluorosilanes as shown in table 5 are seen to be intermediate between those of the corresponding fluorosilanes and chlorosilanes. Swarts observed that the replacement of chlorine in a polychlorinated organic compound by fluorine gave a regular, almost constant, lowering of the boiling point. From the following table (p. 119), it is clear that the Swarts rule is applicable to the alkyltrichlorosilanes.

The solubilities of the chlorofluorosilanes in organic solvents resemble those of the organofluorosilanes. They all hydrolyze, but more slowly with increasing fluorine content and with increasing size of the organic radical. It is thought probable from the behavior of the *n*-butyl compounds that the silicon–chlorine bond is more susceptible to solvolysis than is the silicon–fluorine bond (24e).

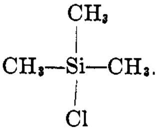
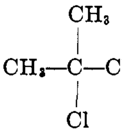
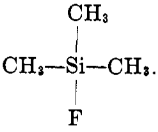
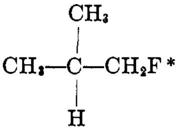
Boiling-point differences of ethyl- and isopropyl-trihalogenosilanes

COMPOUND	BOILING POINT	DIFFERENCE	AVERAGE
	°C.	°C.	
$C_2H_5SiCl_3$	97.9		34.1
		35.7	
$C_2H_5SiCl_2F$	62.2		
		35.0	
$C_2H_5SiClF_2$	27.2		
		31.0	
$C_2H_5SiF_3$	−4.2		
i-$C_3H_7SiCl_3$	119.4		34.5
		35.4	
i-$C_3H_7SiCl_2F$	84.0		
		35.2	
i-$C_3H_7SiClF_2$	48.8		
		33.1	
i-$C_3H_7SiF_3$	15.7		

This suggests that it might be possible to achieve only partial alcoholysis of the n-butylchlorofluorosilanes with the production of mixed alkoxyfluorosilanes.

In the absence of moisture, alkylchlorofluorosilanes seem to be inert to iron, steel, copper, platinum, mercury, and nichrome (24e).

If one considers the alkylhalogenosilanes as carbon compounds in which an atom of silicon has replaced an atom of carbon, it is surprising to note the slight effect on the boiling point which this replacement has, as shown in the following table.

FORMULA	BOILING POINT	FORMULA	BOILING POINT
	°C.		°C.
$CH_3SiCl_2CH_3$	70.0	$CH_3CCl_2CH_3$	69.7
$CH_3SiClFCH_3$	36.4	$CH_3CClFCH_3$	35.0
$CH_3SiF_2CH_3$	2.7	$CH_3CF_2CH_3$	−0.6 to −0.2
 $CH_3-\overset{\displaystyle CH_3}{\underset{\displaystyle Cl}{Si}}-CH_3$	57.3	 $CH_3-\overset{\displaystyle CH_3}{\underset{\displaystyle Cl}{C}}-CH_3$	51–52
 $CH_3-\overset{\displaystyle CH_3}{\underset{\displaystyle F}{Si}}-CH_3$	16.4	 $CH_3-\overset{\displaystyle CH_3}{\underset{\displaystyle H}{C}}-CH_2F$*	16

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* The corresponding carbon analog could not be found. This compound is nearly analogous.

3. *Properties of the organofluorosilanes*

The physical properties of organofluorosilanes are shown in table 5. The change in boiling points with successive replacements of fluorine atoms by alkyl groups is shown in figure 2.

In the liquid state the alkylfluorosilanes are colorless mobile liquids, soluble in petroleum ether (77), benzene, toluene, various chlorinated organic solvents, such as carbon tetrachloride, tetrachloroethylene, chlorobenzene, dichlorobenzene, ether, and ethyl acetate (24c, 24e, 100, 333).

The thermal stability of organofluorosilanes is remarkable. Trifluoromethylsilane is quite stable at 400°C. and decomposes only slowly at 600°C. Even dibutyldifluorosilane can be heated in a glass tube to 300°C. without apparent decomposition (268).

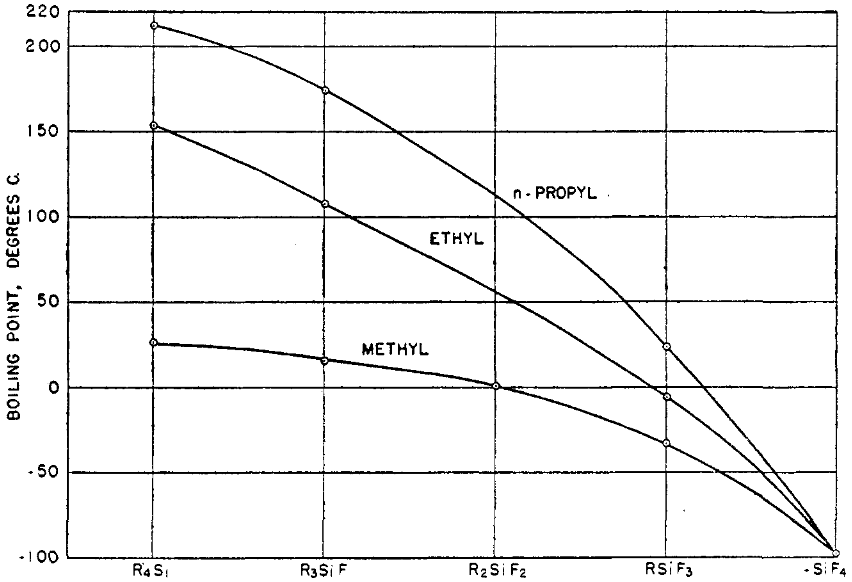

FIG. 2. Change in boiling points with successive replacement of fluorine atoms by alkyl groups.

In general, the organofluorosilanes differ from the other halosilanes in being more difficult to hydrolyze. This resistance to hydrolysis increases with replacement of fluorine by alkyl groups; for example, ethyltrifluorosilane fumes in moist air and hydrolyzes immediately in contact with water (73), while diethyldifluorosilane sinks in water as oily drops and only after 12 hr. standing does a thin film of hydrolysis products appear at the interface. Triethylfluorosilane is even more resistant to hydrolysis. However, all three are quickly hydrolyzed in basic solutions.

Similarly, in an alkyltrifluorosilane, increase in the size of the alkyl group retards hydrolysis. In methyl-, ethyl-, and propyl-trifluorosilanes the odor of the compounds is masked by that of the hydrolytic product, hydrogen fluoride, while in the case of *n*-butyltrifluorosilane, hydrolysis is so slow that the peculiar sharp suffocating odor of the compound itself can be recognized.

When *n*-butyltrichlorosilane is added to acetone, it slowly reacts to give a deep red solution, probably containing mesityl oxide and phorone, a condensation produced by the hydrolytic products of the silane, whereas no reaction takes place with *n*-butyltrifluorosilane (24e).

Similarly, *n*-butyltrichlorosilane readily undergoes alcoholysis but *n*-butyltrifluorosilane merely dissolves in the alcohol (24e).

It is reported that fluorotriphenylsilane is unreactive with water (248), whereas the corresponding chlorotriphenylsilane is hydrolyzed by ice water acidified with sulfuric acid to give triphenylsilanol (191). The corresponding bromo and iodo compounds are rapidly attacked by water (193, 208). Trifluorophenylsilane is quickly hydrolyzed by water, but difluorodiphenylsilane is not hydrolyzed in moist air and even in contact with water only a trace of hydrolytic product appears after a day. Alkalies hydrolyze these two quickly.

In general, the triorganomonofluorosilanes of higher molecular weight are not even readily hydrolyzed by aqueous bases, nor do they react with sodium dissolved in liquid ammonia (100, 268).

Tests so far reveal no tendency of alkyltrifluorosilanes to coördinate with a metal fluoride (24b, 24d), as is the reaction of silicon tetrafluoride.

Halogenation of trialkylfluorosilanes (78) goes in the main as follows:

$$R_3SiF + X'_2 \rightarrow R_2SiFX' + RX'$$

but the reaction is complicated by halogenation of R by hydrogen substitution· The organofluorosilanes give no reaction, at temperatures up to their boiling points, with mercury, nichrome, and iron (24b–24g).

E. THE ALKYLALKOXY- AND AROXY-SILANES, $R_nSi(OR')_{4-n}$

Closely related to the organosilicon halides are the alkyl-and aryl-substituted silicon ethers. While these compounds may be prepared by the reaction of the corresponding chlorosilanes with alcohols or phenols, they may also be prepared by the reaction of the appropriate Grignard reagent with an orthosilicate having the desired R′ groups. The resulting alkylalkoxysilanes are colorless liquids of pleasant odor, capable of many of the reactions of the corresponding halosilanes. The ether groups are readily removed by hydrolysis in the presence of strong mineral acids, and much more slowly in pure water. Hydrolysis yields the same silanols as are obtained by the hydrolysis of the corresponding halosilanes; hence the organic-substituted silicon ethers also are satisfactory intermediates for the preparation of silicon polymers through condensation of silanols (8, 10, 234).

A list of the known alkoxy- and aroxy-organosilanes, together with their properties and the references to the original preparations, is given in table 6.

F. ORGANOSILANOLS, $R_nSi(OH)_{4-n}$, ETC.

The formation of silanols by the hydrolysis of halogenosilanes and alkoxy-

TABLE 6

Alkoxy- and aroxy-organosilanes

COMPOUND	MELTING POINT	BOILING POINT	d	n_D	REFERENCES
	°C.	°C.			
$(CH_3)_3SiOCH_3$		57.2		1.3679[a]	(307)
$(CH_3)_3SiOC_2H_5$		75.0	0.7573[b]	1.3741[a]	(54, 307)
$(CH_3)_3SiOC_2H_4Cl$		134.3	0.9443[b]	1.4140[a]	(262, 312)
$(CH_3)_3SiOC_4H_9(n)$		124.6	0.7774[b]	1.3925[a]	(307)
$(CH_3)_2Si(OC_2H_5)_2$		111	0.890[b]	1.3839[a]	(234, 278)
$(CH_3)_2Si(OC_2H_4Cl)_2$		213	1.135[b]	1.4420[a]	(262, 312)
$(CH_3)_2Si(OC_2H_4Br)_2$		92 (2.5 mm.)			(262)
$(CH_3)_2Si(OC_4H_9(n))_2$		187	0.8434[b]	1.4058[a]	(308)
$(CH_3)_2Si(OC_4H_9(n))Cl$		142			(308)
$CH_3Si(OC_2H_5)_3$		151	0.938[b]	1.3869[a]	(205, 207, 278)
$CH_3Si(OC_2H_4Cl)_3$		137 (6 mm.)	1.257[b]	1.4562[a]	(262, 312)
$CH_3Si(OC_2H_4Br)_3$		131 (1 mm.)			(262)
$CH_3SiH(OC_2H_4Cl)_2$		96 (18 mm.)	1.1643[b]	1.4431[a]	(262, 312)
$CH_3Si(OC_6H_9(n))_3$		115 (10 mm.)	0.8775[b]	1.4106[a]	(308)
$[n\text{-}C_4H_9OSi(CH_3)_2]_2O$		225	0.8733[b]	1.4051[a]	(308)
$[n\text{-}C_4H_9O][(CH_3)_2SiO]_3C_6H_9(n)$		125 (10 mm.)	0.8932[b]	1.4053[a]	(308)
$(C_2H_5)_3SiOC_2H_6$		153	0.8414		(199, 203)
$(C_2H_5)_2Si(OC_2H_5)_2$		155	0.8752[c]		(199, 203)
$(C_2H_5)_2SiCl(OC_2H_5)$		147			(199, 203)
$C_2H_5Si(OCH_3)_3$		126	0.9747[c]		(202, 207)
$C_2H_5Si(OC_2H_5)_3$		159	0.9207	1.3853	(5, 9, 88, 91, 92, 203, 276, 277)
$C_2H_5SiCl(OC_2H_5)_2$		151			(203)
$C_2H_5Si(OC_3H_7(n))_3$		203		1.4017[d]	(276, 277)
$C_2H_5Si(OC_4H_9(n))_3$		237		1.4128[e]	(276, 277)
$C_2H_5Si(OC_4H_9(i))_3$		102 (8 mm.)			(139)
$C_2H_5Si(OC_5H_{11}(n))_3$		285	0.891	1.4210[d]	(276)
$C_2H_5Si(OC_6H_{11}(i))_3$		153 (17 mm.)			(139, 276)
$n\text{-}C_3H_7Si(OC_2H_5)_3$		180	0.852	1.4076	(249, 276)
$i\text{-}C_3H_7Si(OC_2H_5)_3$		178	0.9194		(9)
$CH_2{=}CHCH_2Si(OC_2H_5)_3$		175	0.9229	1.3952	(9, 10)
$n\text{-}C_4H_9Si(OC_2H_5)_3$		191	0.895[h]	1.3976[i]	(276, 278)
$i\text{-}C_4H_9Si(OC_2H_5)_3$		186	0.9104	1.3908	(5, 9)
$(i\text{-}C_4H_9)SiCl(OCH_3)(OC_2H_5)$		155			(178)
$i\text{-}C_5H_{11}Si(OC_2H_5)_3$		198	0.8955	1.3982	(9, 249)
$n\text{-}C_6H_{13}Si(OC_2H_5)_3$		210	0.8938	1.4167	(9)
$(C_6H_{11})_2(C_6H_5)Si(OC_6H_{11})$	103–4	200 (0.5 mm.)			(52)
$(C_6H_5)_2Si(OC_2H_5)_2$		303			(180)
$(C_6H_5)_2Si(OC_2H_4Cl)_2$		144 (0.1 mm.)	1.2027[b]	1.5510[a]	(312)
$(C_6H_5)_2Si(OC_6H_5)_2$	70–1				(167, 181)
$(C_6H_5)_2Si(OC_6H_5)Cl$		253 (40 mm.)			(167)
$C_6H_5Si(OC_2H_5)_3$		233	1.0133[c]		(145, 204, 207, 231, 276)

TABLE 6—*Concluded*

COMPOUND	MELTING POINT	BOILING POINT	d	n_D	REFERENCES
	°C.	°C.			
$C_6H_5Si(OC_2H_4Cl)_3$		158 (1 mm.)	1.2680^b	1.5077^a	(262, 312)
$C_6H_5Si(OC_3H_7(n))_3$		192 (7 mm.)	1.036^b	1.5025^a	(276)
$C_6H_5Si(OC_4H_9(i))_3$		156 (10 mm.)			(139)
$C_6H_5Si(OC_5H_{11}(i))_3$		196 (18 mm.)			(139)
$C_6H_5Si(OC_6H_5)_3$	40	250 (13 mm.)			(138)
$(C_6H_5)(p\text{-}BrC_6H_4)Si(OC_2H_5)_2$		201 (17 mm.)	1.2488^b		(106)
$[(C_6H_5)(p\text{-}BrC_6H_4)Si(OC_2H_5)]_2O$		318 (20 mm.)	1.3369^b		(106)
$[C_6H_5Si(OC_2H_5)_2]_2O$		258 (75 mm.)			(231)
$p\text{-}BrC_6H_4Si(OCH_3)_3$		136 (13.5mm.)	1.3493^b		(106)
$p\text{-}BrC_6H_4Si(OC_2H_5)_3$		150 (12 mm.)	1.2244^b		(106)
$p\text{-}BrC_6H_4Si(OC_3H_7(n))_3$		176 (14 mm.)	1.1553^b		(106)
$p\text{-}BrC_6H_4Si(OC_4H_9(i))_3$		191 (14 mm.)	1.0923^b		(106)
$p\text{-}NH_2C_6H_4Si(OC_2H_5)_3$		148 (14 mm.)			(76)
$p\text{-}(CH_3)_2NC_6H_4Si(OC_2H_5)_3$		181 (14 mm.)			(76)
$C_6H_5CH_2Si(OC_2H_5)_3$		248	0.9864		(249)
$C_6H_5C{\equiv}CSi(OC_2H_5)_3$		142 (6 mm.)	0.986^j	1.4898^k	(355)
$(C_6H_5C{\equiv}C)_2Si(OC_2H_5)_2$		185 (12 mm.)	1.0001^l	1.529^m	(355)
$2,4\text{-}(CH_3)_2C_6H_3Si(OC_2H_5)_3$		270			(145)
$\alpha\text{-}C_{10}H_7Si(OC_2H_5)_3$		294			(143, 144, 145, 249)
$\beta\text{-}C_{10}H_7Si(OC_2H_5)_3$		272			(145)

a, n_D^{20}; b, d_4^{20}; c, d^0; d, n_D^{23}; e, n_D^{24}; f, d^{23}; g, d^{24}; h, d_4^{29}; i, n_D^{29}; j, d_{22}^{22}; k, n_D^{21}; l, d_9^9; m, n_D^9.

silanes has been discussed in the two preceding sections. It was pointed out that all the silanols are subject to condensation with the elimination of water and the formation of siloxanes, and that the rate of condensation depended upon the size and number of the organic groups as well as on the external factors of temperature and catalysts.

Those organosilanols which are sufficiently stable to permit isolation are listed in table 7. Some of these, like triethylsilanol, may be distilled without appreciable condensation (200, 203, 307); others, like diphenylsilanediol, may be purified by crystallization in inert solvents. The ready condensation of diphenylsilanediol in solution by strong acids and alkalies offers a remarkable example of specific catalysis (35).

Besides the simple organosilanols of the type $R_nSi(OH)_{4-n}$ there are listed some α,ω-siloxanediols with siloxane chains of varying length. These are prepared by the hydrolysis of α,ω-dichlorosilanes, which in turn are obtained by the partial hydrolysis and condensation of dialkyldichlorosilanes (35). It remains doubtful whether such a chain can be extended by the reaction of the terminal hydroxyl group with fresh dichlorosilane to split out hydrogen chloride and add a siloxane unit. These α,ω-siloxanediols may also be prepared by careful fractionation of hydrolysis products of the dichlorosilane and by reaction of a cyclic siloxane with water (157, 160, 184, 185, 283, 284, 285, 286, 287, 288).

TABLE 7

Organosilanols—including polymeric diols

COMPOUND	MELTING POINT	BOILING POINT	d	n_D	REFERENCES
	°C.	°C.			
$(CH_3)_3SiOH$		100	0.8112[a]	1.3880[b]	(307)
$(CH_3)_2(Cl_2CH)SiOH$		89 (40 mm.)			(198a)
$(CH_3)(C_2H_5)(C_6H_5)SiOH$		115 (17 mm.)			(175, 176)
$(CH_3)(C_6H_5CH_2)_2SiOH$		241 (60 mm.)			(176)
$(C_2H_5)_3SiOH$		153.5	0.8647[a]		(106, 200, 203)
$(C_2H_5)_2Si(OH)_2$	96	140 dec.			(57, 58)
$(C_2H_5)_2(C_6H_5)SiOH$		165 (60 mm.)			(176)
$(C_2H_5)_2(C_6H_5CH_2)SiOH$		165 (40 mm.)			(175, 176)
$(C_2H_5)(n\text{-}C_3H_7)(C_6H_5)SiOH$		250			(150)
$(C_2H_5)(n\text{-}C_3H_7)(C_6H_5CH_2)\text{-}SiOH$		155 (25 mm.)			(147, 151, 175, 176, 223)
$(C_2H_5)(i\text{-}C_4H_9)(C_6H_5CH_2)\text{-}SiOH$		163 (25 mm.)			(215)
$(C_2H_5)(C_6H_5)Si(OH)_2$	70				(283, 286)
$(C_2H_5)(C_6H_5CH_2)_2SiOH$	54				(282)
$(C_2H_5)(C_6H_5CH_2)Si(OH)_2$	100				(283, 286)
$HO[Si(C_2H_5)(C_6H_5)O]_2H$	87.5				(283, 286)
$(n\text{-}C_3H_7)_3SiOH$		207			(257, 258)
$(n\text{-}C_3H_7)_2Si(OH)_2$	100				(57)
$(n\text{-}C_4H_9)_2Si(OH)_2$	97				(57)
$(i\text{-}C_5H_{11})_3SiOH$		270			(351)
$(C_6H_{11})(C_6H_5)Si(OH)_2$	123–4 dec.				(51)
$(C_6H_{11})_2(C_6H_5)SiOH$	145–6				(51)
$(C_6H_5)_3SiOH$	155			1.1777	(63, 136, 175, 177, 208, 223, 319)
$(C_6H_5)_2Si(OH)_2$	132; 148; 155				(35, 138, 156, 159, 185, 224, 353)
$(C_6H_5)(C_6H_5CH_2)Si(OH)_2$	106				(224, 283, 286)
$HO[Si(C_6H_5)_2O]_2H$	113–4				(35, 157, 160, 185)
$HO[Si(C_6H_5)_2O]_3H$	111–2				(35, 157, 160, 184, 185)
$HO[Si(C_6H_5)_2O]_4H$	128.5				(184, 185)
$(C_6H_5CH_2)_3SiOH$	106				(62, 136, 175, 282)
$(C_6H_5CH_2)_2Si(OH)_2$	101				(62, 282, 284, 285)
$HO[Si(C_6H_5CH_2)_2O]_2H$	76				(284, 288)
$HO[Si(C_6H_5CH_2)_2O]_3H$	82				(287, 288)
$(p\text{-}CH_3C_6H_4)_3SiOH$	99–100				(340)
$(p\text{-}CH_3C_6H_4)_2Si(OH)_2$	113–6				(271)

a, d^{20}_4; b, n^{20}_D.

The silanols, R_3SiOH, where the R's may be all the same or different, are also prepared by reaction of $[R_2SiO]_x$ with the desired Grignard reagent and subsequent hydrolysis of the addition product (175, 176).

Silanol hydroxyl groups in general will react with methylmagnesium iodide to liberate methane, and this reaction is used as a method of determining hydroxyl groups in complex siloxane structures (307).

G. ESTERS, $CH_3COOSiR_3$ AND $(R_3SiO)_2SO_2$

The esters of the organosilanols are formed by the interaction of the silanol with either inorganic or organic acids or their anhydrides. These compounds differ from the ethers or alkoxysilanes in that the silanol has behaved as an alcohol rather than as a silicic acid; hence an acid radical replaces the alkoxy or aroxy radical found in the ethers. In general, the formation of these compounds is carried out by reaction of an acid with the halogenosilane or by interchange of an acid anhydride with an alkoxysilane or siloxane. The following reactions will illustrate the methods which have been used:

(1) $R_3SiOR' + (CH_3CO)_2O = R_3SiOCOCH_3 + R'OCOCH_3$
(2) $R_3SiX + AgOCOCH_3 = R_3SiOCOCH_3 + AgX$
(3) $R_3SiOH + CH_3COCl = R_3SiOCOCH_3 + HCl$
(4) $2R_3SiX + H_2SO_4 = (R_3Si)_2SO_4 + 2HX$
(5) $(R_3Si)_2O + SO_3 = (R_3Si)_2SO_4$
(6) $3(R_3Si)_2O + P_2O_5 = 2(R_3Si)_3PO_4$

The resulting esters, together with their properties and the pertinent references, are given in table 8.

H. THE LINEAR AND CYCLIC ORGANOSILOXANES

The molecular condensation of silanols to siloxanes becomes a very important reaction by which the organosiloxane polymers are formed in practice. However, it should not be concluded that intermolecular condensation is the only mechanism by which such siloxanes may be formed. The preparation of ethyl silicone by the oxidation of tetraethylsilane (290a, p. 73) takes place without benefit of intermediate silicols, and of course the formation of silicon dioxide by the burning of silicon in dry oxygen is the ultimate example of the formation of siloxane linkages without condensation. Most unoxidized compounds of silicon are driven to seek the oxidized forms by the thermodynamic drive of a high heat of oxidation, and hence will move in that direction when the conditions are appropriate.

The name *siloxane* is derived from the names for a series of hydrides in which the silicon atoms are separated by oxygen, as in disiloxane, $H_3SiOSiH_3$. If the hydrogen atoms were fully substituted, we would have an organodisiloxane of the type $R_3SiOSiR_3$. If prosiloxane, $(H_2SiO)_x$, should undergo similar substitution, the product would be a polyorganosiloxane, $(R_2SiO)_x$. Such a substance could be prepared by condensation of a corresponding diol, $R_2Si(OH)_2$, in which case the siloxane chains would have terminal hydroxyl groups and therefore could undergo further condensation with similar molecules or with uncondensed diols. The length of the siloxane chain of the type —$R_2SiOR_2SiOR_2SiO$— therefore would be limited only by conditions which inhibit or do not adequately encourage condensation of the terminal hydroxyl groups.

Since a growing siloxane chain may become long enough for its two terminal hydroxyl groups to condense, there is a possibility that it will go over to a cyclic anhydride. Such a cyclic substance could not then undergo further reaction or rearrangement unless means were provided for the opening of siloxane bonds. For this reason the cyclic siloxanes of the type $(R_2SiO)_x$ are relatively stable substances with vapor pressures that decrease regularly as the value of x increases. No evidence for a cyclic dimer has been reported, but cyclic configurations from trimer to nonomer are known (114, 115, 266, 365). Usually both cyclic and linear types are obtained from the condensation of a given silanediol, but the proportions of each are variable over wide limits depending upon the conditions used.

TABLE 8

Esters

COMPOUND	MELTING POINT	BOILING POINT	d	n_D	REFERENCES
	°C.	°C.			
$[(CH_3)_3Si]_2SO_4$	45–6				(266)
	56–8				(333)
$[(C_2H_5)_3Si]_2SO_4$		170 (12 mm.)		1.4442^a	(333)
$[(CH_3)_3Si]_3PO_4$		86 (4 mm.)		1.4090^a	(308)
$(CH_3)_3SiOCOCH_3$		103			(312)
$(C_2H_5)_3SiOCOCH_3$		168	0.9039^b		(201, 203)
$(C_2H_5)Si(OC_2H_5)_2(OCOCH_3)$		191.5	1.020^c	1.4048^a	(277)
$(n\text{-}C_3H_7)_3SiOCOCH_3$		214			(257, 258)
$(C_6H_5)_3SiOCOCH_3$	91.5				(177, 178)

a, n_D^{20}; b, d^0; c, d_4^{20}.

Cyclic dimethylsiloxanes obtained by the hydrolysis of dichlorodimethylsilane have been separated from the linear dimethylsiloxanes and isolated from each other by fractional distillation (114, 266), the total yield of cyclic forms constituting approximately 50 per cent of the hydrolyzate. The remaining linear siloxanes may then be converted quite completely into cyclic forms by heating to 350°C. or 400°C. in the absence of oxygen, at which temperatures the siloxane bonds rearrange and the volatile cyclosiloxanes distil off as they form. The pyrolysis of dimethylsiloxanes apparently takes place without rupture of the methyl–silicon bond, and therefore is a "clean" reaction which leaves no residue (266, 322). Conversion of cyclic to linear dimethylsiloxanes requires low-temperature rearrangement by reagents capable of opening the siloxane bonds of the cyclic molecule, and recombination of the fragments in linear form (266).

Properties of the organosiloxanes and references to the pertinent articles are given in table 9.

TABLE 9

Organosiloxanes

COMPOUND	MELTING POINT	BOILING POINT	d	n_D	REFERENCES
	°C.	°C.			
$CH_3[(CH_3)_2SiO]_1Si(CH_3)_3$		100.5	0.7619[a]	1.3774[b]	(53, 115, 307, 365)
$CH_3[(CH_3)_2SiO]_2Si(CH_3)_3$	*ca.* −80	153	0.8200[a]	1.3848[b]	(115, 266, 365)
$CH_3[(CH_3)_2SiO]_3Si(CH_3)_3$	*ca.* −70	194	0.8536[a]	1.3895[b]	(115, 266, 365)
$CH_3[(CH_3)_2SiO]_4Si(CH_3)_3$	*ca.* −80	229	0.8755[a]	1.3925[b]	(115, 266, 365)
$CH_3[(CH_3)_2SiO]_5Si(CH_3)_3$	< −100	142 (20 mm.)	0.8910[a]	1.3948[b]	(115, 266, 365)
$CH_3[(CH_3)_2SiO]_6Si(CH_3)_3$		184.5 (40 mm.)	0.911	1.3965	(365)
$CH_3[(CH_3)_2SiO]_7Si(CH_3)_3$		202 (39.3 mm.)	0.913	1.3970	(365)
$CH_3[(CH_3)_2SiO]_8Si(CH_3)_3$		199 (16 mm.)	0.918	1.3980	(365)
$CH_3[(CH_3)_2SiO]_9Si(CH_3)_3$		203 (10 mm.)	0.925	1.3988	(365)
$CH_3[(CH_3)_2SiO]_{10}Si(CH_3)_3$		202 (4.7 mm.)	0.930	1.3994	(365)
$[(ClCH_2)(CH_3)_2Si]_2O$		204.5	1.045[a]	1.4390[b]	(198)
$(ClCH_2)(CH_3)_2SiOSi(CH_3)_3$		151.7	0.9105[a]	1.4106[b]	(198)
$[(CH_3)_2(CHCl_2)Si]_2O$		150 (40 mm.)	1.2213[a]	1.4660[b]	(198a
$[(CH_3)(C_6H_5)_2Si]_2O$	51–2				(165)
$[(CH_3)(C_6H_5CH_2)_2Si]_2O$	56				(175)
$[(CH_3)_3SiO]_3SiCH_3$	*ca.* −80	190	0.8497[a]	1.3880[b]	(115, 266)
$[(CH_3)_2SiO]_3$	64	134			(114, 128, 266, 365)
$[(CH_3)_2SiO]_4$	17.5	175	0.9558[a]	1.3968[b]	(114, 115, 266, 365)
$[(CH_3)_2SiO]_5$	−38	210	0.9593[a]	1.3982[b]	(114, 115, 266, 365)
$[(CH_3)_2SiO]_6$	−3	245	0.9672[a]	1.4015[b]	(114, 115, 266, 365)
$[(CH_3)_2SiO]_7$	−26	154 (20 mm.)	0.9730[a]	1.4040[b]	(114, 115, 266, 365)
$[(CH_3)_2SiO]_8$	31.5	175 (20 mm.)		1.4060[b]	(80, 114, 266, 365)
$[(CH_3)_2SiO]_9$		*ca.* 188 (20 mm.)		1.4070[b]	(266)
$[(CH_3)_2SiO]_3](ClCH_2)$-$(CH_3)SiO]$	−1	214	1.0444[a]	1.4158[b]	(198a)
$(CH_3)_8Si_5O_6$	118	203			(322)
$(CH_3)_{10}Si_6O_7$	51	232			(322)
$(CH_3)_8Si_6O_8$	119	220			(322)
$(CH_3)_{10}Si_7O_9$	150	248			(322)
$(CH_3)_{10}Si_8O_{11}$	139	257			(322)
$(CH_3SiO_{1.5})_n$	Sublimes	without melting			(322)
$(CH_3)_8Si_5O_6$	121	204			(322)
$(CH_3)_{10}Si_6O_7$	57	230			(322)
$(CH_3)_{12}Si_7O_8$	31	254	1.0352[c]	1.4031[d]	(322)
$(CH_3)_{14}Si_8O_9$	−12	157 (20 mm.)	1.0260[a]	1.4032[b]	(322)

TABLE 9—*Concluded*

COMPOUND	MELTING POINT	BOILING POINT	d	n_D	REFERENCES
	°C.	°C.			
$[(C_2H_5)_3Si]_2O$		231	0.8590	41.430[b]	(58a, 87, 89, 193, 203)
$[(C_2H_5)(n\text{-}C_3H_7)(C_6H_5\text{-}CH_2)Si]_2O$		246 (20 mm.)			(161, 223)
$[(C_2H_5)(i\text{-}C_4H_9)(C_6H_5\text{-}CH_2)Si]_2O$		251 (25 mm.)			(215)
$[(C_2H_5)(C_6H_5)_2Si]_2O$	65.5				(222, 223)
$[(C_2H_5)(C_6H_5CH_2)_2Si]_2O$	55				(282)
$[(C_2H_5)(C_6H_5)SiO]_3$	177.5				(128)
$[(C_2H_5)(C_6H_5CH_2)SiO]_3$		310 (22 mm.)			(282)
$[(n\text{-}C_3H_7)_3Si]_2O$		285			(258)
$[(i\text{-}C_5H_{11})_3Si]_2O$		365			(351)
$[(C_6H_{11})_2SiO]_3$	237–9				(51)
$[(C_6H_{11})(C_6H_5)SiO]_3$	117–8				(51)
$[(C_6H_6)_3Si]_2O$	222				(177, 178, 319, 320)
$[(C_6H_5CH_2)_3Si]_2O$	205				(75, 231)
$[(p\text{-}CH_3C_6H_4)_3Si]_2O$	223–4				(340)
$[(C_6H_5)_2SiO]_3$	190	295 (1 mm.)			(35, 62, 122, 157, 160, 185, 357)
$[(C_6H_5)_2SiO]_4$	201 188	335 (1 mm.)	1.185[e]		(35, 36, 122, 157, 160, 184, 185)
$[(C_6H_5CH_2)_2SiO]_3$	98				(288, 357)
$[(p\text{-}CH_3C_6H_4)_2SiO]_3$	261–2				(271)

a, d_4^{20}; b, n_D^{20}; c, d_4^{20} of supercooled liquid; d, n_D^{20} of supercooled liquid; e, density of crystals.

See also alkoxysiloxanes, α,ω-siloxanediols, α,ω-dichlorosiloxanes, and organopolysilanes in their respective tables.

I. SILAZANES AND RELATED COMPOUNDS

Ammonia reacts with silicon tetrachloride first to form a hexaammonate and then to replace the four chlorine atoms with amino groups (290a, p. 10). A similar reaction occurs with all of the chlorosilanes, and provides a method for the preparation of silazanes and other substances having silicon–nitrogen bonds. For example, two molecules of chlorotrimethylsilane condense with one molecule of ammonia to form hexamethyldisilazane (307):

$$2(CH_3)_3SiCl + 3NH_3 = (CH_3)_3SiNHSi(CH_3)_3 + 2NH_4Cl$$

This process is seen to be analogous to that of hydrolysis of the chlorotrimethylsilane, followed by condensation of the silanol. A similar reaction with dichlorosilanes or trichlorosilanes opens the possibility of preparing many polymeric substances which are the nitrogen equivalents of the organopolysiloxanes or silicones. However, the possible utility of such substances is impaired by the fact that the silicon–nitrogen bond is quite readily hydrolyzed to regenerate ammonia and form a corresponding siloxane.

The successful attachment of three trimethylsilyl groups to nitrogen has not been reported. Two such groups may be attached quite readily, but there appears to be a hindrance to the reaction of a third (311). Primary and secondary amines also react with chlorosilanes to form silicon–nitrogen bonds, and this reaction provides a method for making silylamines having various organic groups linked directly to nitrogen (311). Examples of such compounds are given in table 10, along with the known silazanes and their physical constants.

TABLE 10

Silazanes

COMPOUND	MELTING POINT	BOILING POINT	d	n_D	REFERENCES
	°C.	°C.			
$(CH_3)_3SiNHCH_3$		71	0.7395[a]	1.3905[b]	(311)
$(CH_3)_3SiNHC_2H_5$		90.5		1.3912[b]	(311)
$(CH_3)_3SiN(C_2H_5)_2$		126.3		1.4112[b]	(311)
$[(CH_3)_3Si]_2NH$		126.2	0.7741[a]	1.4078[b]	(307, 311)
$[(CH_3)_3Si]_2NCH_3$		145			(311)
$(C_2H_5)_3SiNH_2$		137.3		1.4259[b]	(311, 329)
$(C_2H_5)_3SiNHC_2H_5$					(193)
$[(C_2H_5)_3Si]_2NH$					(193)
$(C_2H_5)_2(CH_3CHCl)SiNH_2$		93 (38 mm.)		1.4570[b]	(329)
$(C_2H_5)(n\text{-}C_3H_7)(C_6H_5)SiNHC_6H_4CH_3$					(150)
$(n\text{-}C_3H_7)_3SiNH_2$		189		1.4359[b]	(329)
$(C_6H_5)_3SiNH_2$	55–6				(194)
$[(C_6H_5)_3Si]_2NH$	175				(281)
$(C_6H_5)_3Si\cdot C_2H_5NH_2$	45				(192)

a, d_4^{20}; b, n_D^{20}.

V. The Silicone Polymers

As has been shown above, the partial oxidation of an organosilane or the condensation of an organosilanol will yield an organosiloxane. If there are three organic groups and one hydroxyl group on each silicon atom, the molecule is seen to be monofunctional and hence may condense with only one similar molecule to produce an organodisiloxane (307). If each silicon atom bears two organic groups and two hydroxyl groups, the molecule becomes bifunctional and is capable of forming straight-chain siloxanes which are multiples of the unit structure $[R_2SiO]$. Such polymeric siloxanes may reach a very high molecular weight, being limited only by cyclization or by the attachment of chain-terminating groups that block further reaction (123, 128, 266). In like manner, the silicon atom which bears one organic substituent and three hydroxyl groups becomes trifunctional and is capable not only of propagating a siloxane chain but also of forming an oxygen bridge or cross link to a similar trifunctional unit in a neighboring chain (301). Silicic acid, which may be considered to exist momentarily during the hydrolysis of silicon tetrachloride, is tetrafunctional and so may form two corresponding links to neighboring structures (290).

With mono-, di-, tri-, and tetra-functional units available, it is seen that a wide variety of siloxane chains may be built, and that the various types may have properties which depend upon the degree of cross linking as well as the nature of the organic groups which are attached to silicon. The name *silicone* was given to substances of the empirical formula R_2SiO by Kipping (158), because he thought they were analogous to the ketones, but he was the first to recognize that these substances are in fact polymeric and show no resemblance, chemical or otherwise, to the organic ketones. Kipping also recognized that the silicones became polymeric through a process of intermolecular condensation (244, 245), and he was able to isolate several of the lower-molecular-weight polymers as well as some of the intermediate condensation products to prove his point. The name *silicone*, instead of dropping out of usage as an inept analogy, has persisted and has become a generic term for all polymeric organosiloxanes (306), even though they may be cross linked and so contain an average of less than two organic groups per silicon atom. For this reason it has been necessary to name pure compounds as individual siloxanes and to use the word silicone only to denote a general type of organopolysiloxane.

Only a few general types of alkyl and aryl silicones need be considered here, for a detailed description of the useful polymers is more properly the function of the technical literature.

In the alkyl series the first and perhaps the best-known organopolysiloxane is methyl silicone (291, 301). This may take the form of an oil (266, 365), elastomer (16, 368), or a resinous substance (301), depending upon the molecular size, the degree of cross linking, and (to some extent) the method of manufacture. Of the various types of polymer, the simplest from the point of structure is the oil, which is composed of the linear polymethylsiloxanes shown in table 8 and their longer-chain homologs. As the average number of siloxane units in the chain increases, the resulting oil becomes more viscous, less volatile, and of somewhat higher melting point. The physical chemistry of the series up to the linear decamer has been studied very thoroughly (114, 115, 266, 365), and it has been found possible to express the vapor pressure and heat of vaporization of any individual compound at a given temperature as a function of the number of siloxane units, according to the following equation:

$$\Delta H_{\text{vap.}} \text{ linear} = 4.70 + 1.65x \text{ kg.-cal.}$$

where x is the number of siloxane units in the chain. The activation energy of viscous flow similarly may be expressed as a function of the same variables:

$$E_{\text{vis.}} \text{ linear} = 1.74 + 1.49 \log x \text{ kg.-cal.}$$

Expressions for heat of vaporization and energy of flow have been derived in the same way for the equivalent cyclic polymethylsiloxanes, as follows:

$$\Delta H_{\text{vap.}}\ \text{cyclic} = 5.45 + 1.35x\ \text{kg.-cal.}$$

$$E_{\text{vis.}}\ \text{cyclic} = 0.98 + 3.96 \log x\ \text{kg.-cal.}$$

The complete comparison shows some interesting differences: for a given number of siloxane units the cyclic compound has a higher viscosity, a greater increase in viscosity with temperature, and a higher vapor pressure than the linear compound.

Among the linear polymethylsiloxanes of higher molecular weight the ratio of energy of vaporization to activation energy of viscous flow approaches a constant value of approximately 3.8; in the cyclic series the same ratio approaches the value of 2.3. The fact that these values become constant with increasing molecular weight is interpreted as meaning that the liquids appear to flow as segments rather than as complete molecules, as was also concluded by Eyring after his investigation of high-molecular-weight hydrocarbons. An interesting comparison may be made between the units of flow in the methyl silicone and the hydrocarbon series (365).

	UNITS OF FLOW	
	Hydrocarbon	Silicone
Composition	$C_{25}H_{50}$	$(CH_3)_{14}Si_7O_7$
Molecular weight	350	519
Volume, Å.^{3}	640	920
$E_{\text{vis.}}$	6 to 7 kg.-cal.	3.8 kg.-c

In the silicone oils a smaller amount of energy is capable of opening a hole sufficiently large for the larger unit of flow to pass through. This in turn reflects a smaller attraction between neighboring chains or molecules than is experienced in the hydrocarbon series. Since a very long dimethylsiloxane polymer appears to be encased in hydrocarbon groups when it is set up as a scale model, it is difficult to see why such hydrocarbon-encased chains should not attract each other to about the same extent as do the long hydrocarbon chains themselves.

Silicone oils are noted particularly for their very small change of viscosity with temperature. This property makes the silicone oils more suitable as lubricants, dielectric fluids, and hydraulic fluids under a wide range of temperatures than the hydrocarbon oils. The lower limit of usefulness of the silicone oils extends down to the temperature of solid carbon dioxide. For this reason they have found application at very low temperatures, even though at first they were thought important for their high thermal stability and their resistance to oxidation in service at elevated temperatures (7, 32a, 34, 75a, 141, 142a).

If the molecular weight of a polymeric dimethyl silicone is not limited purposely by the attachment of chain-terminating units, but rather is extended greatly by the action of condensation or rearrangement catalysts, there is produced an elastic gel (368) instead of an oily polymer. This gel, which is properly called an elastomer, may be milled with reinforcing fillers and various curing agents, and then heat treated to produce a so-called silicone rubber. This rubber has the high heat resistance that is characteristic of silicone oils and resins, and retains its rubbery properties at about 100°C. beyond the useful temperature limit of service for natural rubber. It also shows small change of physical properties with temperature, and so remains useful at temperatures as low as −50°C. (290).

The methyl silicone resins are cross-linked polymers with an average of less than two methyl groups per silicon atom. They decrease in density and refractive index, and require a more drastic curing cycle, as the methyl-to-silicon ratio is increased (301). In the range 1.0 to 1.3 methyl groups per silicon atom the resins precipitate readily from solution and cure at moderate temperatures to a hard, rather brittle mass. Resins with CH_3/Si ratios of 1.3 to 1.6 require a temperature of 150–250°C. to harden, but provide a more flexible and durable resin. At higher CH_3/Si ratios the polymer constituents may become volatile before their molecular weight has been sufficiently increased by condensation. Those resins in the stated ranges find application as laminating resins, as insulating materials, and in protective coatings (55, 290, 291, 298, 310, 367).

Ethyl silicone resins (6, 119, 124, 125, 126, 128, 233) differ from the methyl in being softer, more flexible, and slower to condense for a given ratio of organic groups to silicon atoms. For this reason, a smaller proportion of ethyl groups suffices to produce a resin with physical properties similar to those of a given methyl silicone resin. The higher alkyl silicone resins become progressively softer and more readily oxidized as the alkyl chains are lengthened; they do not have the thermal stability and chemical inertness which are important advantages to the methyl silicones, and hence are not as interesting in a practical way. Higher trichlorosilanes of the type $RSiCl_3$, in which R represents an alkyl group of five or more carbon atoms, hydrolyze to soluble resinous substances instead of to the insoluble white powders ("siliconic acids") which are formed upon hydrolysis of the lower alkyl trichlorosilanes. Similarly, benzyltrichlorosilane hydrolyzes to a soluble resinous condensation product which may further be condensed to an insoluble resin (231, 249). The corresponding cyclohexyl compound forms polymeric compounds which were described by Kipping as "gluelike" in consistency (256).

Some marked contrasts are encountered in the series of aryl silicones. Diphenylsilanediol is a rather stable white crystalline substance which begins to condense to phenyl silicone only at its melting point (148°C.) or higher. However, it too responds to the action of condensing agents (35, 159); if the crystals of the diol are dissolved in ether and treated with a small amount of concentrated hydrochloric acid, the cyclic trimer of phenyl silicone (hexaphenylcyclotrisiloxane) is formed almost exclusively, but if the diol is dissolved in boiling alcohol and a small amount of strong caustic is added, crystals of the cyclic tetramer (octaphenylcyclotetrasiloxane) are formed with little or no trimer. Crystals of the trimer may also be converted to the tetramer by dissolving them and adding a few drops of strong alkali, so it must be concluded that the specificity of acids and alkalies as catalysts is concerned with their ability to rearrange siloxane bonds as well as their influence upon the condensation of hydroxyl groups.

Diphenyl silicone of high molecular weight is a brittle rosin-like substance with a melting point that continues to rise with further condensation. These thermoplastic polymers show very high resistance to oxidation, even exceeding that of methyl silicones, but the phenyl groups may be split off by the action of strong mineral acids (128). Chlorination of the phenyl groups (292) (by chlorination of dichlorodiphenylsilane before hydrolysis) produces a similar brittle sticky resin which does not burn if the number of chlorine atoms is almost equal to the number of hydrogen atoms in each phenyl nucleus.

The xylyl, naphthyl, and higher aryl silicones (207, 231, 245, 341) also are thermoplastic, brittle, and sticky. A phenoxyphenyl silicone of this type, with high thermal stability, has been reported (294).

By introducing both alkyl and aryl groups into an organosiloxane polymer, an increase in physical strength and toughness may be obtained. For example, some popular compositions for insulating and protective resins are methyl phenyl silicones in which the molar proportion of phenyl to methyl may be anywhere from 1:10 through 1:1. Such methyl phenyl silicone resins (26, 295, 336) may be made either by the hydrolysis and condensation of methylphenyldichlorosilane, or by the hydrolysis of a suitable mixture of methyl- and phenyl-chlorosilanes, followed by intermolecular condensation of the hydrolysis products to get a random distribution of methyl and phenyl silicone units in the polymer. Various degrees of cross-linking are employed to give the hardness and rate of cure which are required for the application at hand. In these as in all silicone resins the use of rearrangement or condensation catalysts may greatly accelerate the curing process.

Ethyl phenyl silicones (13, 121, 123, 128) may be prepared in much the same manner as methyl phenyl silicone, and are useful as coating compositions and in electrical insulations. Many other mixed alkyl-aryl silicones may be made, and various substituents may be put on the alkyl and aryl groups to make the composition flame-proof or to provide other special properties. Considering the number of usable organic groups, and the number of variations within each group through the use of substituents, it is seen that an almost infinite variety of organosiloxane polymers is possible. Only a few of these have been discussed here, and indeed only a few have been prepared and described in the literature (10b, 14, 16, 22, 33, 49a, 95a, 96, 108a, 113, 140a, 142a, 145a, 191, 211, 251, 251a, 270, 305b, 315a, 359a).

VI. WATER-REPELLENT FILMS

The ability of organosilicon compounds to render certain surfaces water-repellent is a recent discovery (259) in the field. The application depends upon the fact that some organosilicon compounds have a very high contact angle to liquid water (137, 254) and a low solubility in water.

There are three general methods that may be used for applying organosilicon films to surfaces. In the first, organohalogenosilanes are caused to react with hydroxyl groups on the surface to be treated, leaving a film of organosiloxane polymer which is the effective agent in making the surface water-repellent (254, 259, 290, 351a). This reaction may be carried out in the vapor phase if the organosilicon halide is sufficiently volatile to build up an appreciable partial pressure in the treating atmosphere. A mixture of methylchlorosilanes has been especially valuable for use in this way. Reactive silanes which are not sufficiently volatile to be used in the vapor phase may be applied as a solution in an inert solvent, from which an organosiloxane film is deposited by reaction with surface hydroxyl groups as before. Such films deposited by reaction are not removed by organic solvents.

The second general method for applying films makes use of oily dimethylsiloxane polymer which is applied to the surface (preferably in dilute solution) and then heated in air to a temperature of 300°C. or more, whereupon the film becomes chemically attached to the surface and is not thereafter removed by organic solvents (137, 214a). In the third method, suitable varnishes of high water-repellent characteristics are applied to the surface to be treated. Evaporation of the solvent in such a varnish then leaves a film of organosilicon resin which may require further baking or treating to make it durable and effective (255). Films deposited by this method are not chemically bound to the surface and hence have only the usual adhesion of a varnish film.

Some measurements (254) which have been made on water-repellent films deposited by the first method (that is, by the reaction of methylchlorosilanes in the vapor phase with hydroxyl-containing surfaces) are of interest here. These experiments were conducted with steatite, a magnesium silicate composition which is used as a dielectric in high-frequency applications, but presumably the conclusions also apply to films deposited by reaction with any surface having on it a film of absorbed water. It was found that the methylchlorosilane vapor did not produce any water-repellent film on glass which had been dried by heating to 350°C. in vacuum, but would react with glass which had been exposed to room temperature and humidity. The film on steatite was found to be 1.9×10^{-5} cm. thick, and since a scale model of the unit $(CH_3)_2SiO$ shows that its thickness is about 6×10^{-8} cm., the film must be approximately 300 molecules thick. It is known that the absorbed film of water on quartz and on glass is about 100 molecules thick (the actual thickness depending upon the relative humidity of the surrounding air), and therefore it may be concluded that the methylchlorosilane vapor reacts with the absorbed water, molecule for molecule, and replaces it with a corresponding film of organosiloxane polymer. Since the model of a single dimethylsiloxane unit measures about 3 by 7Å., one mole of dimethyldichlorosilane would yield a monomolecular film having an area of 21×10^{-16} sq. cm. $\times$ Avogadro's number, or 1.26×10^9 sq. cm. It is seen that a small amount of chlorosilane vapor is capable of making a considerable surface area water-repellent, and that the actual area so covered will depend upon the actual thickness of the water film which it replaces.

Paper, cotton cloth, wool, leather, wood, and many similar substances may be treated with methylchlorosilane vapor to make them water-repellent, and the film so deposited is not removed by organic solvents or by washing with soap and water. It may be removed only by severe abrasion or by the chemical action of dilute hydrofluoric acid, ammonium bifluoride solutions (24a), or alcoholic sodium hydroxide, reagents which are capable of attacking a siloxane bond (290a, p. 84).

Water-repellent films are applied by the second method to insulators and similar ceramic objects, especially when such objects have metal inserts or coatings which would be damaged by the hydrochloric acid produced during a reaction with chlorosilanes. Apparatus or assembled objects which can neither be heated to high temperature nor be exposed to chlorosilane vapor may be given a water-repellent film by the application of a varnish according to the third method. A suitable varnish for this process contains the methylsiloxane unit, [CH_3SiHO] (255).

VII. SPECIAL INVESTIGATIONS OF PHYSICAL PROPERTIES

Because of its position in the Periodic System, silicon and its compounds are of special interest for comparison with organic compounds and with compounds of the fourth group metals. For this reason some organosilicon compounds have been examined very carefully, not only in order to get good values of melting point, boiling point, and density, but also to determine many less usual properties which relate in some way to the molecular structure of the compounds. The result is an accumulation of excellent measurements on a few of the compounds that happen to be of particular importance.

The crystal structures of dibenzylsilanediol (288), diphenylsilanediol, and the cyclic diphenylsiloxanes have been thoroughly investigated in order to establish the identity of the diol condensation products (36, 122, 185). Tetramethylsilane and the methylchlorosilanes have been investigated by electron diffraction, and have yielded pertinent information on the carbon–silicon and silicon–chlorine bond distances (28, 29, 30, 31, 32, 214). The Raman spectrum of tetramethylsilane is also reported in some detail (4, 279, 326, 358), and calculations have been made for the bond force constants in this compound.

Tetraphenylsilane has been examined thoroughly by crystallographic methods, and an interesting comparison of the fourth group elements (carbon, silicon, germanium, tin, and lead) has resulted from a study of their tetraphenyl compounds (19, 99, 273).

The heat capacity, entropy, and heats of fusion and vaporization for tetramethylsilane have been determined, and there are extensive data on the vapor pressure and heats of vaporization of all the silicon hydrides as well as their alkyl and halogen derivatives (11, 12, 24, 24b–24g, 112, 142, 366). The vapor pressures of the polymeric dimethylsiloxanes have been of interest not only in connection with the uses to which these substances are put, but also for the calculation of heats of vaporization. Precise measurements of viscosity leading to values of the activation energy for viscous flow have allowed comparisons with the energy of vaporization, and from that ratio have come conclusions about the unit of flow in the methylsiloxane polymers (114, 115, 365). The heat capacity of tetraphenylsilane also is known (327).

The isotopic composition of silicon from terrestrial sources and from meteorites has been investigated by preparing alkyl derivatives of silicon from both sources and measuring the densities of these liquids very carefully. The studies have led to the conclusion that the ratio of silicon isotopes is the same in both cases (132, 133, 134, 135).

Measurements of the surface tension and density of several organic derivatives of silicon have given the values of 27.8 for the atomic parachor of silicon (114, 348).

The molar refractions of a large number of organosilicon compounds have been determined (40, 308a), and it is found that the values for the atomic refraction of silicon vary considerably depending upon various substituents on the silicon. It has been suggested that a system of bond refractions, or of bond and group refractions, be substituted for the usual atomic and molecular refractions as a method for determining the purity of compounds or deducing their structure. Given sufficiently reliable data on such bond refractions, it becomes possible to calculate in advance the specific refraction of a compound that is to be prepared.

Since the methylchlorosilanes are made and used in considerable quantity and are quite volatile in nature, it has been necessary to determine the flammability limits of methylchlorosilane vapors in air in order to avoid explosive mixtures during the handling of these substances. It was found (12a) that the lower flammability limit for dichlorodimethylsilane was 3.4 per cent by volume in air, and that for trichloromethylsilane was 7.6 per cent by volume. Combustion of the mixtures with air deposited a very fluffy and finely divided silicon dioxide.

The kinetics of the decomposition of tetramethyl-, tetraethyl-, and tetrapropyl-silanes has been studied (112, 359). The solubility of tetraethylsilane in various solvents is accurately known (21).

Roentgenographic investigations of the structures of methylpolysiloxanes and other organosilicon compounds have been made (80, 136, 371), and data on vapor pressures of chlorotrimethylsilane (349) and ethyl- and phenyl-fluorosilanes (73) have been published.

VIII. ISOMERISM

Organosilicon compounds, like organic compounds, may exist in isomeric forms due to structural or geometrical considerations. Isomerism in the organosilicon compounds can be more complex than that of the similar carbon compounds, owing to the presence of the silicon atoms. In general, the ordinary isomerism that occurs in organic compounds can be manifested in the organic part of the organosilicon compound, but it is in turn made more complex by the presence of the silicon atom.

The structural type of isomerism may occur in the organic radical, occur at the silicon atom, or occur at both. An example of the first type is $n\text{-}C_4H_9SiCl_3$ and $i\text{-}C_4H_9SiCl_3$ (37, 41), while the second type is illustrated by decamethyltetrasiloxane, $(CH_3)_3SiO[(CH_3)_2SiO]_2Si(CH_3)_3$, and 3-trimethylsiloxyheptamethyltrisiloxane, $[(CH_3)_3SiO]_3SiCH_3$ (266). The third type is illustrated by butyltrimethylsilane and triethylmethylsilane (362).

The number of isomers which may occur because of geometrical considerations is more limited, since certain geometrical factors that cause isomerism in carbon compounds have not been observed in organosilicon compounds. No known compounds exist in which silicon is doubly bonded to another atom (165, 315), a fact which would indicate that isomerism of the type existing in compounds such as maleic and fumaric acids does not exist. This type of isomerism can exist, however, in the organic side chain.

Kipping, in his earliest work, was interested in synthesizing organosilicon compounds in which the silicon atom was an asymmetric center. He was able to resolve several of the racemic mixtures he had prepared (46, 47, 147, 148, 149, 150, 151, 152, 153, 161, 174, 215, 216, 223).

IX. Physiological Properties

Ethyl orthosilicate is known to have a hemolytic effect on experimental animals when inhaled or ingested. This effect does not appear to involve any specific action of the silicon, but rather is analogous to the action of ether and the higher alcohols of the red blood cells. The silicic acid or silica formed by hydrolysis of orthosilicates apparently has no physiological response. Methyl silicate shows a specific effect in that the liquid or its vapor seems capable of causing severe irritation or ulceration of the cornea upon actual contact with the eyes (10b). This effect does not seem related to any action of silica or to the action of methyl alcohol upon the optic nerve, and hence it cannot be attributed to hydrolysis products of the methyl silicate. These observations (290a, p. 14) suggest that the substituted alkoxysilanes may have specific physiological effects as solvents or as local irritants, but no such effects have been reported.

The organosilicon halides are capable of hydrolysis on the skin or in the body fluids, and the resulting hydrohalogen acids may be irritating or destructive if they are liberated in sufficient quantity. However, the portion of the molecule containing the carbon–silicon bond does not appear to have any physiological effect. Organosiloxane polymers are bland to the skin and cause no dermatitis; it has not been demonstrated whether they are absorbed in appreciable quantities through the skin, but from their behavior in other circumstances it seems unlikely that even absorbed organosilicon compounds would produce any harmful effects.

The lower alkylfluorosilanes hydrolyze fairly rapidly in moist air and hence exhibit a toxicity due to the hydrolysis product, hydrogen fluoride; butyltrifluorosilane hydrolyzes very slowly and appears to be somewhat toxic *per se*. Inhalation of small quantities of the vapor causes headache and nausea (24e).

The two butylchlorofluorosilanes do not seem to be toxic, save for the action of their hydrolysis products.

The chloromethylsilanes, also being highly volatile, are in danger of being inhaled in quantity during their use. The hydrogen chloride which is liberated by their hydrolysis is irritating; hence all these substances have about the same odor and effect as silicon tetrachloride when inhaled. The products of hydrolysis other than hydrochloric acid undoubtedly are polymethylsiloxanes, and there has been some question as to whether these polymers might accumulate in the lungs upon continued exposure to the vapors. However, x-ray examinations of the lungs of laboratory workers over a period of years have failed to reveal any deposits of silicon-containing material, and it must be concluded that any organosiloxanes so formed are sufficiently soluble in body fluids to be removed. No effect akin to the condition known as silicosis has been experienced.

It may be concluded from these observations that silicon has not been known to cause any specific poisoning analogous to heavy metal poisoning, nor do the organosilicon compounds show any physiological responses that could be attributed to their silicon content or to their carbon–silicon bonds (290a, p. 103).

X. Analytical Methods

The traditional methods for determining silicon as silica in natural products involve the ignition or ashing of the sample to recover the silica. Such methods are entirely inapplicable to the analysis of organosilicon compounds, because pyrolysis products or volatile fragments will be lost during the strong heating. It has been necessary to determine silicon by a process of wet oxidation in sealed tubes (274), or by complete combustion in a sealed bomb (352). Wet oxidation with sulfuric (177) and nitric acids in open tubes, or by a Kjeldahl digestion with concentrated sulfuric acid, have been used under precautions to avoid loss of silicon. All these methods give silicon dioxide, which may be weighed as such or may be determined colorimetrically as the blue silicomolybdate (290a, p. 106).

Carbon and hydrogen in organosilicon compounds may be determined by combustion, provided that a sufficiently high temperature is maintained (41). Most organosiloxanes require for their oxidation a temperature considerably higher than that ordinarily used for the combustion of organic compounds. The early investigators used platinum foil or platinized asbestos as filling in their combustion tubes in order to have them function properly at these higher temperatures. With some modification, microcombustion may be used as a more rapid and more convenient method.

By modifying the combustion tube itself so that it may be weighed, it becomes possible to determine carbon, hydrogen, and silicon simultaneously in a single sample (301). The sample is oxidized slowly at a temperature of 200–600°C. in pure oxygen, and the products passed over platinum gauze heated to 800°C. to insure complete combustion. Carbon dioxide and water are collected and weighed as usual, and the silicon dioxide remains within the combustion tube and is weighed as such. Because the combustion tube must be kept small enough to fit in an analytical balance, samples are limited to about 0.05 g. maximum.

Halogen atoms attached to silicon may be determined by hydrolyzing the sample and then determining the halide ion volumetrically, or more conveniently by titrating the hydrohalogen acid which is produced (128; 290a, p. 109). If the halogen is fluorine, alkaline hydrolysis followed by determination of the fluorine by the lead chlorofluoride method is advisable (24b). Any organic halogen which is readily hydrolyzable will be indistinguishable from the halogen attached to silicon.

Non-hydrolyzable organic halogen may be determined by fusion in a Parr bomb, possibly using the same sample that is used for determination of silicon. In halogenosilanes with halogen substituents on the organic groups this method naturally will give only total halogen.

Hydrogen which is present as silane groups will be included in the total hydrogen obtained by combustion, but in many cases it can be determined separately by hydrolyzing the sample in a concentrated solution of sodium hydroxide and measuring the evolved hydrogen (347). Silicon–silicon bonds usually also react with the aqueous alkali and, like the silane hydrogen, will produce one equivalent of hydrogen per silicon–silicon bond (187). It is necessary therefore to know whether both silicon–hydrogen and silicon–silicon are present, and, if so, to determine one independently.

Hydroxyl groups in organosiloxanes may be determined by reaction with methylmagnesium iodide in an apparatus designed to collect and measure the evolved methane (307). Total nitrogen may be determined by a standard Kjeldahl procedure, using concentrated sulfuric acid and a mercury catalyst (41). The same digestion mixture may be used for the determination of the silicon by filtering the silica from the diluted acid before alkali is added for the distillation of the ammonia.

There is an interesting possibility of cleavage of silicones by anhydrous hydrogen fluoride in the presence of a dehydrating agent to give a quantitative yield of organofluorosilanes analogous to the organochlorosilanes from which the silicone originally was prepared (24a).

Specific and molar refractions have been used to confirm the composition of organosilicon compounds. The methyl-to-silicon ratio of the methylpolysiloxanes can be determined from measurements of specific refraction (308a).

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