An Introduction to the

CHEMISTRY

of the

SILICONES

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By

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To **P. G. F.**

PREFACE

The organic compounds of silicon, which have been the subject of many scholarly researches during the past 80 years, at last show promise of emerging from the laboratory and finding a place in industry. An understanding of the behavior of organosilicon materials is necessary to their intelligent use and, inasmuch as the chemistry of these substances ordinarily is not treated in our textbooks, it is possible that a compact yet comprehensive survey of our present knowledge in this field would be of service to chemists, engineers, and industrial designers.

This volume has just such a purpose. The first few chapters review the silanes and their derivatives in some detail, in order to provide an understanding of the fundamental chemistry of the nonsilicate compounds of silicon. The later chapters emphasize the silicone polymers which have achieved commercial importance and deal with the methods for their preparation, their chemical and physical properties, and their possible uses. The processes available for large-scale production are treated separately, and a review of methods of analysis is included. In order not to burden the text with definitions and explanations of nomenclature which might already be familiar to some readers, an extensive glossary of terms is appended.

An exhaustive review of the literature on organic compounds of silicon cannot very well be included in a volume intended for the nonspecialist. However, many references are provided, and tables of most of the known compounds and their properties are included in the appropriate chapters. The reader will find comprehensive reviews of publications in Friend's *Textbook of Inorganic Chemistry*, Volume 11, Part 2; Krause and von Grosse's *Chemie der Metallorganischen Verbindungen*, Dolgow's *Chemistry of the Silico-Organic Compounds*, and Bygden's *Silizium als Vertreter des Kohlenstoffs organischen Verbindungen*. A more recent and more complete compilation of the literature on organic compounds of silicon would be welcomed by every investigator in the field.

Since this work presents a point of view rather than an uncritical compilation of published fact, the author must assume entire responsibility for the opinions expressed. However, he is greatly indebted to his coworkers in the research laboratory of the General Electric Com-

pany for helpful advice and criticisms.   In a larger sense this work is
the result of many years of common endeavor in a most interesting field
of research.

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INTRODUCTION

Silicon is the most plentiful electropositive element on the earth's crust, being three times as abundant as aluminum and six times as abundant as iron. Yet the only compounds of silicon which have been important to human history are those natural forms of silica and the silicate minerals which are used in the building arts and in ceramic technology. Only within the past 90 years have hydrides and organic derivatives of silicon been synthesized, and the chlorides 30 years before; up to a few years ago it could be said that all these substances were still relatively unknown products of the laboratory, unimportant save for their scientific interest. The chemistry and technology of silicon continued to be dominated entirely by consideration of the inorganic silicates.

It has seemed quite natural to think of silicon only in terms of the oxide, for practically all of the earth's silicon is bound up with oxygen. Together these two elements constitute some 76 per cent of the solid crust of the earth, and there is more than enough oxygen to combine with all the silicon. Free silicon therefore does not occur in nature, nor do its organic compounds.* The only natural substance which has been demonstrated to have carbon–silicon bonds is the rare mineral moissanite, which is silicon carbide, and this ordinarily is not thought of as an organosilicon compound.

The lack of natural products undoubtedly hindered the early studies of organic compounds of silicon, for synthetic methods had to be developed from the very beginning. Fortunately the problem received the attention of some of the ablest investigators of the nineteenth century, such men as Friedel, Crafts, and Ladenburg, who were able to make the first organic compounds of silicon by what now seem to be laborious methods. Then in 1901 Kipping began his monumental re-

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* It is true that straw and feathers contain silicon, for its oxide is found in the ash when these materials are burned, but the mechanism by which this silicon entered into the plant or animal is not understood, and it has not been demonstrated that silicate esters or organosilicon compounds are involved.

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searches which were to extend over 43 years, and which stand as the basis of most of our present knowledge of organosilicon compounds. Much as these men and many others [1] have contributed, the science of organosilicon chemistry is still rather meager in content and limited in scope, considering the abundance of silicon and the versatility of its chemical behavior. Possibly the lack of simple inexpensive methods of synthesis has hindered more widespread laboratory study and has deterred commercial exploitation of the known materials; possibly chemical science has been concerned with many other interesting things and has been slow to consider the possibilities of silicon.

The demonstrated utility of organosilicon materials has wrought a great change, however. The period since 1940 has seen rapid development of the organosiloxanes or silicone polymers, and some of the organosilicon intermediates are coming into further importance of their own. To serve this newly awakened interest, this book seeks to review the reactions and properties of all the nonmineral compounds of silicon in terms of their potential usefulness, and to consider organosilicon compounds in particular as promising new synthetic substances which may fill a need heretofore unsatisfied by the natural and by the conventional synthetic materials.

In later chapters it will be necessary to limit the term "organosilicon" to those compounds in which carbon is linked directly to silicon. The esters or ethers of silicic acid, in which organic groups are linked to the silicon atom through oxygen, have structures and properties which warrant setting them aside in a separate class, here treated less thoroughly than the class of organosilicon compounds. Such esters are described more completely elsewhere,[2] and long since have acquired a commercial importance and a literature of their own.

In this chapter we shall consider briefly the chemical behavior of silicon and its simple compounds with hydrogen, the halogens, and alkoxy or aroxy groups. These covalent compounds in themselves do not contain carbon–silicon bonds, but a preliminary study of their behavior serves two important purposes: it provides an introduction to the chemistry of the more complex substances to follow, and it provides the background necessary to an understanding of those organosilicon compounds which also have halogen, hydrogen, or alkoxy groups attached to the silicon atoms.

[1] See bibliography in Krause and von Grosse, Die Chemie der metallorganischen Verbindungen, pp. 290–5 (Borntraeger, Berlin, 1937; photolithographed by J. W. Edwards, Ann Arbor, Mich., 1943).

[2] Post, The Chemistry of the Aliphatic Orthoesters, Am. Chem. Soc. Monograph 92 (Reinhold Publishing Company, New York, 1943); King, *J. Oil Colour Chem. Assoc.* 13, 28 (1930); Frydlender, *Rev. prod. chim.* 33, 720 (1930).

CHEMICAL BEHAVIOR OF SILICON

As an element, silicon is a hard brittle metallic-looking substance which crystallizes in the diamond lattice. It is produced commercially by the electrothermal reduction of silica, resulting in a product which contains about 97 per cent silicon.* The element shows no visible oxidation or corrosion at ordinary temperatures and oxidizes very slowly below red heat. Halogens attack it more readily, and chlorination proceeds satisfactorily at 250° C. to form the silicon chlorides which are perhaps the best-known volatile compounds of silicon. Whenever the element is exposed to nascent hydrogen, or its metallic compounds are treated with acids, some hydrides usually are formed, as may be noticed by the odor which such hydrides impart to the gas evolved when cast iron is dissolved in dilute acids. A mixture of concentrated nitric and hydrofluoric acids will dissolve pure silicon, but mineral acids singly will not do so. Hot concentrated solutions of alkalies will dissolve it, however, with the evolution of hydrogen.

In its chemical behavior, silicon usually is tetracovalent, as might be expected from its position in the fourth group of the periodic system. However, since it lies in the second short period its maximum covalency is not four but six,[3] in which respect it differs markedly from carbon. This hexacovalency is attained only with elements like fluorine (as in the fluosilicate ion, $SiF_6^=$) and oxygen (as in the acetylacetonate [4]), which have a combination of high nuclear charge and small atomic volume. In its organic compounds silicon remains tetravalent like carbon, but it must always be borne in mind that the electropositive nature and the hexacovalency of silicon may become evident under a variety of conditions and may cause vigorous reactions which are unknown to the analogous carbon compounds. Two examples of this are the hydration and rapid hydrolysis of the silicon halides, and the rupture of silicon–silicon chains by water and by hydroxyl ions,[5] reactions which will appear strange to students of organic chemistry.

In these and in the many other ways in which silicon differs markedly from carbon, the differences arise from the larger size of the silicon atom, with the correspondingly greater screening of its nuclear charge. Therefore, any attempt to force silicon into the framework of classical organic chemistry or to predict the reactions of silicon purely by analogy

[3] Sidgwick, The Electronic Theory of Valency, Chap. 9 (Oxford University Press, 1932); Sidgwick, *Trans. Faraday Soc.* 19, 469 (1923); Sidgwick and Callow, *J. Chem. Soc.* 125, 532 (1924).

[4] Sidgwick, *loc. cit.*, p. 155.

[5] For a more detailed explanation of the co-ordination of water and OH ion in these cases, see Sidgwick, *loc. cit.*, pp. 155–60.

* A more recently available purified form contains about 99.8 per cent silicon.

with those of carbon compounds is likely to fail because of this funda-
mental difference.   If the chemical behavior of silicon is to be predicted
by analogy, it must be predicted from a consideration of the behavior
not only of carbon but also of boron, germanium, and tin, according
to the well-known diagonal and subgroup relationships within the
periodic table.*

Another dominant chemical characteristic of silicon is its tendency
to oxidize.   The molar heat of oxidation of silicon is very high (198
kcal., more than twice that of carbon), so that oxidizable compounds
will revert to silica readily and rapidly if the necessary oxygen and the
activation energy are provided.   Hence, under favorable conditions
silicon will abandon linkage with hydrogen, carbon, sulfur, and even
the halogens in order to revert to the oxide.   Combustion is not the
only mechanism for such oxidation; the silicon may seek combination
with oxygen through hydrolysis, alcoholysis, and other similar re-
actions with oxygen-containing substances.   The various covalent
compounds of silicon differ greatly in the ease and rate with which
they undergo these various forms of oxidation, but the thermodynamic
possibility is always present.   The scarcity of unoxidized compounds
of silicon in nature is but an illustration of this tendency.

In brief, then, silicon is an electropositive element with some of the
properties of the metals.   It commonly exhibits a covalency of four,
but is capable of a maximum covalency of six in combination with
atoms of relatively small volume and high nuclear charge.   Chemically
it resembles boron and germanium as closely as carbon and shows
an exceptionally strong preference for combination with oxygen.

THE HYDRIDES

From the standpoint of structure, the simplest covalent com-
pounds of silicon are the hydrides, and the simplest hydride is SiH_4,
which has been named monosilane (or simply silane).[6]   The higher
hydrides Si_2H_6 (disilane), Si_3H_8 (trisilane), Si_4H_{10} (tetrasilane), and
so forth, form a homologous series which bears a structural resemblance
to the methane series of saturated hydrocarbons.   The length of the
silicon chain appears to be limited by an inherent instability which
is unknown in carbon chains, for the higher silanes are unstable and

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[6] The nomenclature used herein is intended to conform to the system proposed
by Sauer, *J. Chem. Education* **21**, 303 (1944).   The term " silane " was first used by
Stock, *Ber.* **49**, 108 (1916), and has the advantage of brevity over Kipping's " sili-
cane," *Proc. Chem. Soc.* **28**, 243 (1912).

* If the reader has any doubts about this point, let him attempt to predict the
behavior of the hydrides of silicon from a consideration of the hydrocarbons.   It
will soon be seen that the hydrides of boron offer a much closer analogy.

the highest member of the series so far reported is hexasilane, Si_6H_{14}. All these silanes can be prepared by the action of mineral acids upon the crude magnesium silicide which results from the reduction of silica by magnesium. Under the conditions reported by Stock,[7] hydrides corresponding to one fourth of the silicon contained in the silicide were obtained in the proportions of 40 per cent SiH_4, 30 per cent Si_2H_6, 15 per cent Si_3H_8, 10 per cent Si_4H_{10}, and the remainder as higher hydrides.

Monosilane is quite stable thermally, being decomposed to silicon and hydrogen only at red heat. The higher silanes decompose at progressively lower temperatures: disilane dissociates at 400° to 500° C., and hexasilane decomposes quite completely at room temperature over a period of several months. The higher hydrides do not break down to elementary hydrogen and silicon, but undergo a series of complicated rearrangements resulting in mixtures of simple gaseous hydrides and solid unsaturated hydrides:

$$Si_5H_{12} = 2(SiH) + Si_2H_6 + SiH_4$$
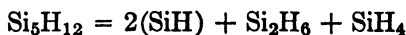
Such a disproportionation might result from the preliminary dissociation of a part of the Si_5H_{12}, followed by hydrogenation of the remainder to form monosilane and disilane. This spontaneous disproportionation of the higher hydrides explains why long chains of silicon atoms have not been found.

Of greater importance from the standpoint of possible use is the susceptibility of the hydrides to oxidation. Here there is no marked differentiation; all the silanes are extremely sensitive to oxygen and will ignite in air. The reaction proceeds with an explosive puff, evidently because hydrogen is a preliminary product:[8]

$$SiH_4 + {}_-O = H_2SiO + H_2$$
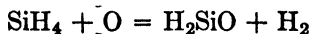
The hydrogen which is liberated by this initial oxidation forms with oxygen an explosive mixture which is detonated by the rapidly rising temperature of the system. The introduction of a chlorine atom or methyl group into the monosilane molecule suffices to render it no longer spontaneously inflammable in air, but the remaining hydrogen atoms can be removed readily by mild oxidation, so that the substances are good reducing agents. In fact, any silicon–hydrogen bond may be expected to oxidize at elevated temperatures in air, and at a rate far greater than that of an Si—CH_3 bond, for example.

[7] Stock and Somieski, *Ber.* 49, 111 (1916); Stock, *Ber.* 50, 169 (1917); Stock, Stiebeler, and Zeidler, *Ber.* 56, 1695 (1923).

[8] Stock and Somieski, *Ber.* 55, 3961 (1922).

The oxidation of silanes also can be accomplished by solutions of potassium permanganate, mercuric salts, ferric compounds, and cupric salts. Plain water also will oxidize the silicon–hydrogen bond in the presence of hydroxyl ions as catalysts:[5]

$$Si — H + H_2O = Si — OH + H_2$$
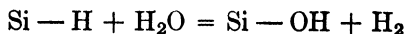
Thus in vessels of fused quartz the silanes do not react with water,[9] but the alkali extracted by the water from an ordinary glass flask (or from chips of ordinary glass introduced into the silica vessel) suffices to catalyze the reaction. The hydrogen is liberated quantitatively from any silion–hydrogen bond by dilute solutions of the alkalies, one molecule of hydrogen for each silicon–hydrogen bond.

The silicon–silicon bond likewise is attacked by aqueous alkalies and is oxidized by the water with attendant liberation of one mole of hydrogen:

$$Si — Si + 2H_2O = 2Si — OH + H_2$$
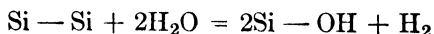
The hydroxyl ions again act catalytically, and it has been proposed[10] that they do so by preliminary co-ordination to the covalently unsaturated silicon atoms. The complete hydrolysis of disilane in alkaline solution therefore produces seven equivalents of hydrogen and leaves only hydrated silica as a residue:

$$H_3Si — SiH_3 + 4H_2O = 2SiO_2 + 7H_2$$
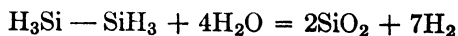
The silanes react violently with free chlorine and bromine, but a controlled halogenation may be achieved by the action of hydrogen chloride or hydrogen bromide in the presence of the corresponding aluminum halide as catalyst:

$$HCl + SiH_4 \xrightarrow{AlCl_3} SiH_3Cl + H_2$$

$$HCl + SiH_3Cl \xrightarrow{AlCl_3} SiH_2Cl_2 + H_2 \qquad etc.[11]$$
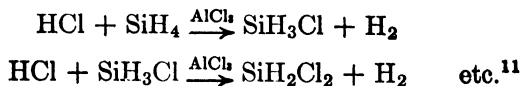
The aluminum chloride seems necessary, for without it the reaction does not proceed even at elevated temperatures. With it, even a mixture of silane and chlorosilane will react,

$$SiH_4 + SiH_2Cl_2 \xrightarrow{AlCl_3} 2SiH_3Cl$$
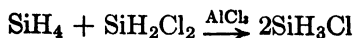
a rearrangement which is reminiscent of Calingaert's redistribution

[9] Stock and Somieski, *Ber.* 51, 989 (1918).

[10] Sidgwick, The Electronic Theory of Valency, p. 159 (Oxford University Press, 1932).

[11] Stock and Somieski, *Ber.* 52, 695 (1919).

reaction,[12] but not analogous because an energy change is involved.

Another method of chlorinating silanes and one which emphasizes the differences between carbon and silicon involves the use of chloroform or carbon tetrachloride as a source of halogen:

$$Si_3H_8 + 4CHCl_3 = Si_3H_4Cl_4 + 4CH_2Cl_2$$
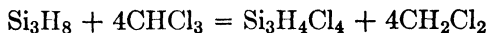
The reaction is explosively violent if oxygen is present, but is controllable if aluminum chloride is used as a catalyst. It is interesting to note that monosilane is inert to chloroform, and that only the higher hydrides undergo this exchange of hydrogen for chlorine.[13]

Trichlorosilane, $SiHCl_3$, is more easily prepared directly from silicon than by the progressive chlorination of monosilane. Anhydrous hydrogen chloride reacts with silicon, ferrosilicon, or calcium silicide at 350° to 450° to form a mixture of silicon tetrachloride, trichlorosilane, and higher chlorides of silicon, from which the trichlorosilane can be distilled. The greater accessibility of this silane derivative has led to its being used more widely than the others as an intermediate for preparing trialkoxy- and trialkylsilanes by the reactions corresponding to those used for silicon tetrachloride.

All the chlorosilanes similarly may be used as intermediates for the preparation of many interesting substances. They may be methylated with zinc dimethyl,[14] for example, to form monomethyl- and dimethylsilanes, CH_3SiH_3 and $(CH_3)_2SiH_2$. Stock and Somieski in this way succeeded in obtaining 36 cc. of the gaseous dimethylsilane, of which they hydrolyzed 5.57 cc. in a few drops of aqueous alkali in order to measure the evolved hydrogen:

$$(CH_3)_2SiH_2 + 2NaOH = (CH_3)_2Si(ONa)_2 + 2H_2$$
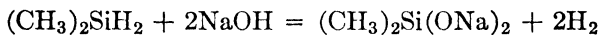
They found that the sodium salt remained dissolved in the alkaline solution, but after this was acidified an oily phase separated, presumably a polymeric form of dimethyl silicone, $(CH_3)_2SiO$. However, their maximum yield could not have been more than 0.019 g.; they did not analyze or characterize the material, nor conduct any tests which might have demonstrated its properties or utility.

The chlorosilanes also react with ammonia to form amines:

$$3SiH_3Cl + 4NH_3 = (SiH_3)_3N + 3NH_4Cl$$
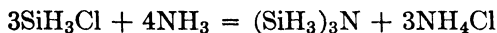
[12] Calingaert and Beatty, *J. Am. Chem. Soc.* **61**, 2748 (1939); Calingaert, Beatty, and Neal, *J. Am. Chem. Soc.* **61**, 2755 (1939); Calingaert and Soroos, *J. Am. Chem. Soc.* **61**, 2758 (1939); Calingaert, Soroos, and Hnizda, *J. Am. Chem. Soc.* **62**, 1107 (1940); Calingaert, Soroos, Hnizda, and Shapiro, *J. Am. Chem. Soc.* **62**, 1545 (1940).

[13] Stock and Stiebeler, *Ber.* **56**, 1087 (1923).

[14] Stock and Somieski. *Ber.* **52**, 695 (1919).
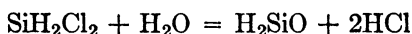
and

$$SiH_2Cl_2 + 3NH_3 = SiH_2NH + 2NH_4Cl$$
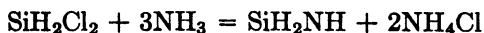
The product of the first reaction is volatile, but the product of the second polymerizes to a silicalike substance. Closely analogous are the products of hydrolysis:

$$2SiH_3Cl + H_2O = H_3Si - O - SiH_3 + 2HCl$$

and

$$SiH_2Cl_2 + H_2O = H_2SiO + 2HCl$$

The $H_3Si - O - SiH_3$ (disiloxane) is a volatile substance having a boiling point close to that of $H_3Si - SiH_3$ (disilane). It is the first of a long series of siloxanes having the characteristic silicon–oxygen–silicon linkage, about which much more is said in a later chapter. The compound H_2SiO (which already has been encountered as a partial oxidation product of monosilane) has been named prosiloxane [15] and is of particular interest to this discussion because it is capable of appearing in many polymeric forms. Thus a solution of dichlorosilane in benzene hydrolyzes to form a benzene-soluble hexamer, $(H_2SiO)_6$. Hydrolysis of dichlorosilane alone yields a temporarily monomeric prosiloxane, but this soon polymerizes to liquid and then to solid forms.[16] The highly polymerized solid substance closely resembles silica, but like any other silane it evolves hydrogen when treated with alkali:

$$(H_2SiO)_x + 2xNaOH = xNa_2SiO_3 + 2xH_2$$
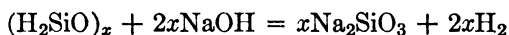
Prosiloxane therefore is the first and simplest example of a polymeric siloxane which is capable of many forms, depending on the degree of association. The dimethylsiloxane which was shown to result from the hydrolysis of dimethylsilane may be considered to be the methyl derivative of prosiloxane and has been shown to exhibit the same tendency to polymerize.

It will be noted that the introduction of oxygen into the molecular structure of the silanes or their derivatives brings about a distinct departure in physical properties from those of the unoxidized silanes or of the corresponding carbon compounds. Thus the normal silanes exhibit at least a physical resemblance to their organic counterparts, as is shown by the constant ratio of absolute boiling points given in Table I,

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[15] Stock, *Ber.* **50**, 1769 (1917).
[16] Stock, Somieski, and Wintgen, *Ber.* **50**, 1764 (1917); Stock and Somieski, *Ber.* **52**, 695 (1919).

reaction of silica with hydrochloric acid similar to that with hydrofluoric acid therefore seems ruled out, and silica is so insoluble in hydrochloric acid as to make possible its analytical dehydration in this reagent without loss. However, silica is attacked by chlorine in the presence of reducing agents, and phosgene converts it to silicon tetrachloride at 700° or less.

As a group, the tetrahalides of silicon are volatile acid-smelling substances ranging from a gas (SiF_4, boiling point $-65°$ at 2.4 atmospheres) to a solid (SiI_4, melting point 121° and boiling point 290°). All may be prepared by direct action of the respective halogen upon elementary silicon or its alloys, and the fluoride and chloride may be prepared by the reactions of silica previously given. The tetrahalides are characterized chemically by their ability to form co-ordination or " addition " compounds, and by the readiness with which they hydrolyze. With ammonia, for example, silicon tetrachloride first forms a hexammonate, $SiCl_46NH_3$, which upon heating passes through the stages $Si(NH_2)_4$, $Si(NH_2)_2NH$, $Si(NH)_2$, and finally to Si_3N_4. The reactions with water follow a parallel course and ultimately result in silica. The other three tetrahalides undergo similar reactions.

The ease with which the tetrahalides dissociate thermally increases rapidly in the series from tetrafluoride to tetraiodide. While the chlorine–silicon bond ordinarily is not considered mobile, it undergoes an interesting redistribution reaction with the isocyanate bond in the preparation of chloroisocyanates of silicon.[18]

The tetrahalides are the cheapest, most readily available monomeric covalent compounds of silicon, and hence are important as starting materials for the synthesis of many other compounds. The halogen atoms readily are replaced stepwise by alkoxy and aroxy groups through reaction with the corresponding alcohol or phenol. As is discussed in greater detail in the next chapter, hydrocarbon groups may be attached directly to the silicon by reaction with zinc alkyls,[19] with mercury aryls,[20] with sodium alkyls and aryls,[21] and with the organomagnesium halides or Grignard reagents.[22] Of these, the Grignard reagents usually offer the greatest convenience in laboratory synthesis

[18] Anderson, *J. Am. Chem. Soc.* **66**, 934 (1944); *ibid.* **67**, 2176 (1945).

[19] Friedel and Crafts, *Ann.* **136**, 203 (1865); Friedel and Ladenburg, *Ann.* **159**, 259 (1871), *ibid.* **203**, 251 (1880).

[20] Ladenburg, *Ann.* **164**, 302 (1872), *ibid.* **173**, 151 (1874).

[21] Polis, *Ber.* **18**, 1540 (1885); Kipping and Lloyd, *J. Chem. Soc.* **79**, 449 (1901); Schumb, Ackerman, and Saffer, *J. Am. Chem. Soc.* **60**, 2486 (1938); Schumb and Saffer, *J. Am. Chem. Soc.* **63**, 93 (1941).

[22] Kipping, *Proc. Chem. Soc.* **20**, 15 (1904); Dilthey, *Ber.* **37**, 319, footnote 2 (1904).

and for this reason have been the most widely employed. Silicon tetrachloride usually is used for such syntheses because it is available commercially in large quantities, but the tetrafluoride also has been suggested for such use.[23] The tetrachloride also is used for the preparation of orthosilicic esters and as a source of pure silica and silicon.

The replacement of the halogen in silicon halides by hydrogen with aluminum or other metal as a halogen absorber [24] reverses the exothermic halogenation of silanes already described in this chapter. The Hurd method accomplishes this by mixing hydrogen with the vapor of a silicon halide (such as silicon tetrachloride, for example) and passing the mixed gases over heated aluminum powder. Aluminum chloride is formed, and hydrogen is transferred to the silicon. The net change can be represented as

$$Si - Cl + H + Al = Si - H + Al - Cl$$
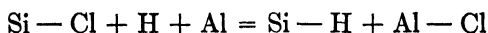
Zinc may be used in place of aluminum in a similar reaction. The method also may be used for the vapor-phase hydrogenation of organosilicon halides such as methyltrichlorosilane:

$$6CH_3SiCl_3 + 3H_2 + 2Al = 6CH_3SiHCl_2 + 2AlCl_3$$
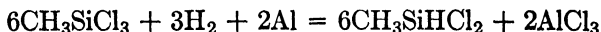
The reaction may involve the intermediate formation of a metal hydride which undergoes metathesis with the silicon halide, but no evidence for such a mechanism has been accumulated.

Another characteristic reaction of the silicon halides is the reaction with ethylene oxide to form a β-chloroethyl or β-bromoethyl group:[25]

$$Si-Cl + CH_2CH_2O = Si-OCH_2CH_2Cl$$

$$Si-Br + CH_2CH_2O = Si-OCH_2CH_2Br \qquad etc.$$
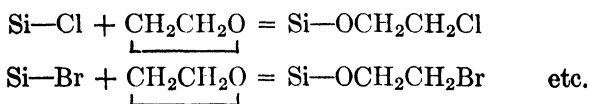
This general reaction allows the conversion of a halogen group to an ester group without the evolution of hydrohalogen acid and therefore without the corrosion problem that would attend such evolution. The reaction is particularly useful for changing organosilicon halides to esters in order to separate them more easily.

Just as the chemistry of the silicon hydrides is not limited to that of monosilane, so the silicon halides are not represented solely by the simple tetrahalides so far considered. In addition to these there are several series of higher halides, such as the higher chlorides Si_2Cl_6,

[23] U. S. patent 2 238 669 to Richard H. Wiley.

[24] Hurd, *J. Am. Chem. Soc.* 67, 1545 (1945).

[25] U. S. patents 2 381 137 and 2 381 138 to W. I. Patnode and R. O. Sauer; 2 381 139 to R. O. Sauer.

Si_3Cl_8, Si_4Cl_{10}. These correspond to Si_2H_6, Si_3H_8, and Si_4H_{10}, with chlorine atoms replacing the hydrogen. Such chains of silicon atoms encased in chlorine are the products of direct chlorination of silicon, particularly under special conditions of low temperature and slow flow or high dilution of the chlorine with inert gas.[26]   It is Schumb's theory that the atoms linked to each other on the surface of the silicon crystal pick up chlorine atoms by virtue of their free valences, and that whole groups or chains of such silicon atoms may be lifted off and carried away if the action of the chlorine is slow and stepwise.   Under conditions of slow flow and low temperature (temperature 150°, time 12 days for a 250-g. charge) the product of chlorination contains 65 per cent $SiCl_4$, 30 per cent Si_2Cl_6, 4 per cent Si_3Cl_8, and 1 per cent of higher chlorides.   At considerably higher temperatures, or with copious supply of chlorine, silicon tetrachloride becomes the sole product.

The higher chlorides of silicon also may be prepared by an electric-discharge method,[27] by the action of $SiCl_4$ on silicon,[28] and by substitution of chlorine for iodine in hexaiododisilane.[29]

These higher chlorides of silicon hydrolyze in the same way as does the tetrachloride, and they likewise undergo similar reactions with Grignard reagents and with sodium alkyls or aryls.[30]   Under some conditions, however, the silicon–silicon bond is cleaved by sodium.[31] The silicon–silicon chains are destroyed by the action of aqueous alkalies, liberating hydrogen at the rate of one molecule of H_2 per silicon–silicon bond, just as are the higher silanes.

THE ESTERS

As was mentioned in the previous section, the halides of silicon react with alcohols to form alkoxy derivatives which are volatile colorless liquids of pleasant odor:

$$SiCl_4 + 4C_2H_5OH = Si(OC_2H_5)_4 + 4HCl$$
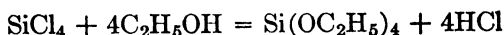
Such products traditionally are known as organic orthosilicates, being considered esters of the hypothetical orthosilicic acid, $Si(OH)_4$.   There is no particular basis for this view other than one of formal analogy to the orthocarbonates, for silicic acid is not acidic in the sense of

[26] Schumb and Gamble, Inorganic Syntheses, Vol. 1, p. 42 (McGraw-Hill Book Company, Inc., 1939).

[27] Besson and Fournier, *Compt. rend*. 152, 603 (1911).

[28] Troost and Hautefeuille, *Ann. chim. phys*. [5] 7, 459 (1871).

[29] Friedel, *Compt. rend*. 73, 1011 (1871); Friedel and Ladenburg, *Ann*. 203, 253 (1880).

[30] Schumb and Saffer, *J. Am. Chem. Soc*. 61, 363 (1939).

[31] Schumb, Ackerman, and Saffer, *J. Am. Chem. Soc*. 60, 2486 (1938).

furnishing hydrogen ions. In fact, the alcohol may be more acidic than the supposed silicic acid, as in the case of combination with phenol:

$$SiCl_4 + 4C_6H_5OH = Si(OC_6H_5)_4 + 4HCl$$
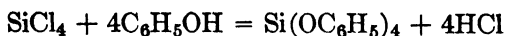
Here the phenyl silicate represents a compound of an acidic " alcohol " with a nonacidic " acid." Considerations such as these have led to the term *ether* as a more correct name from the standpoint of organic chemistry, and yet not all the carbon ethers hydrolyze as readily as do these silicon analogs. The names "tetraethoxysilane" and "tetraphenoxysilane" would be more correct, although unwieldy.

It has long been known that the reaction of silicon tetrachloride with alcohols and phenols usually yields other products as well as the orthosilicates. Incomplete " esterification " gives volatile alkoxychlorosilanes, for example,[32] a process which can be facilitated by using benzene as an inert solvent.[33] If any water is present, condensed esters of the type $(RO)_3Si—O—Si(OR)_3$ are obtained. These higher-boiling alkoxysiloxanes probably result from the partial hydrolysis of the ester followed by intermolecular condensation of the silicols so formed, for hexamethoxydisiloxane has been made from methyl silicate by boiling it with a solution of water in methanol. As the stepwise hydrolysis is continued, condensed esters of higher and higher molecular weights may be produced, giving rise to the viscous transparent paint vehicles such as are derived from ethyl silicate and are used for preserving porous stone or as heat-resistant coatings.[34]

The tendency to hydrolyze by a relatively slow and controllable stepwise reaction is characteristic of all the silicon orthoesters. When ethyl silicate, for example, is poured into water it remains immiscible and hydrolyzes at the interface over a period of many days or even months. If both the ester and the water are dissolved in alcohol, however, a much faster reaction in the homogeneous medium becomes possible. If a drop of strong acid then is added to the solution, the hydrolysis is further accelerated to such an extent that the solution becomes warm and silica is precipitated as solid or gel. If less than the equivalent amount of water is used, there is formed a viscous nonvolatile liquid which may be stored for long periods. The addition of further water (as in mixing an ethyl silicate paint) then

[32] Friedel and Crafts, *Ann.* **136**, 203 (1865).
[33] Kalinin, *Compt. rend. Acad. Sci. URSS* **18**, 433 (1938).
[34] King, *Paint Oil Chem. Rev.* **15**, 26 (1936); British patent 494 848 to Auden and Staudinger.

allows the hydrolysis to proceed to the gel stage *in situ*, and ultimately the film reverts to silica.

The other silicon esters differ from ethyl silicate in their rates of hydrolysis, but all respond to catalysts and all give silica as end product:

$$Si(OR)_4 + 2H_2O = SiO_2 + 4ROH$$
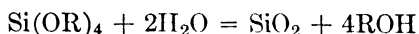
Since the alcohol is regenerated and the net result is the same as though the original silicon halide had been hydrolyzed directly, it is obvious that the esters may be regarded as hydrolytic intermediates which allow the over-all process of hydrolysis to be controlled and directed. The commercial value of the esters therefore lies in their ability to deposit silica in a desired form and at a well-defined rate. Besides their use as stone preservatives, esters like ethyl silicate are used as sources of pure ion-free silica and as additives to organic paints and lacquers to provide a harder, more resistant film. A disperse sol of silica in *n*-propanol (possibly derived from propyl silicate) is available commercially for related applications.

Besides hydrolysis, the silicic esters show many more of the reactions which have been described for the halides. For example, the alkoxy group reacts with the Grignard reagent to attach organic groups directly to the silicon atom in stepwise fashion:

$$Si(OR)_4 + R'MgX = R'Si(OR)_3 + Mg(OR)X$$
$$R'Si(OR)_3 + R'MgX = R'_2Si(OR)_2 + Mg(OR)X \qquad \text{etc.}[35]$$
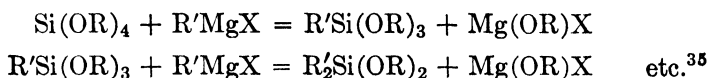
An excess of the ester may serve as solvent for the reaction, making unnecessary the use of ether, with consequent advantage over the same reaction for the halide.[36] Zinc alkyls similarly will undergo metathesis with silicate esters and attach organic groups to the silicon.[37] Treatment of an ester with a halogenating agent such as phosphorus pentachloride or benzoyl chloride will reconvert it to the corresponding silicon chloride.

Of particular interest to the user are the physiological reactions of the silicon esters within the human body. Ethyl silicate apparently is readily absorbed,[38] and has a hemolytic effect such as is produced by ether, chloroform, or the higher alcohols. Inhalation of air containing 9 to 20 mg. per liter or absorption of comparable quantities by other methods is fatal to experimental animals because of this

[35] U. S. patent 2 380 057 to R. R. McGregor and E. L. Warrick.

[36] Andrianov and Gribanova, *J. Gen. Chem. USSR* 8, 552 (1938); Andrianov and Kamenskaya, *J. Gen. Chem. USSR* 8, 969 (1938).

[37] Ladenburg, *Ann.* 173, 143 (1874).

[38] Report of Detroit Dept. Health, Oct. 1, 1937.

hemolysis, but at lower concentration no silicosis or any other unique effect attributable to the silicon content has been demonstrated.[39] Methyl silicate likewise has no physiological response peculiar to its silicon content, but the liquid or its vapor appears to cause severe irritation or even ulceration of the cornea of the eye in some cases.

The reaction of silicon tetrachloride with polyhydric alcohols produces a condensation polymer which may be called a silicon polyester. Some interesting condensation polymers related to these are produced by the reaction of ethyl silicate with glycols and phenols.[40]

In the foregoing discussion there has been no intention of minimizing the importance or the scientific interest of the remaining types of volatile covalent compounds of silicon, such as the silylamines.[41] Emphasis has been placed on the hydrides, halides, and esters, only because they are more important to the present methods for preparing the organosilicon products described in later chapters.

It has repeatedly been evident that the various substituent groups on silicon could be interchanged and that many " mixed " compounds containing various combinations of hydrogen, halogen, and ester groups are possible. If we represent halogen by X, organic groups by R, and ester groups by OR, then the volatile covalent compounds of silicon described herein may be represented by the general formula $SiH_aX_b(OR)_c$, where a, b, and c have values from 0 to 4 and $a + b + c = 4$. Since there are four halogens and almost limitless organic and ester groups, it is seen that the chemistry of even these simple silicon compounds is very extensive. Relatively few of the possible compounds have been prepared and described. The index which follows includes only a sufficient number of representative compounds from each group to demonstrate the trends in physical properties. For more complete lists of the known compounds it is necessary to consult the usual compendia and abstract indexes.

[39] Holzapfel, Z. Ver. deut. Ing. 87, 605 (1943).
[40] Holzapfel, Kolloid-Z. 100, 380 (1942).
[41] Examples are described by Stock, The Hydrides of Boron and Silicon, p. 30.

INDEX OF REPRESENTATIVE COMPOUNDS AND THEIR PROPERTIES

Compound	Formula	M.P., °C.	B.P., °C.	Density (Liquid)
Monosilane	SiH_4	−185	−112	0.68/−185°
Disilane	Si_2H_6	−133	−14.5	0.686/−25°
Trisilane	Si_3H_8	−117	52.9	0.743/0°
Tetrasilane	Si_4H_{10}	ca. −90	ca. 109	0.825/0°
Difluorosilane	SiH_2F_2	−119	−77.5	
Trifluorosilane	$SiHF_3$	−131	−97.5	
Silicon tetrafluoride	SiF_4	−95.7	−65 (1810 mm.)	1.15/−113°
Monochlorosilane	SiH_3Cl	−118	−30.4	1.42/−122°
Dichlorosilane	SiH_2Cl_2	−122	8.3	
Trichlorosilane	$SiHCl_3$	−127	31.8	1.35/0°
Silicon tetrachloride	$SiCl_4$	−70	57.6	1.48/20°
Monobromosilane	SiH_3Br	−94	1.9	1.53/0°
Dibromosilane	SiH_2Br_2	−70.1	ca. 66	2.17/0°
Tribromosilane	$SiHBr_3$	−73.5	111.8	2.81/20°
Silicon tetrabromide	$SiBr_4$	5	153	
Monoiodosilane	SiH_3I	−56.5	45.8	3.31/20°
Triiodosilane	$SiHI_3$	8	220	
Silicon tetraiodide	SiI_4	121	290	
Disiloxane	$(SiH_3)_2O$	−144	−15.2	0.881/−80°
Hexachlorodisiloxane	$(SiCl_3)_2O$	−33	137	
Hexabromodisiloxane	$(SiBr_3)_2O$	27.9	118 (15 mm.)	

INDEX OF REPRESENTATIVE COMPOUNDS AND THEIR PROPERTIES (*Continued*)

Compound	Formula	M.P., °C.	B.P., °C.	Density (Liquid)
Trisilylamine	$(SiH_3)_3N$	−106	52	0.895/−106°
Hexachlorodisilane	Si_2Cl_6		147	
Octochlorotrisilane	Si_3Cl_8		216	
Decachlorotetrasilane	Si_4Cl_{10}		150 (15 mm.)	
Methyl silicate	$Si(OCH_3)_4$		121	1.031/23°
Ethyl silicate	$Si(OC_2H_5)_4$		165.5	0.933/20°
Butyl silicate	$Si(OC_4H_9)_4$		163 (20 mm.)	0.953/25°
Amyl silicate	$Si(OC_5H_{11})_4$		148 (3 mm.)	0.893/25°
Phenyl silicate	$Si(OC_6H_5)_4$	48		
Benzyl silicate	$Si(OC_7H_7)_4$	32.5	305 (12 mm.)	
Hexamethoxydisiloxane	$(CH_3O)_6Si_2O$		201	
Hexaethoxydisiloxane	$(C_2H_5O)_6Si_2O$		235	

THE ORGANOSILICON MONOMERS

We turn now to the true organic compounds of silicon, those in which alkyl or aryl groups are linked directly to silicon through carbon–silicon bonds. For our purpose it will be convenient to apply the term to all those substances which have from one to four such organic groups linked to silicon, thereby including within one class the so-called " normal " alkyls of the type SiR_4 and all the organo-substituted halides, hydrides, esters, and hydroxides. The present discussion will be limited to the monomeric compounds (that is, those in which there is no repeating structure within the molecule) and will be concerned principally with the substances which are important as organosilicon reagents and as intermediates for the preparation of the silicone polymers.

It has been pointed out repeatedly[1] that the organic compounds of silicon differ greatly from other organometallic compounds in their exceptional thermal stability and resistance to chemical attack. To a chemist engaged in experiments with the unstable alkyls of mercury or the highly reactive and spontaneously inflammable alkyls of zinc, it must be remarkable indeed to read that silicon tetramethyl is unaffected by concentrated sulfuric acid and that silicon tetraphenyl distils undecomposed above 530° C. It must be remembered, however, that such considerations are purely relative. If we consider thermal dissociation alone, the bond energy of the carbon–silicon bond is 57.6 kcal. per mole and that for the carbon–carbon bond is 58.6 kcal. per mole,[2] so that organosilicon compounds *in general* are about as thermally stable as carbon compounds. The mere inclusion of a silicon atom within a predominantly organic structure does not guarantee the stability of the molecule in some mysterious way. It is more likely to change the properties of the substance very little.*

[1] Krause and von Grosse, Die Chemie der metallorganischen Verbindungen, pp. 254–5 (Borntraeger, Berlin, 1937).

[2] Pauling, The Nature of the Chemical Bond, p. 53 (Cornell University Press, 1940).

* Except, of course, in those positions where the larger size of the silicon atom comes into play to relieve a steric strain, as in $(C_6H_5)_3Si—Si(C_6H_5)_3$ compared with $(C_6H_5)_3C—C(C_6H_5)_3$.

In its resistance to oxidation, the carbon–silicon bond seems superior to the carbon–carbon bond. The variations between different organosilicon compounds in this respect are extreme, however, and it would be well not to interpret too broadly any generalizations about the stability or nonreactivity of these substances. Some particular configurations of silicon and organic groups (Si—CH$_3$ and Si—C$_6$H$_5$, for example) are undeniably stable and difficult to oxidize, being much more so than their hydrocarbon counterparts; it is the problem of the research chemist to use such configurations to the best advantage in the design of heat-stable molecules, and to avoid the less stable structures. Even the most refractory of organosilicon groupings is a source of weakness in an organosilicon oxide, for example, because the composite is less stable than silica itself. In this respect a silicone resin represents a partial sacrifice of the stability of silica in order to gain plasticity and flexibility by the inclusion of organic groups.

METHODS OF ESTABLISHING CARBON–SILICON BONDS

Before taking up the separate classes of monomeric organosilicon compounds, it would be well to consider the available methods for attaching organic groups to silicon atoms. The separate compounds which have been reported then will be seen to fall into groups or classes, each derived by the application of one or more of the general methods of synthesis. As might be supposed, the different classes of compound often are prepared most conveniently by different methods.

There are two general types of synthesis for organosilicon compounds: the *substitution* methods and the *direct* method. In the substitution methods, a silicon halide or ester is employed as starting material, and the halogen atoms or ester groups are replaced successively by reaction with a suitable organometallic compound or its progenitors. In the direct method, a hydrocarbon halide reacts directly with elementary silicon under certain favorable conditions to produce a mixture of organosilicon halides. Both types have been studied extensively, and, although not all of the resulting information is available for publication, it is possible to discuss in a general way the chemical features of each method. No attempt will be made at this time to compare the economic aspects of the different methods or to assess their commercial values; such comparisons involve a number of industrial considerations which are beyond the scope of this chapter.

The Substitution Methods. In the following paragraphs the substitution methods are taken up in their approximate chronological order under the subheadings **1, 2, 3,** and **4.** Then follows a brief discussion of the direct method and its proposed mechanism. In order

to keep the discussion general in nature and to avoid repetition of footnotes, references to specific applications of the various methods are given later in the chapter as the compounds so prepared are described.

1. SUBSTITUTION BY ALKYLS OF ZINC, MERCURY, AND ALUMINUM. The reaction of alkyls of zinc with ethyl silicate or silicon tetrachloride was the first to be used for the preparation of organosilicon compounds. During the period 1863 to 1880 Friedel and Crafts and later Ladenburg employed zinc dimethyl and zinc diethyl to prepare the corresponding alkyls of silicon and many of the intermediate substitution products as well. The reactions were conducted in sealed tubes heated to about 160° and were of a straightforward metathetical type:

$$2Zn(C_2H_5)_2 + SiCl_4 = 2ZnCl_2 + Si(C_2H_5)_4$$
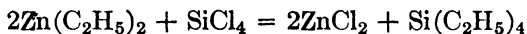
In much the same way they prepared hexaethyldisilane from hexa-iododisilane and zinc ethyl.

A variation of the method was described in 1884 by Pape, who used a mixture of silicon tetrachloride and propyl iodide with metallic zinc instead of preparing the zinc dipropyl separately. Another variation, exploited by Friedel and Ladenburg, eliminated the sealed tube by introducing metallic sodium along with the zinc alkyl and silicate ester:

$$Zn(C_2H_5)_2 + Si(OC_2H_5)_4 + 2Na = (C_2H_5)_2Si(OC_2H_5)_2$$
$$+ 2NaOC_2H_5 + Zn \qquad \text{etc.}$$
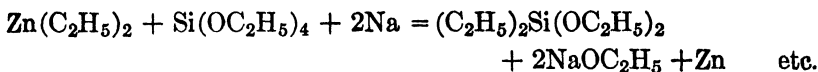
Starting with three pounds each of the zinc diethyl and ethyl silicate, Ladenburg prepared all of the ethylethoxysilanes and described their properties. He also was able to show that the reaction was not a simple reduction of ethoxy groups to ethyl groups by the action of sodium, for methyl silicate and zinc ethyl gave *ethyl*methoxysilanes. It is probable that the sodium reacted first with the zinc alkyl, as proposed by Ladenburg,

$$Zn(C_2H_5)_2 + 2Na = 2NaC_2H_5 + Zn$$
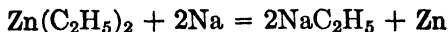
and that the sodium ethyl was the real alkylating agent. Such a sequence is in keeping with Gilman's rules for the formation of one organometallic compound from another and would explain the enhanced reactivity toward ethyl silicate at moderate temperatures.

Zinc alkyls also have been caused to react with trichlorosilane to produce trialkylsilanes, R_3SiH. Thus zinc propyl and trichlorosilane react to form tripropylsilane, but Pape found that at the same time considerable tetrapropylsilane was produced, according to the repre-

sentation,

$$4Zn(C_3H_7)_2 + 2SiHCl_3 = SiH(C_3H_7)_3 + Si(C_3H_7)_4 + Zn$$
$$+ 3ZnCl_2 + C_3H_8$$
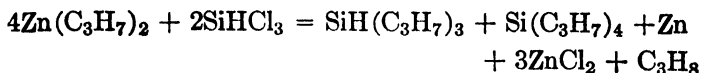
This result can be explained only by the partial hydrogenation of zinc propyl by silicon–hydrogen bonds under the particular conditions of the experiment (150° for 6 hours in a sealed tube), and may be taken as another example of the strong reducing action of the silane bond.

No similar destruction of silicon–hydrogen groups was encountered in the gas-phase methylation of chlorosilanes with zinc methyl as reported by Stock and Somieski in 1919. Vapor-phase alkylation of the silicon halides by the use of zinc and an alkyl halide more recently has been greatly extended as a general method by Hurd,[3] who passed the mixed vapors of the silicon halide and alkyl halide over a heated bed of the granular metal. As an example, dimethyldichlorosilane and methyl chloride were passed through granular zinc at 375° to yield a mixture of trimethylchlorosilane and unreacted dimethyldichlorosilane. A similar reaction conducted with powdered aluminum in place of the zinc converted 30 per cent of the dimethyldichlorosilane to trimethylchlorosilane and also produced a small amount of silicon tetramethyl. In the same way, silicon tetrachloride and trichlorosilane, as well as the methylchlorosilanes and bromosilanes, react with methyl chloride, ethyl chloride, methyl bromide, and the like, in the presence of excess zinc or aluminum, to substitute organic groups for one or more of the halogen atoms attached to silicon.

It is proposed[3] that in this vapor-phase alkylation an alkyl of zinc or aluminum first is formed and that this reacts immediately with the silicon halide:

$$2Zn + 2CH_3Cl = Zn(CH_3)_2 + ZnCl_2$$
$$Zn(CH_3)_2 + 2CH_3SiCl_3 = 2(CH_3)_2SiCl_2 + ZnCl_2$$
$$2Al + 3CH_3Cl = CH_3AlCl_2 + (CH_3)_2AlCl$$
$$CH_3AlCl_2 + CH_3SiCl_3 = (CH_3)_2SiCl_2 + AlCl_3 \qquad \text{etc.}$$
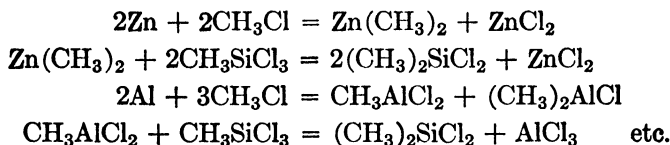
At higher temperatures the methylchlorosilanes themselves appear to react with aluminum, furnishing methyl groups for the further alkylation of some molecules at the expense of others which are reduced to free silicon. This actually is a form of disproportionation, in which organic groups are stripped from some silicon atoms and attached to others. In this and the similar reactions zinc or aluminum acts as halogen acceptor.

[3] Hurd, *J. Am. Chem. Soc.* **67**, 1545 (1945).

Although these liquid-phase and vapor-phase alkylations serve well to attach aliphatic groups to silicon, they are not so satisfactory for the substitution of aromatic groups. Very early in the history of organosilicon chemistry, Ladenburg found that the aryl compounds of mercury were more effective reagents than those of zinc. For example, mercury diphenyl reacted with silicon tetrachloride in a sealed tube at 300° to form phenyltrichlorosilane:

$$Hg(C_6H_5)_2 + SiCl_4 = C_6H_5SiCl_3 + C_6H_5HgCl$$
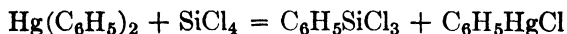
A similar reaction with mercury ditolyl at 320° produced tolyltrichlorosilane. No modifications of the method have come into common use.

2. SODIUM CONDENSATION. The coupling of an organic halide and a silicon halide by reaction with metallic sodium (the so-called Wurtz reaction) was first applied by Pape in 1884. Silicon tetrachloride and isoamyl or isobutyl chloride were found to react with sodium at reflux temperatures when a little ethyl acetate was added to get the reaction started:

$$SiCl_4 + 4C_4H_9Cl + 8Na = Si(C_4H_9)_4 + 8NaCl$$
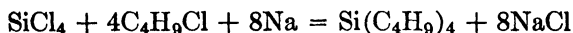
A similar condensation of ethyl bromide and silicon tetrachloride with sodium was used by Kipping and Lloyd in 1907 to prepare silicon tetraethyl.

Although the reactions of various organosilicon halides with sodium have been studied extensively, the Wurtz reaction as a method for attaching organic groups to silicon never achieved the popularity of the Grignard reaction or even of the other methods for organosilicon synthesis, chiefly because the difficulty of control made it reasonably successful only as a means of preparing tetra-alkyls. The partially substituted silicon halides, for example, appeared only in low yields because the reaction as usually conducted went right on to complete substitution. One explanation is based on the heterogeneity of the system: a molecule of silicon tetrachloride which comes in contact with the relatively enormous surface of a lump of sodium has available an excess of sodium atoms and derives enough energy from the first substitution

$$2Na + Si—Cl + R—Cl = Si—R + 2NaCl$$
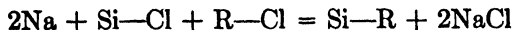
to go right on with the substitution of the remaining three silicon-chlorine bonds. Only by limiting the supply of R—Cl, as by extreme dilution, could this process by limited. Local overheating due

to the energy of condensation makes even the control by dilution seem questionable.

This liberation of energy by the reaction just shown was found by Schumb [4] and his coworkers also to be sufficient to cleave the silicon-silicon bond. The action of sodium on mixtures of ethyl bromide, chlorobenzene, or n-amyl chloride with hexachlorodisilane resulted only in tetrasubstituted monosilanes and no disilane derivatives. In the same way, the silicon–oxygen–silicon bond of hexachlorodisiloxane was split by sodium in the presence of ethyl bromide or chlorobenzene and yielded only silicon tetraethyl or tetraphenyl.

These results led Schumb and Saffer to devise a two-stage synthesis [5] which allows a much better control. The sodium first is allowed to react with a halide such as chlorobenzene in a solvent to yield phenyl sodium. After the heat of this reaction is dissipated, the phenyl sodium is mixed with the silicon halide in solution, and a milder reaction ensues. In this way hexaphenyldisilane was made from hexachlorodisilane, and hexaphenyldisiloxane from hexachlorodisiloxane. Moreover, phenyltrichlorosilane was made by the action of less than one equivalent of sodium phenyl on silicon tetrachloride. The use of a separately prepared sodium alkyl in this way provides the same degree of control as in a Grignard synthesis, and the reactions indeed are very similar. Organolithium compounds probably could be used in the same way.

3. SUBSTITUTION BY ORGANOMAGNESIUM COMPOUNDS. When Victor Grignard first developed the separate preparation of the organomagnesium halides as reagents, he not only opened a wide field of synthesis in organic chemistry but also gave a great impetus to organosilicon chemistry. Within a short time Kipping [6] and Dilthey [7] had applied the Grignard reaction to the preparation of organic derivatives of silicon tetrachloride. Subsequent refinement of technique by Kipping and his students then made the Grignard method more popular than any other for preparing a great variety of organosilicon compounds.

As usually carried out, the Grignard synthesis is a two-stage method. The reaction of a suitable alkyl or aryl halide [8] with magnesium turnings suspended in a straight-chain aliphatic ether gives

[4] Schumb, Ackerman, and Saffer, *J. Am. Chem. Soc.* **60**, 2486 (1938).

[5] Schumb and Saffer, *J. Am. Chem. Soc.* **63**, 93 (1941).

[6] Kipping, *Proc. Chem. Soc.* **20**, 15 (1904).

[7] Dilthey, *Ber.* **37**, 319, footnote 2 (1904).

[8] The " suitability " of the halide is defined by the possibility of its reaction with its own magnesium derivatives. See Gilman, Organic Chemistry, second edition, Vol. 1, Chap. 5 (John Wiley & Sons, Inc., 1943).

the corresponding alkyl or aryl magnesium halide, or, more correctly, an equilibrium mixture of the organomagnesium halide with magnesium dialkyl and magnesium dihalide.* This mixture, still in the anhydrous solvent, then is added in appropriate quantity to a solution of a silicon halide or ester, usually with cooling and stirring. Magnesium halide (or alkoxide, if an ester is used) seoarates as a precipitate, and the substituted silicon compounds remain in the solvent, from which they usually may be separated by distillation.

For sluggish reactions involving the higher aryl magnesium halides, a variation of procedure is used in which the solvent is evaporated from the mixture of Grignard reagent and silicon halide and the partially reacted substances are heated to a temperature of 160° to 180° for several hours.[9] The organosilicon compounds then may be separated by destroying any excess Grignard reagent and recrystallizing the product from a suitable solvent.

Another variation used by Kipping and others simplifies the synthesis to a one-stage reaction. Magnesium is suspended in an ether solution of silicon tetrachloride, and the organic halide is introduced dropwise or in portions. The other variation of adding magnesium to the mixed halides also has been tried but is not convenient. Adding the mixed halides to magnesium in ether is less awkward.

Some reagents for the Grignard synthesis can serve as their own solvents. In the previous chapter it was pointed out that ethyl silicate is such a solvent, and that alkyl- or arylethoxysilanes may be made by adding the appropriate organic halide to a stirred mixture of magnesium and ethyl silicate.[10] In the same way excess chlorobenzene is a solvent for the preparation of phenyl magnesium chloride.[11]

In all variations of the Grignard reaction, and indeed in all similar substitution reactions involving alkyls of zinc, mercury, or sodium, a mixture of products is obtained. As the organometallic compound is added to the silicon halide the primary substitution product is formed, and this then may react with the additional reagent just as did the original unsubstituted halide. If silicon tetrachloride be taken as an example, the successive substitution products will be $RSiCl_3$, R_2SiCl_2, R_3SiCl, and R_4Si. Of these, the first three still may react with the substitution reagent. Any attempt to prepare an inter-

[9] Cusa and Kipping, *J. Chem. Soc.* **1933**, 1040; Schumb and Saffer, *J. Am. Chem. Soc.* **61**, 363 (1939).

[10] U. S. patent 2 380 057 to R. R. McGregor and E. L. Warrick.

[11] Gilman and Brown, *J. Am. Chem. Soc.* **52**, 3330 (1930); German patents 660 075 and 697 420.

* The conditions for starting and operating this reaction are too well described in elementary textbooks and laboratory manuals to be repeated here.

mediate substitution product therefore must result in a mixture of the desired compound with its less highly and more highly alkylated homologs. The situation has been treated mathematically as a system of consecutive competitive reactions[12] in which the molar proportions of all the possible products at any given time are functions of the molar proportion of reagent added and the relative reactivities of the individual products. This general treatment shows agreement with the experimental yields of the different substitution products only when the reactivity of the symmetrical R_2SiX_2 is assigned a value much lower than that of the unsymmetrical $RSiCl_3$. This implies that the molecular configuration has more to do with reactivity than has the number of reactive groups, or (to put it another way) the capacity for reaction. The circumstance acts to make the Grignard reaction more favorable to the production of compounds of the type R_2SiCl_2 than it otherwise would be.

In all of the organosilicon syntheses so far discussed, an organometallic compound has been used as the substitution reagent, whether prepared separately or not. From an over-all point of view, a metal is used as condensing agent or halogen acceptor, and the organic groups are transferred from a more reactive metal to a less reactive metalloid (silicon) in exchange for halogen or its equivalent. Of the several methods, the Grignard reaction has become the most widely used because the organomagnesium compound is the most easily prepared.

4. ABSORPTION OF HYDROCARBONS. One of the newest substitution methods does not involve conversion of free metal to metallic halide as a part of the process. Instead, unsaturated hydrocarbons or carbon monoxide are absorbed directly by silicon tetrachloride at pressures of 10 to 100 atm. and in the presence of metallic chlorides or oxychlorides as catalysts.[13] If ethylene is absorbed, the product is β-chloroethyltrichlorosilane:

$$CH_2{=}CH_2 + SiCl_4 \rightarrow Cl{-}C_2H_4{-}SiCl_3$$
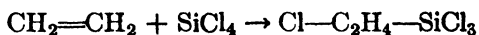
This is not substitution in the sense employed in the foregoing discussions, but rather is addition followed by rearrangement. The net effect, however, is a replacement of halogen by a halogenated alkyl group.

When acetylene is absorbed, again under pressure and in the presence of aluminum chloride or mercury oxychloride as catalyst, the

[12] Fuoss, *J. Am. Chem. Soc.* **65**, 2406 (1943).
[13] Russian certificate of invention 44 934 issued to I. I. Shtetter (application filed June 2, 1935).

product has a β-chlorovinyl group attached to silicon:

$$CH\equiv CH + SiCl_4 \rightarrow ClCH=CH-SiCl_3$$
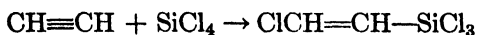
and, if carbon monoxide is employed, a carbonyl chloride group is formed:

$$CO + SiCl_4 \rightarrow O=\overset{\overset{\textstyle Cl}{\textstyle |}}{C}-SiCl_3$$
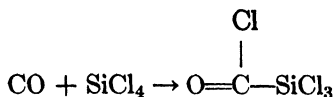
These reactions appear to cease when one equivalent of the hydrocarbon or monoxide is absorbed, so that the method seems limited to the preparation of halogen-substituted trichlorosilanes. However, the products are attractive as intermediates for the preparation of many other organosilicon compounds. No mechanism is offered for the reaction. If the salts of aluminum, copper, mercury, or nickel which are disclosed as catalysts undergo any intermediate reactions with the hydrocarbon, such reactions must be cyclic because the catalyst is not consumed. The fact that molar quantities of catalyst are required for the reaction may be evidence for such intermediate reactions. No subsequent publications on the method have appeared, and so it is difficult to evaluate its importance in comparison with the earlier syntheses.

A somewhat similar process makes use of the gas-phase reaction of aliphatic hydrocarbons with a silicon halide[14] at a high temperature. Thus a mixture of silicon tetrachloride and an aliphatic hydrocarbon may be heated to a temperature above 450° (but below the temperature of thermal decomposition of the hydrocarbon) to produce organosilicon halides.

Direct Synthesis. The direct method for preparing organosilicon halides represents a distinct departure from all the substitution variations developed over the past 80 years in that, instead of fully halogenating the silicon and then successively replacing the halogen atoms with organic groups, it attaches both halogen atoms and organic groups to silicon in one operation.[15] This appears to be a general reaction in which hydrocarbon halides react with elementary silicon in the liquid or vapor phase and in the presence or absence of a catalyst to produce a mixture of organosilicon halides. The most useful variations are those in which alkyl or aryl chlorides or bromides in the vapor phase are passed through a heated mixture of silicon and a
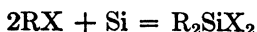
[14] U. S. patent 2 379 821 to H. C. Miller and R. S. Schreiber.
[15] Rochow, *J. Am. Chem. Soc.* **67,** 963 (1945); U. S. patent 2 380 995.
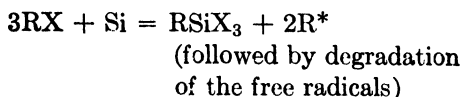
metallic catalyst; under such conditions acceptable yields of R_2SiX_2 are obtained in a single pass through the reactive mass.
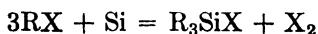
Under optimum conditions the predominant reaction may be represented as

$$2RX + Si = R_2SiX_2$$

A number of side reactions occur simultaneously, such as

$$3RX + Si = RSiX_3 + 2R*$$
$$\text{(followed by degradation of the free radicals)}$$

and

$$3RX + Si = R_3SiX + X_2$$

followed by

$$2X_2 + Si = SiX_4$$

The degradation of free radicals also may supply hydrogen for the formation of hydrides:

$$2RX + Si \rightarrow RSiHX_2 + \text{hydrogen} + \text{carbon}$$
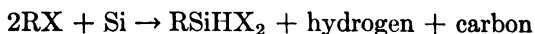
These reactions are written only as summaries of the chemical changes which take place. No single compound is obtained, but rather a mixture of related organosilicon halides from which the individual substances must be separated by distillation. The composition of the mixture is influenced by the temperature of the reacting mass, the type of catalyst used (if any), the manner in which the catalyst is associated with the silicon, and possibly the time of contact. These factors allow some flexibility in directing the reaction toward obtaining a preponderance of one particular compound, but the related substances always are formed to some extent.

A consideration of the equations previously given will show that the method is most economical of materials when two moles of the halide RX produce one mole of organosilicon halide R_2SiX_2. The production of any other compounds, unless in balanced proportions, represents a loss of organic groups or halogen. The direct synthesis therefore is best suited to the preparation of dialkyl- or diaryldihalosilanes, and the operation of the reaction is more satisfactory if limited further to the chlorosilanes and bromosilanes. If compounds of the type R_3SiCl or R_4Si are required, the corresponding dichlorosilane may first be made by the direct method and then alkylated further by the use of the Grignard or some other substitution method.

The actual operation of the direct method involves heating a mass of powdered silicon (preferably associated with a catalyst) in

a reaction tube, passing the vapors of the hydrocarbon halide through the heated mass, condensing the products, and separating the individual organosilicon halides.   In general, the lowest temperature which will suffice to initiate the reaction has been found to be the most satisfactory for producing maximum yields of R_2SiX_2.   As the temperature is raised above this threshold value, the rate of reaction increases but the possibility of pyrolysis of free radicals also rises, so that the resulting mixture of organosilicon compounds becomes richer in halogen and correspondingly poorer in organic groups.   The optimum operating temperature depends upon the nature of the hydrocarbon halide and is different for each substance; for the lower alkyl chlorides and bromides it usually lies between 275° and 375° C.

A catalyst for the direct reaction is desirable, not only to improve the reactivity and yield, but also to " smooth " the reaction and make the result more reproducible than otherwise would be the case.   One effective catalyst is metallic copper, which may be powdered and mixed with the silicon or (better still) sintered with the silicon by heating the mixture in hydrogen.[16]   The initial distribution of the catalyst has much to do with the behavior of the reaction during the early stages, as is evident upon consideration of the proposed mechanism for the reaction.[17]

When a crystal of pure silicon is embedded in copper and exposed to methyl chloride at 350° C., the interface between the two solids is seen to recede, and both copper and silicon are removed from the point at which they are in contact or in close proximity.   The fact that either element is a catalyst for the removal of the other suggests that the mechanism depends upon mutual interaction, rather than upon adsorption, for example.   To find out what happened to the copper, thin films of evaporated copper on glass were heated in an atmosphere of methyl chloride, and it was found that approximately half of the copper was transported in the form of a volatile labile compound, whereas the other half remained in the form of a transparent layer of crystals of cuprous chloride.   The first step therefore appears to be

$$2Cu + CH_3Cl = \overline{CuCH_3} + CuCl \qquad (1)$$
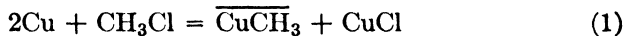
The copper methyl is unstable at the temperature of reaction and soon decomposes to metallic copper and free methyl radicals, the latter being identified by their ability to " wipe off " a mirror of lead on glass (the Paneth test).   This decomposition occurs in about 0.003 second

[16] U. S. patents 2 380 997 to W. I. Patnode; 2 380 996 to E. G. Rochow and W. I. Patnode.
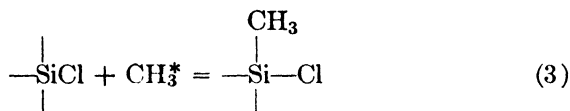[17] Hurd and Rochow, *J. Am. Chem. Soc.* **67**, 1057 (1945).

at 250° C., so that the free methyl groups are available for reaction with silicon only in the immediate vicinity of the copper. It follows that copper placed some distance from silicon cannot facilitate the formation of organosilicon compounds.

It can be shown independently that cuprous chloride, the other product of reaction 1, is reduced by elementary silicon at 265° or more:

$$CuCl + Si = Cu + \overset{\displaystyle |}{\underset{\displaystyle |}{-Si}}-Cl \tag{2}$$
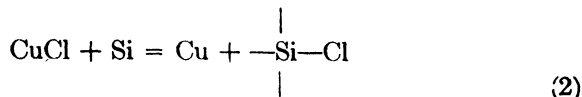
This regenerates the other half of the copper used in reaction 1, so that it is again available for reaction with the organic halide. The copper used as " catalyst " in the direct synthesis therefore undergoes two cycles of reaction, and is redeposited near the original scene of reaction, ready to be used over again. This explains why 10 per cent by weight of copper in the silicon mixture is ample for full effect, and even 3 per cent by weight (mole fraction 0.013) has a marked effect.

At first it was thought that the copper methyl might react with the silicon halide in the manner of a Grignard reagent, but copper ethyl and copper phenyl prepared in ether suspension did not react with silicon tetrachloride. Neither did free methyl radicals from lead tetramethyl react with elementary silicon, but they did add on silicon that was being chlorinated. This suggests that the third step in the mechanism is the addition of methyl groups to the chlorinated silicon formed in the cuprous chloride reduction:

$$\overset{\displaystyle |}{\underset{\displaystyle |}{-Si}}Cl + CH_3^* = \overset{\displaystyle CH_3}{\underset{\displaystyle |}{\overset{\displaystyle |}{-Si}}}-Cl \tag{3}$$

Such a structure may then add more chlorine or more methyl groups or both, until it is tetrasubstituted and removed from the scene of reaction. In this way there is produced a mixture of compounds of the type

$$(CH_3)_a SiCl_{4-a}$$
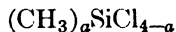
where a has values from zero to four.

Thus the function of the copper catalyst in the synthesis of methylchlorosilanes seems to be to transport the free methyl groups and to prolong their life in the form of copper methyl, and also to transfer the chlorine from methyl chloride to silicon. It is probable that copper acts similarly in the reaction of other hydrocarbon halides with silicon, and that similar metals also may undergo the same cycle of reactions.

For example, silver is known to be a preferred catalyst for the direct synthesis of phenylchlorosilanes from chlorobenzene and silicon,[18] and since silver chloride readily is reduced by silicon it may be inferred that the sequence of reactions is the same as that for copper.   Other metals may exercise catalytic effects on the reaction through entirely different mechanisms, of course.

These five general methods of establishing carbon–silicon bonds constitute the tools for synthesizing organosilicon compounds.   Each has its place in laboratory or large-scale preparations, as is evident in the following discussions, and it is unlikely that any one method will supplant the others.   It seems more probable that the methods will supplement each other, and that there will continue to be a place for any new syntheses that can be devised.

THE ALKYLS

In the usage of organometallic chemistry the term " metal alkyl " designates both aliphatic and aromatic hydrocarbon derivatives of the metal,* and it is so used here.   The simple alkyls of silicon therefore comprise all of the compounds of the type SiR_4, where R is any hydrocarbon radical.

Silicon tetramethyl[19] and tetraethyl[20] were the first such simple alkyls of silicon to be prepared.   The tetramethyl originally was made by the reaction of zinc dimethyl with silicon tetrachloride in a sealed tube at 200°, but it now is prepared more conveniently by the action of an excess of methyl magnesium bromide or chloride on silicon tetrachloride, followed by distillation of the ether and tetramethyl and absorption of the ether in cold sulfuric acid.[21]   The tetramethyl is a colorless unreactive liquid of very little odor, boiling at 26° C.   Silicon tetraethyl similarly may be made by the action of zinc ethyl on silicon tetrachloride at 160°, by the action of zinc ethyl and sodium on ethyl silicate,[22] by sodium condensation of ethyl bromide and silicon tetrachloride,[23] or by the Grignard synthesis.[24]   It can easily be separated from ether by distillation because it boils at 154°.   The ethyl groups may be chlorinated without breaking the

[18] Rochow and Gilliam, *J. Am. Chem. Soc.* **67**, 1772 (1945).
[19] Friedel and Crafts, *Ann.* **136**, 203 (1865).
[20] Friedel and Crafts, *Ann.* **127**, 31 (1863).
[21] Bygden, *Ber.* **44**, 2640 (1911).
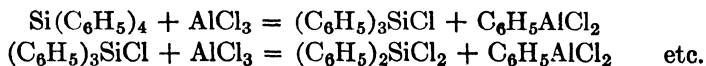[22] Ladenburg, *Ann.* **164**, 302, 330 (1872).
[23] Kipping and Lloyd, *J. Chem. Soc.* **79**, 456 (1901).
[24] Krause and von Grosse, reference 1, pp. 260–1.
* Krause and von Grosse (reference 1) also use the term "alkyl" inclusively, and the terms "alphyl" and "aryl" as subdivisions under it.

carbon–silicon bond,[25] and if the chlorine is in the *alpha* position it may be removed as hydrogen chloride, leaving a vinyl group attached to silicon.[26] In the same way, when silicon tetrapropyl is brominated and then heated, hydrogen bromide splits out, leaving tripropylallyl-silane.[27]

Silicon tetraphenyl is easily prepared from chlorobenzene and silicon tetrachloride[28] or tetrafluoride[29] by sodium condensation, and by the Grignard reaction from bromobenzene and silicon tetrachloride or sodium fluosilicate.[30] It crystallizes in colorless plates which melt at 233° and are said to boil above 530°. All four phenyl groups may be nitrated with fuming nitric acid without splitting off the phenyl groups, but heating with bromine and water in a sealed tube causes fission. Aluminum chloride reacts with silicon tetraphenyl stepwise,

$$Si(C_6H_5)_4 + AlCl_3 = (C_6H_5)_3SiCl + C_6H_5AlCl_2$$
$$(C_6H_5)_3SiCl + AlCl_3 = (C_6H_5)_2SiCl_2 + C_6H_5AlCl_2 \quad \text{etc.}$$

and finally degrades the compound to silicon tetrachloride and leaves a tarry residue containing the phenyl groups.

In those reactions involving substitution on the phenyl groups which are attached to silicon, it appears that the silicon may exert either a *meta*-directing influence[31] or an *ortho–para* influence, depending upon the other groups on the silicon. Thus a triphenylsilyl group is *meta* directing, but halogens or aliphatic groups on the silicon cause it to direct substitution quite strongly to the *ortho* and *para* positions.

Other examples of aromatic " normal " alkyls are the tetra-*m*-tolyl (m.p 151°)[32] and the tetra-*p*-tolyl (m.p. 228°).[33] Silicon tetra-benzyl[34] more properly is grouped as an aliphatic compound, but it closely resembles silicon tetraphenyl in that it is a very stable substance of high melting point and exceedingly high boiling point (550°).

There are many " mixed " alkyls in which different aliphatic and aromatic groups are linked to a single silicon atom. Some of these have been made by altering one of the four groups of a tetra-alkyl

[25] Friedel and Crafts, *Ann.* **138**, 19 (1866).

[26] Ushakov and Itenberg, *J. Gen. Chem. USSR* **7**, 2495 (1937).

[27] Pape, *Ann.* **222**, 373 (1884).

[28] Polis, *Ber.* **18**, 1540 (1885); Manulkin and Yakubova, *J. Gen. Chem. USSR* **10**, 1300 (1940).

[29] U. S. patent 2 238 669 to R. H. Wiley.

[30] Soshestvenskaya, *J. Gen. Chem. USSR* **8**, 294 (1938); *ibid.* **10**, 1689 (1940); Manulkin and Yakubova, *J. Gen. Chem. USSR* **10**, 1300 (1940).
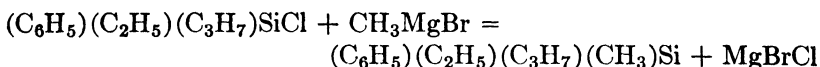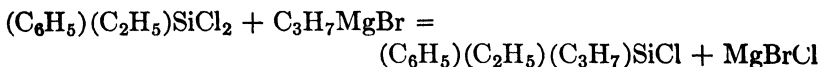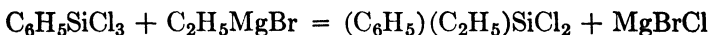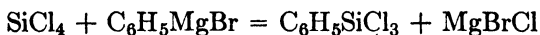
[31] Kipping and Blackburn, *J. Chem. Soc.* **1932**, 2200.

[32] Polis, *Ber.* **18**, 1540 (1885).

[33] Kipping and Lloyd, *J. Chem. Soc.* **79**, 449 (1901).

[34] Smith and Kipping, *J. Chem. Soc.* **101**, 2553 (1912).

(as in the preparation of tripropylallylsilane from silicon tetrapropyl), but most have been made by the successive replacement of the chlorine in silicon tetrachloride with different radicals supplied by Grignard reagents, as in these examples:

$$SiCl_4 + C_6H_5MgBr = C_6H_5SiCl_3 + MgBrCl$$

$$C_6H_5SiCl_3 + C_2H_5MgBr = (C_6H_5)(C_2H_5)SiCl_2 + MgBrCl$$

$$(C_6H_5)(C_2H_5)SiCl_2 + C_3H_7MgBr =$$
$$(C_6H_5)(C_2H_5)(C_3H_7)SiCl + MgBrCl$$

$$(C_6H_5)(C_2H_5)(C_3H_7)SiCl + CH_3MgBr =$$
$$(C_6H_5)(C_2H_5)(C_3H_7)(CH_3)Si + MgBrCl$$

A table of 21 such mixed alkyls, together with their physical properties, methods of preparation, and literature references, is given in Krause and von Grosse.[35]   Those with four different groups represent compounds of an asymmetric silicon atom, and their derivatives exhibit optical isomerism.[36]   The p-bromoderivative of triethylphenyl-silane,* $(C_2H_5)_3Si—C_6H_4—Br$, reacts with magnesium to form a Grignard reagent, and this has been employed to synthesize silicon-containing derivatives of tin, lead, and arsenic.[37]

THE ALKYLSILANES

Organic derivatives of trichlorosilane (" silicochloroform," $SiHCl_3$) are obtained readily by applying the methods previously described for the alkylation of silicon tetrachloride.   Thus trimethylsilane[38] results from the action of zinc methyl on trichlorosilane, and triphenyl-silane[39] results from the action of the phenyl Grignard reagent.   Tri-t-butylsilane and tri-i-amylsilane have been obtained by sodium condensation of the respective chlorides with trichlorosilane.[40]   Triethylsilane was obtained by the reaction between zinc ethyl, sodium, and ethyl silicate.[41]

No method has been reported for the direct alkylation of mono-

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[35] Krause and von Grosse, reference 1, pp. 264–5.

[36] Challenger and Kipping, Proc. Chem. Soc. 26, 65 (1910); Challenger and Kipping, J. Chem. Soc. 97, 755 (1910).

[37] Grüttner and Krause, Ber. 50, 1559 (1917).

[38] Taylor and Walden, J. Am. Chem. Soc. 66, 842 (1944).

[39] Reynolds, Bigelow, and Kraus, J. Am. Chem. Soc. 51, 3067 (1929).

[40] Taurke, Ber. 38, 1664 (1905).

[41] Ladenburg, Ann. 164, 302, 327 (1872).

* Following the recommended system of nomenclature (reference 6, Chapter 1), the alkyls having two or more different groups on the silicon are named as derivatives of silane and the term " silicon tetra- " is reserved for those compounds in which the four substituents are all alike.

silane.   In order to make methylsilane, CH_3SiH_3, it was necessary to convert silane to monochlorosilane and then treat this with zinc methyl.[42]   By chlorinating again and repeating the reaction with zinc methyl, dimethylsilane was obtained.   A similar series of reactions was used to prepare cyanosilane[43] from monosilane:

$$SiH_4 + HI \xrightarrow{AlI_3} SiH_3I + H_2$$

$$SiH_3I + AgCN \longrightarrow SiH_3CN + AgI$$
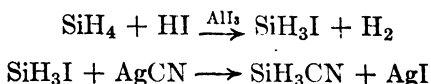
THE ALKYLHALOSILANES

Particular emphasis is due the organosilicon halides, or alkylhalosilanes, because these substances are the intermediates from which silicone polymers are made.   Their reactive halogen linkages allow them to be converted readily into silicols, alkoxysilanes, or siloxane polymers which retain the organosilicon grouping present in the halide. Besides this, some alkylchlorosilanes now are important in their own right as reagents for imparting water-repellent films to many different surfaces.

Since no one method of synthesis is suitable for the preparation of all alkylhalosilanes, the more favorable methods for each different type of compound are pointed out in the following discussion.   Details concerning the practical operation of the various methods are reserved for a later chapter on large-scale preparations.

The **trialkylhalosilanes** include a growing group of *trialkylfluorosilanes* derived from silicon tetrafluoride by action of Grignard reagents.   Even with an excess of the reagent, it has been found difficult to force the process beyond the stage of trisubstitution; the markedly low reactivity of the single fluorine atom in compounds of the type R_3SiF makes these the chief end products of the Grignard reaction.[44]   Six such trialkylfluorosilanes are included in the index at the end of this chapter.   In each instance the fluorine is reported to be much less active to reagents and more difficult to hydrolyze than is chlorine or bromine in the analogous compounds R_3SiCl and R_3SiBr.

The known *trialkylchlorosilanes* range from trimethylchlorosilane[45] (b.p. 57.6°) to tribenzylchlorosilane[46] (b.p. 300° to 360° at 100 mm.) in volatility.   The bromoanalogs range from triethylbromosilane

[42] Stock and Somieski, *Ber.* **52**, 706 (1919).

[43] Eméleus, Maddock, and Reid, *J. Chem. Soc.* **1941**, 353.

[44] Me loks, *J. Gen. Chem. USSR* **7**, 2007 (1937); *ibid* **8**, 291 (1938); Gierut, Sowa, and Nieuwland, *J. Am. Chem. Soc.* **58**, 897 (1936).

[45] Taylor and Walden, *J. Am. Chem. Soc.* **66**, 842 (1944); Gilliam and Sauer, *J. Am. Chem. Soc.* **66**, 1793 (1944).

[46] Martin and Kipping, *J. Chem. Soc.* **95**, 302 (1909).

(b.p. 161°) to triphenylbromosilane (m.p. 120°). There is also a group of mixed trialkylchlorosilanes, of which benzylethylpropyl-chlorosilane[47] is an example; these are prepared by the stepwise substitution of the chlorine in silicon tetrachloride by successive treatment with single equivalents of three different Grignard reagents.*

The trialkylchlorosilanes undergo all of the reactions which are typical of the halides of silicon, although the violence of these reactions is reduced by the moderating influence of the three organic groups. Reaction with dry ammonia produces ammonium chloride and a disilazine, R_3Si—NH—SiR_3. Hydrolysis leads to the trialkylsilanols, R_3SiOH, which in turn may condense by dehydration in the manner of all hydroxides of silicon:

$$, \; 2R_3SiOH = R_3Si\text{—}O\text{—}SiR_3 + H_2O$$

The trialkylsilanols, being monofunctional, are capable only of condensation to the organodisiloxane as shown, and, since this reaction occurs relatively slowly under the influence of the R_3Si— group, it provides a basis for thorough study of the condensation process. It is found that the size of the organic group R has the major influence on the rate of condensation. Trimethylsilanol condenses so rapidly that it can be isolated only by a special technique,[48] but triphenylsilanol may be distilled at a temperature of 170° to 180° and a pressure of 1 mm. without condensing to hexaphenyldisiloxane.

The **dialkyldihalosilanes** are represented by dimethyl- and diphenyldibromosilanes, and by a considerable number of dichlorosilanes ranging from dimethyldichlorosilane[49] (b.p. 70°) to di-p-tolyldichlorosilane (b.p. 239° at 50 mm.). The earliest to be prepared, diethyldichlorosilane, was first obtained by preparing diethyldiethoxysilane from ethyl silicate and then replacing the ethoxy groups with chlorine by means of the reaction with benzoyl chloride.[50] Now these important intermediates are prepared in greater quantity by the Grignard synthesis or by the direct method.

The dialkyldihalosilanes react with alcohols to form esters of the type $R_2Si(OR')_2$, and they also hydrolyze to form dialkylsilanediols or dialkylsilicols, $R_2Si(OH)_2$. These silicols condense intermolecularly to form polymeric organosiloxanes. The rate of condensation is

[47] Kipping, *J. Chem. Soc.* **91**, 722 (1907).

[48] Sauer, *J. Am. Chem. Soc.* **66**, 1707 (1944).

[49] Gilliam, Liebhafsky, and Winslow, *J. Am. Chem. Soc.* **63**, 801 (1941); U. S. patent 2 286 763 to E. G. Rochow.

[50] Ladenburg, *Ann.* **164**, 310 (1872).

* A list of representative alkylhalosilanes is given in the compound index at the end of this chapter. For a description of those compounds reported before 1936, see Krause and von Grosse, reference 1, pp. 274–8.

governed principally by the size of the R group, being greatest for dimethylsilanediol and successively less for the silicols with larger and larger R groups. Diphenylsilanediol, for example, may be obtained as a stable white crystalline compound by hydrolyzing diphenyldichlorosilane in a mixture of water, toluene, and tertiary amyl alcohol,[51] but dimethylsilanediol condenses so rapidly that it has never been isolated. The lower aliphatic silanediols therefore remain purely hypothetical compounds, the possible existence of which is inferred from the existence of the trimethyl- and triethyl-silanols and from the existence of the more stable homologs.

The **alkyltrihalosilanes** are represented by methyltrichloro-silane and many other higher trichlorosilanes. The first ones to be reported (phenyl- and p-tolyltrichlorosilanes[52]) were prepared by the action of the respective mercury alkyls upon silicon tetrachloride, but all now may be prepared by the action of approximately one molar equivalent of Grignard reagent upon silicon tetrachloride. In the reaction of monochlorohydrocarbons with silicon[15] a consider-able proportion of alkyl- or aryltrichlorosilane appears in the product, especially when the conditions are such as to favor pyrolysis of the organic radicals. Certain chloroalkyltrichlorosilanes are prepared most readily by the absorption of olefins in silicon tetrachloride, as has been described.

Methyltrichlorosilane[49] (b.p. 66°) is the simplest member of this series, and α-naphthyltrichlorosilane (b.p. 170° at 22 mm.) is perhaps the most complex. A group of representative alkyltrichlorosilanes will be found in the index of compounds at the end of this chapter. All of the alkyltrichlorosilanes hydrolyze and are commonly supposed to form silanetriols:

$$RSiCl_3 + 3H_2O = RSi(OH)_3 + 3HCl$$
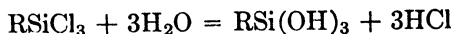
No such compound has ever been isolated and identified, however. A single organic group seems to exert insufficient retarding influence on the condensation of the silanetriol, and so it proceeds immedi-ately to split out water and to form polymeric products. At one time it was thought that the condensation produced a "siliconic acid" analogous to a carboxylic acid:

$$C_2H_5Si(OH)_3 = H_2O + C_2H_5SiOOH$$
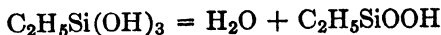
This supposed "siliconic acid" is a white silicalike solid, however, and obviously is polymeric rather than of the monomeric form shown.

[51] Burkhard, *J. Am. Chem. Soc.* **67**, 2173 (1945).
[52] Ladenburg, *Ann.* **173**, 151, 165 (1874).

All the other supposed silanetriols likewise form viscous, glassy, or silicalike polymers, and so it must be concluded that intermolecular condensation takes place and a three-dimensional silicon-and-oxygen network results. Use is made of this property in constructing organosiloxane polymers, as is described later.

Allyltrichlorosilane, allyldichlorosilane, and diallyldichlorosilane have been made by the direct reaction of allyl chloride with silicon.[53] The reaction is vigorous, and unless carefully controlled it produces enough heat to pyrolyze allyl groups, liberating hydrogen (part of which appears as $C_3H_5SiHCl_2$) and depositing carbon. The physical properties of these interesting substances are given in the table which follows this chapter; the boiling point for diallyldichlorosilane is given only approximately as 83° to 84° at 50 mm. because the compound polymerizes very readily during distillation. The homologs with a single allyl group may be distilled at atmospheric pressure without difficulty, and so it must be concluded that any inhibiting effect of the silicon atom on polymerization of the allyl group becomes ineffective when two allyl groups are linked to the same silicon.

Methylallyldichlorosilane, $(CH_3)(C_3H_5)SiCl_2$, and dimethylallylchlorosilane, $(CH_3)_2(C_3H_5)SiCl$, have been prepared by the action of methyl magnesium bromide on allyltrichlorosilane obtained by the direct reaction. These compounds, like the parent allyltrichlorosilane, may be distilled at atmospheric pressure (the boiling points are 119° and 112°, respectively) without appreciable polymerization.[53]

Vinylchlorosilanes also have been prepared by the direct reaction of vinyl chloride with silicon, but the comparative unreactivity of the chlorine attached to a vinyl group keeps the yields low. However, vinyltrichlorosilane and divinyldichlorosilane both have been isolated from the reaction mixture,[53] and their constants appear in the table. Both compounds also may be made by chlorinating the corresponding ethylchlorosilanes (which may be made by the direct reaction) and then extracting hydrogen chloride with a tertiary amine such as quinoline:

$$CH_3CHClSiCl_3 \rightarrow CH_2{=}CHSiCl_3 + HCl$$
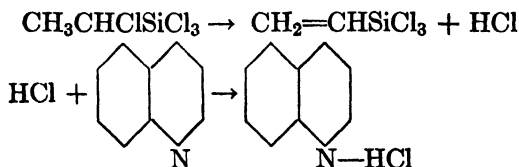
Methylvinyldichlorosilane then may be prepared by methylation of the vinyltrichlorosilane.[53]

[53] Hurd, *J. Am. Chem. Soc.* 67, 1813 (1945).

THE ALKYLALKOXYSILANES

A special class of alkylhalosilanes is the "mixed" group containing both Si—H and Si—X linkages. Methyldichlorosilane, CH_3SiHCl_2, for example, is both a hydride and a halide. It and the related methylchlorosilane, CH_3SiH_2Cl, were obtained from methylsilane by the action of hydrogen chloride,[54] and other examples result from the partial alkylation of "silicochloroform":

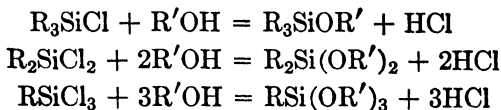$$RMgCl + SiHCl_3 = RSiHCl_2 + MgCl_2$$
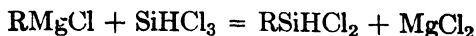
Methyldichlorosilane is also a by-product of the direct action of methyl chloride on silicon, particularly under conditions which allow pyrolysis of some of the methyl groups:

$$2CH_3Cl + Si = CH_3SiHCl_2 + C + H_2$$
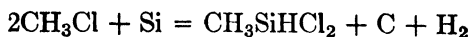
The alkylchlorosilanes containing silicon–hydrogen linkages usually may be hydrolyzed without splitting out the hydrogen, and also may be converted to esters. The hydrogen attached to silicon retains its silane character, however, for it oxidizes readily and is removed quantitatively by treatment with aqueous alkalies.

THE ALKYLALKOXYSILANES

The reaction of the alkylchlorosilanes with alcohols introduces another series of organosilicon compounds, the alkylsilicic esters (or ethers). These substances have some organic groups linked directly to silicon, whereas others are joined through oxygen. They may be considered to derive from the halides through replacement of halogen by alkoxy groups:

$$R_3SiCl + R'OH = R_3SiOR' + HCl$$
$$R_2SiCl_2 + 2R'OH = R_2Si(OR')_2 + 2HCl$$
$$RSiCl_3 + 3R'OH = RSi(OR')_3 + 3HCl$$

It is not necessary that such alkylalkoxysilanes be formed in this manner alone, however, for they can be prepared from the orthosilicates by direct reaction with zinc alkyls[55] or with the Grignard reagent, as was pointed out in the section on the orthoesters. It follows that there may be mono-, di-, and trialkyl derivatives of ethyl silicate just as mono-, di-, and trialkylchlorosilanes are obtained from silicon tetrachloride. The same is true of every other silicon orthoester, so that many different organosilicon compounds are possible even within
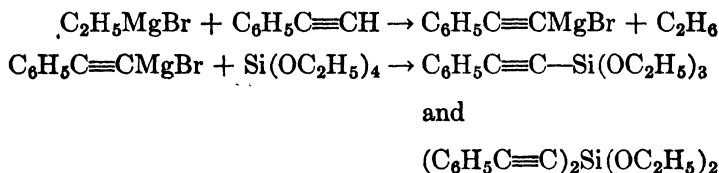
[54] Stock, The Hydrides of Boron and Silicon, p. 28 (Cornell University Press, 1933).
[55] Ladenburg, *Ann.* **173,** 148 (1874).

the limits of the readily available esters and the more common Grignard reagents.

In general, the alkylalkoxysilanes behave like the alkylchlorosilanes in that they hydrolyze to form the various silicols or their dehydration products. It is not necessary to go through the separate classes of compounds, for their reactions and derivatives may be inferred from the known properties of the halides and the previously discussed properties of the silicon esters. Some of the representative compounds are listed in the index which follows this chapter,[56] and a list of alkyltrialkoxysilanes is given in Krause and von Grosse.[57]

Added importance centers on the dialkyldialkoxysilanes in view of the fact that they are satisfactory intermediates for the manufacture of silicone resins. These compounds may be made by a modification of the Grignard method without the use of ether as a solvent,[58] and many of the alkyltriethoxysilanes listed in the compound index at the end of this chapter also were made this way.[59] The allyltriethoxysilane so prepared apparently did not polymerize, but the phenylethynylsilanes prepared by the following reactions

$$C_2H_5MgBr + C_6H_5C\equiv CH \rightarrow C_6H_5C\equiv CMgBr + C_2H_6$$
$$C_6H_5C\equiv CMgBr + Si(OC_2H_5)_4 \rightarrow C_6H_5C\equiv C—Si(OC_2H_5)_3$$

and

$$(C_6H_5C\equiv C)_2Si(OC_2H_5)_2$$

polymerized during the synthesis and the subsequent distillation.[60] It is concluded that the phenylethynyl group is weakly bound to silicon in these compounds, for hydrolysis removes it as phenylacetylene, leaving silica and ethanol.

[56] The esters of trimethylsilanol are from a paper by R. O. Sauer, *J. Am. Chem. Soc.* **66,** 1707 (1944). For preparation of the related compounds, see also Jorg and Stetter, *J. prakt. Chem.* **117,** 305 (1927); Post and Hofrichter, *J. Org. Chem.* **5,** 572 (1940).

[57] Krause and von Grosse, reference 1, p. 288.

[58] Andrianov and Gribanova, *J. Gen. Chem. USSR* **8,** 552, 558 (1938); Andrianov and Kamenskaya, *J. Gen. Chem. USSR* **8,** 969 (1938); U. S. patent 2 380 057 to R. R. McGregor and E. L. Warrick.

[59] Andrianov, *J. Gen. Chem. USSR* **8,** 1255 (1938); Andrianov, *Org. Chem. Ind. USSR* **6,** 203 (1939).

[60] Volnov and Reutt, *J. Gen. Chem. USSR* **10,** 1600 (1940).

INDEX OF REPRESENTATIVE COMPOUNDS AND THEIR PROPERTIES

Compound	Formula	M.P., °C.	B.P., °C.	Density at 20° C.
Silicon tetramethyl	$(CH_3)_4Si$		26	0.646
Silicon tetraethyl	$(C_2H_5)_4Si$		154	0.766
Silicon tetrapropyl	$(n\text{-}C_3H_7)_4Si$		213	0.785
Silicon tetrabutyl	$(n\text{-}C_4H_9)_4Si$		231	0.822
Silicon tetraisoamyl	$(i\text{-}C_5H_{11})_4Si$		275	1.078
Silicon tetraphenyl	$(C_6H_5)_4Si$	233	530	
Silicon tetra-m-tolyl	$(C_7H_7)_4Si$	151		1.118
Silicon tetra-p-tolyl	$(C_7H_7)_4Si$	228		1.079
Silicon tetrabenzyl	$(C_6H_5CH_2)_4Si$	128	>550	1.078
Silicon tetraxenyl	$(C_{12}H_9)_4Si$	274		
Trimethylphenylsilane	$(CH_3)_3C_6H_5Si$		172	
Dimethyldiphenylsilane	$(CH_3)_2(C_6H_5)_2Si$		176/45 mm.	
Methyltriphenylsilane	$CH_3(C_6H_5)_3Si$	67		0.906/0°
Triethylphenylsilane	$(C_2H_5)_3C_6H_5Si$		238	
Diethyldiphenylsilane	$(C_2H_5)_2(C_6H_5)_2Si$		305	
Ethyltriphenylsilane	$C_2H_5(C_6H_5)_3Si$	76		
Methylethylpropylphenylsilane	$(CH_3)(C_2H_5)(n\text{-}C_3H_7)(C_6H_5)Si$		228	
Ethyl-n-propyl-i-butylbenzylsilane	$(C_2H_5)(n\text{-}C_3H_7)(i\text{-}C_4H_9)(CH_2C_6H_5)Si$		282	
Trimethylsilane	$(CH_3)_3SiH$	−150	9	0.68/−80°
Dimethylsilane	$(CH_3)_2SiH_2$	−157	−20	0.62/−57°
Methylsilane	CH_3SiH_3		−57	

INDEX OF REPRESENTATIVE COMPOUNDS AND THEIR PROPERTIES (Continued)

Compound	Formula	M.P., °C.	B.P., °C.	Density at 20° C.
Triethylsilane	$(C_2H_5)_3SiH$		107	0.751/0°
Tripropylsilane	$(n\text{-}C_3H_7)_3SiH$		170	0.772/0°
Tri-i-butylsilane	$(i\text{-}C_4H_9)_3SiH$		204	
Tri-i-amylsilane	$(i\text{-}C_5H_{11})_3SiH$		245	
Triphenylsilane	$(C_6H_5)_3SiH$	38		
Tribenzylsilane	$(C_6H_5CH_2)_3SiH$	91		
Triethylfluorosilane	$(C_2H_5)_3SiF$		109	0.835/25°
Tripropylfluorosilane	$(n\text{-}C_3H_7)_3SiF$		175	0.834/25°
Tributylfluorosilane	$(n\text{-}C_4H_9)_3SiF$		224	0.837/25°
Triamylfluorosilane	$(n\text{-}C_5H_{11})_3SiF$		267	0.839/25°
Triphenylfluorosilane	$(C_6H_5)_3SiF$	64	200/10 mm.	
Tribenzylfluorosilane	$(C_6H_5CH_2)_3SiF$	79	236/7.5 mm.	
Trimethylchlorosilane	$(CH_3)_3SiCl$	−40	57.6	0.846
Trimethylbromosilane	$(CH_3)_3SiBr$		80.0	1.148/25°
Triethylchlorosilane	$(C_2H_5)_3SiCl$		143.5	0.925/0°
Triethylbromosilane	$(C_2H_5)_3SiBr$		161	1.177
Tripropylbromosilane	$(n\text{-}C_3H_7)_3SiBr$		213	
Triisobutylbromosilane	$(i\text{-}C_4H_9)_3SiBr$		245	
Triisoamylbromosilane	$(i\text{-}C_5H_{11})_3SiBr$		278	
Triphenylchlorosilane	$(C_6H_5)_3SiCl$	111		
Triphenylbromosilane	$(C_6H_5)_3SiBr$	120	365	

INDEX OF REPRESENTATIVE COMPOUNDS AND THEIR PROPERTIES (*Continued*)

Compound	Formula	M.P., °C.	B.P., °C.	Density at 20° C.
Tri-p-tolylchlorosilane	$(p\text{-}C_7H_7)_3SiCl$	116		
Tribenzylchlorosilane	$(C_6H_5CH_2)_3SiCl$	141	300–360°/100 mm.	
Allyldimethylchlorosilane	$(CH_2=CHCH_2)(CH_3)_2SiCl$		ca. 112	0.922/27°
Ethyldiphenylchlorosilane	$C_2H_5(C_6H_5)_2SiCl$		208/50 mm.	
Phenylethylpropylchlorosilane	$(C_6H_5)(C_2H_5)(n\text{-}C_3H_7)SiCl$		ca. 250	
Benzylethylpropylchlorosilane	$(C_6H_5CH_2)(C_2H_5)(n\text{-}C_3H_7)SiCl$		174/50 mm.	
Benzylethyl-i-butylchlorosilane	$(C_6H_5CH_2)(C_2H_5)(i\text{-}C_4H_9)SiCl$		200/100 mm.	
Dimethyldibromosilane	$(CH_3)_2SiBr_2$		112.3	1.062
Dimethyldichlorosilane	$(CH_3)_2SiCl_2$	−86	70	
Diethyldichlorosilane	$(C_2H_5)_2SiCl_2$		129	
Divinyldichlorosilane	$(CH_2=CH)_2SiCl_2$		118	1.081 /27°
Dipropyldichlorosilane	$(n\text{-}C_3H_7)_2SiCl_2$		ca. 176	
Allyldichlorosilane	$CH_2=CHCH_2SiHCl_2$		97	1.086 /27°
Diallyldichlorosilane	$(CH_2=CHCH_2)_2SiCl_2$		ca. 83/50 mm.	
Diphenyldichlorosilane	$(C_6H_5)_2SiCl_2$	−22	303	1.19
Di-p-bromophenyldichlorosilane	$(p\text{-}BrC_6H_4)_2SiCl_2$	60	239/21 mm.	
Diphenyldibromosilane	$(C_6H_5)_2SiBr_2$		180/12 mm.	
Di-p-tolyldichlorosilane	$(p\text{-}C_7H_7)_2SiCl_2$		238/50 mm.	
Dibenzyldichlorosilane	$(C_6H_5CH_2)_2SiCl_2$	51	243/100 mm.	
Vinylmethyldichlorosilane	$(CH_2=CH)(CH_3)SiCl_2$		93	1.085/27°
Allylmethyldichlorosilane	$(CH_2=CHCH_2)(CH_3)SiCl_2$		119	1.057/27°

INDEX OF REPRESENTATIVE COMPOUNDS AND THEIR PROPERTIES (*Continued*)

Compound	Formula	M.P., °C.	B.P., °C.	Density at 20° C.
Ethylpropyldichlorosilane	$C_2H_5(n\text{-}C_3H_7)SiCl_2$		153	1.043
Ethylisobutyldichlorosilane	$C_2H_5(i\text{-}C_4H_9)SiCl_2$		169	1.024
Ethylphenyldichlorosilane	$C_2H_5(C_6H_5)SiCl_2$		230	
Ethylbenzyldichlorosilane	$C_2H_5(C_6H_5CH_2)SiCl_2$		169/100 mm.	
Phenylbenzyldichlorosilane	$C_6H_5(C_6H_5CH_2)SiCl_2$		245/100 mm.	
Phenyl-*p*-bromophenyldichlorosilane	$C_6H_5(p\text{-}BrC_6H_4)SiCl_2$		200/14 mm.	1.501
Methyltrichlorosilane	CH_3SiCl_3		66	1.271
Ethyltrichlorosilane	$C_2H_5SiCl_3$		100	1.238
Vinyltrichlorosilane	$CH_2{=}CH{-}SiCl_3$		92	1.264/27°
Propyltrichlorosilane	$n\text{-}C_3H_7SiCl_3$		125	1.196
Allyltrichlorosilane	$CH_2{=}CHCH_2SiCl_3$		117	1.211/27°
Butyltrichlorosilane	$n\text{-}C_4H_9SiCl_3$		149	1.161
Isobutyltrichlorosilane	$i\text{-}C_4H_9SiCl_3$		140	1.161/15°
Isoamyltrichlorosilane	$i\text{-}C_5H_{11}SiCl_3$		56/17 mm	1.07
Phenyltrichlorosilane	$C_6H_5SiCl_3$		199	1.28
Cyclohexyltrichlorosilane	$C_6H_{11}SiCl_3$		208	
p-Tolyltrichlorosilane	$p\text{-}C_7H_7SiCl_3$		219	
Benzyltrichlorosilane	$C_6H_5CH_2SiCl_3$		216	1.283
α-Naphthyltrichlorosilane	$\alpha\text{-}C_{10}H_7SiCl_3$		168/22 mm.	1.376
Methyltribromosilane	CH_3SiBr_3		133.5	
Trimethylsilanol	$(CH_3)_3SiOH$		97	

INDEX OF REPRESENTATIVE COMPOUNDS AND THEIR PROPERTIES (*Continued*)

Compound	Formula	M.P., °C.	B.P., °C.	Density at 20° C.
Triethylsilanol	$(C_2H_5)_3SiOH$		154	0.865
Tripropylsilanol	$(n\text{-}C_3H_7)_3SiOH$		207	
Tri-i-amylsilanol	$(i\text{-}C_5H_{11})_3SiOH$		270	
Triphenylsilanol	$(C_6H_5)_3SiOH$	151		
Tri-p-tolylsilanol	$(p\text{-}C_7H_7)_3SiOH$	100		
Tribenzylsilanol	$(C_6H_5CH_2)_3SiOH$	106		
Methylethylphenylsilanol	$(CH_3)(C_2H_5)(C_6H_5)SiOH$		115/17 mm.	
Diethylphenylsilanol	$(C_2H_5)_2(C_6H_5)SiOH$		165/60 mm.	
Ethylpropylphenylsilanol	$(C_2H_5)(n\text{-}C_3H_7)(C_6H_5)SiOH$		ca. 250	
Methyldibenzylsilanol	$CH_3(C_6H_5CH_2)_2SiOH$		241/60 mm.	
Ethyldibenzylsilanol	$C_2H_5(C_6H_5CH_2)_2SiOH$		210/25 mm.	
Diethylbenzylsilanol	$(C_2H_5)_2(C_6H_5CH_2)SiOH$		165/40 mm.	
Ethylpropylbenzylsilanol	$(C_2H_5)(n\text{-}C_3H_7)(C_6H_5CH_2)SiOH$		155/25 mm.	
Ethyl-i-butylbenzylsilanol	$(C_2H_5)(i\text{-}C_4H_9)(C_6H_5CH_2)SiOH$		163/25 mm.	
Diphenylsilanediol	$(C_6H_5)_2Si(OH)_2$	132		
Dibenzylsilanediol	$(C_6H_5CH_2)_2Si(OH)_2$	101		
Ethylphenylsilanediol	$C_2H_5(C_6H_5)Si(OH)_2$	70		
Ethylbenzylsilanediol	$C_2H_5(C_6H_5CH_2)Si(OH)_2$	99		
Trimethylmethoxysilane	$(CH_3)_3SiOCH_3$		57	
Trimethylethoxysilane	$(CH_3)_3SiOC_2H_5$		75	0.758
Trimethylbutoxysilane	$(CH_3)_3SiOC_4H_9$		123	0.777

INDEX OF REPRESENTATIVE COMPOUNDS AND THEIR PROPERTIES (*Continued*)

Compound	Formula	M.P., °C.	B.P., °C.	Density at 20° C.
Dimethyldiethoxysilane	$(CH_3)_2Si(OC_2H_5)_2$		111	0.890
Dimethyldibutoxysilane	$(CH_3)_2Si(OC_4H_9)_2$		187	0.843
Diethyldiethoxysilane	$(C_2H_5)_2Si(OC_2H_5)_2$		156	0.875/0°
Diphenylethynyldiethoxysilane	$(C_6H_5C\equiv C)_2Si(OC_2H_5)_2$		185/12 mm.	0.928/0°
Methyltriethoxysilane	$CH_3Si(OC_2H_5)_3$		149	0.877
Methyltributoxysilane	$CH_3Si(OC_4H_9)_3$		115/10 mm.	
Ethyltrimethoxysilane	$C_2H_5Si(OCH_3)_3$		126	0.975/0°
Ethyltriethoxysilane	$C_2H_5Si(OC_2H_5)_3$		159	0.921/0°
Isopropyltriethoxysilane	$i\text{-}C_3H_7Si(OC_2H_5)_3$		178	0.919
Isobutyltriethoxysilane	$i\text{-}C_4H_9Si(OC_2H_5)_3$		186	0.910
Isoamyltriethoxysilane	$i\text{-}C_5H_{11}Si(OC_2H_5)_3$		198	0.896
Hexyltriethoxysilane	$C_6H_{13}Si(OC_2H_5)_3$		210	0.894
Allyltriethoxysilane	$C_3H_5Si(OC_2H_5)_3$		175	0.923
Phenyltriethoxysilane	$C_6H_5Si(OC_2H_5)_3$		234	1.013/0°
Phenyltriphenoxysilane	$C_6H_5Si(OC_6H_5)_3$		250/13 mm.	
Benzyltriethoxysilane	$C_6H_5CH_2Si(OC_2H_5)_3$		253	0.986
Phenylethynyltriethoxysilane	$C_6H_5C\equiv C\text{—}Si(OC_2H_5)_3$		141/6 mm.	

TYPES OF ORGANOSILICON POLYMERS

SILICON CHAINS

The organosilicon monomers of Chapter 2 become polymers through repetition of some unit of structure within a larger molecule. In the simplest sense any repetitive arrangement of two or more silicon atoms bearing organic substituents is an organosilicon polymer, regardless of the type of linkage or the number of other elements included within the structure. Thus 1,2-dimethyldisilane, CH_3SiH_2—H_2SiCH_3, is a

dimer in which two methylsilyl groups, $-\overset{\displaystyle H}{\underset{\displaystyle H}{\overset{|}{\underset{|}{Si}}}}-CH_3$, are joined by silicon–silicon linkage. If all the hydrogen atoms of disilane were replaced by methyl groups, the result would be hexamethyldisilane, $(CH_3)Si$—$Si(CH_3)_3$. By the insertion of —$Si(CH_3)_2$— units in the chain of silicon atoms, the fully methylated counterparts of all the higher silanes could be written.

Such organosubstituted silicon chains might be expected to result from the action of Grignard reagents or sodium alkyls upon the higher halides of silicon. Actually these methods have been applied successfully only to hexachlorodisilane.[1] When octachlorotrisilane reacts with phenyl magnesium bromide, one silicon–silicon bond is broken and a mixture of tetraphenylsilane and hexaphenyldisilane is obtained. This cleavage by an alkylating reagent reflects the fundamental instability of the longer silicon chains, previously encountered in the thermal decomposition of the higher silanes and chlorosilanes. Even the treatment of halogenated disilanes with zinc alkyls,[2] Grignard reagents,[3] and metallic sodium[4] results in some fission of the single silicon–silicon bond. The only organosilicon chains of greater length which have been reported were prepared by the action of sodium on
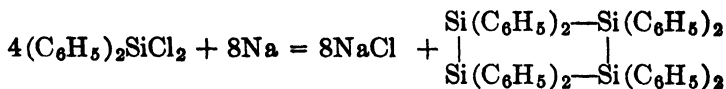
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[1] Schumb and Saffer, *J. Am. Chem. Soc.* **61**, 363 (1939); *ibid.* **63**, 93 (1941).
[2] Friedel and Ladenburg, *Compt. rend.* **68**, 923 (1869); *Ann. chim. phys.* [5] **19**, 401 (1880); *Ann.* **203**, 251 (1880).
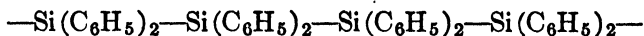[3] Martin, *Ber.* **46**, 2442, 3294 (1913).
[4] Gattermann and Weinlig, *Ber* **27**, 1946 (1894).

diphenyl-, ditolyl-, or dibenzyldichlorosilane:[5]

$$4(C_6H_5)_2SiCl_2 + 8Na = 8NaCl + \begin{array}{l} Si(C_6H_5)_2\text{—}Si(C_6H_5)_2 \\ | \qquad\qquad\quad | \\ Si(C_6H_5)_2\text{—}Si(C_6H_5)_2 \end{array}$$

or the alternative product

$$\text{—}Si(C_6H_5)_2\text{—}Si(C_6H_5)_2\text{—}Si(C_6H_5)_2\text{—}Si(C_6H_5)_2\text{—}$$

The alternative open-chain structure for the product is suggested by the marked unsaturation of one modification of the tetrasilane. Both types are attacked and split by aqueous alkalies.

It follows that, even though suitable procedures were to be found for the alkylation of the longer silicon chains, the products would be subject to oxidation, to thermal dissociation, and to hydrolysis in the presence of alkalies. It seems unlikely that any combination of substituents could stabilize these chains sufficiently to allow their practical application as polymeric materials.

SILICON-CARBON CHAINS

Since the silicon–carbon bond in some selected structures has outstanding thermal stability and is not readily oxidized or hydrolyzed in the manner of the silicon chains, it should be possible to construct many polymers entirely from repeating arrangements of silicon atoms and organic groups. For example, chains of alternate carbon and silicon atoms of the type —C—Si—C—Si—C—Si— might serve as the structural framework, and by suitable choice of substituents for the two kinds of atoms one might produce a wide variety of organosilicon polymers. Only recently has a method been devised for accomplishing this: the action of methylene chloride upon silicon in the presence of a catalyst yields compounds in which the —CH_2—$SiCl_2$— group is repeated.[6] By action of Grignard reagents on the silicon–chlorine bonds, interesting polymers of the unit structure

$$\begin{array}{c} R \\ | \\ \text{—}Si\text{—}CH_2\text{—} \\ | \\ R \end{array}$$
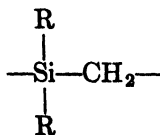
then could be made.

The classical Grignard method of synthesis does not lend itself to the joining of alternate silicon atoms and methylene groups, because

[5] Kipping and coworkers, *J. Chem. Soc.* **119**, 830, 848 (1921); *ibid.* **123**, 2590, 2598 (1923); *ibid.* **1928**, 1431; *ibid.* **1929**, 360, 1176, 2545; *ibid.* **1930**, 1029; *ibid.* **1931**, 1290.
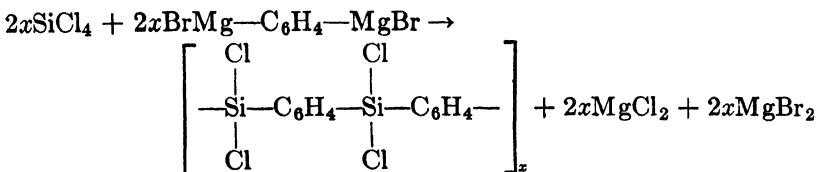
[6] U. S. patents 2 381 000 and 2 381 002 to W. I. Patnode and R. W. Schiessler.

methylene bromide does not form the dimagnesium derivative which would be required to join such a methylene group to two separate silicon atoms.
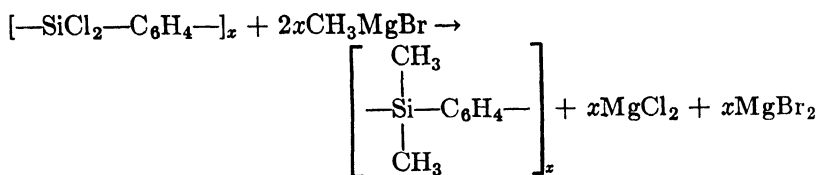
Structures similar to the —CH_2—$SiCl_2$— polymers but with organic groups larger than methylene have been reported.[7] The phenylene radical, —C_6H_4—, is one example which lends itself to the Grignard synthesis; p-dibromobenzene may be converted to the dimagnesium derivative:

$$p\text{-Br}—C_6H_4—Br + 2Mg \rightarrow BrMg\!\!\left\langle\!\!\bigcirc\!\!\right\rangle\!\!MgBr$$
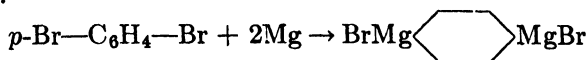
This then is allowed to react with one equivalent of silicon tetrachloride:

$$2x\text{SiCl}_4 + 2x\text{BrMg}—C_6H_4—MgBr \rightarrow$$

$$\left[\begin{array}{cc} \text{Cl} & \text{Cl} \\ | & | \\ —\text{Si}—C_6H_4—\text{Si}—C_6H_4— \\ | & | \\ \text{Cl} & \text{Cl} \end{array}\right]_x + 2x\text{MgCl}_2 + 2x\text{MgBr}_2$$

Since the phenylene group is a rigid planar structure, both ends cannot be attached to the same silicon atom. The group therefore joins two separate silicon atoms, and some form of chain or branched polymer results. The silicon atoms still have an average functionality of two, however, and so they must be "stopped off" in some way. Monovalent organic groups may be used to accomplish this by means of a second Grignard reaction:

$$[—\text{SiCl}_2—C_6H_4—]_x + 2x\text{CH}_3\text{MgBr} \rightarrow$$

$$\left[\begin{array}{c} \text{CH}_3 \\ | \\ —\text{Si}—C_6H_4— \\ | \\ \text{CH}_3 \end{array}\right]_x + x\text{MgCl}_2 + x\text{MgBr}_2$$

After treatment with water to dissolve out the magnesium salts, and after evaporation of the ether which generally is used as solvent, sticky resinous polymers are left. Their rather low melting point (about 100°) suggests that the phenylene–silicon chains are rather short, and probably they are terminated by methyl groups or by phenyl groups derived from the hydrolysis of structures like Si—C_6H_4MgBr.

Organosilicon chains based on combinations of silicon with other divalent organic radicals may be prepared in much the same way. Pentamethylene groups may be employed, for example, because

[7] U. S. patent 2 352 974 to E. G. Rochow.

1,5-dibromopentane forms a dimagnesium derivative which is capable of reacting with two different molecules of silicon tetrachloride. At the same time this double Grignard reagent is capable of a side reaction which is denied to the planar phenylene group: the pentamethylene group may bend around and attach both ends to the same silicon atom. The result is a heterocyclic compound of silicon:[8]

$$CH_2 \Big\langle \begin{array}{c} CH_2-CH_2 \\ CH_2-CH_2 \end{array} \Big\rangle SiCl_2$$
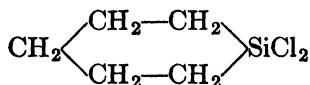
This compound also may be methylated or ethylated with Grignard reagents, but the products are only of passing interest here because they are not polymeric in the sense of repeating the silicon-containing structure. Those pentamethylene groups which are joined to two *different* silicon atoms form organosilicon polymers resembling those obtained with phenylene groups, and indeed the phenylene and pentamethylene groups may be mixed in the same polymer.[7]

The molecular weight of these rather short organosilicon chains may be increased by linking them to each other through siloxane bonds, by the simple expedient of leaving a few unreacted silicon–chlorine groups in the structure. Upon hydrolysis these become Si—OH groups, and heat then brings about intermolecular condensation to join two chains with a siloxane bridge:

$$-Si(CH_3)_2-C_6H_4-\underset{\underset{\underset{-Si(CH_3)-C_6H_4-Si(CH_3)_2-}{|}}{\overset{|}{O}}}{Si(CH_3)}-$$
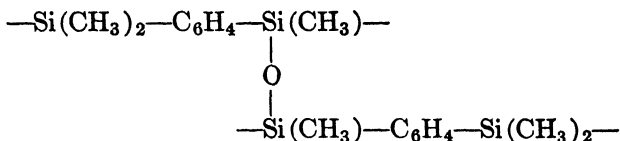
More extensive use is made of this type of cross linking through trifunctional groups in the organosiloxane polymers, as is shown later.

Still another way to form organosilicon chains would be to attach various unsaturated and polymerizable groups to silicon and then induce polymerization of the organic groups as a means of tying together the structure. Thus silicon tetra-allyl, $Si(-CH_2-CH=CH_2)_4$, polymerizes slowly to a gel when heated to 200° and forms a film like that of a drying oil when exposed to air at room temperature for a year or more. Triethylvinylsilane, $(C_2H_5)_3SiCH=CH_2$, as prepared from chlorinated silicon tetraethyl, could not be polymerized by heating with benzoyl peroxide at 80° or 140° for 30 hours, or when heated with 3 per cent of sulfuric acid. It was concluded that silicon does not

[8] Bygdén, *Ber.* **48**, 1236 (1915); Upsala dissertation (1916), pp. 105–07.

activate the vinyl group, but rather renders it inert.[9] Similarly, silicon linked to the phenylethynyl group makes that group rather unreactive in that it is slow to absorb bromine,[10] but the phenylethynylethoxysilanes polymerize during preparation and leave a brittle resin as residue from the vacuum distillation. It seems likely that hexaethynyldisiloxane, $(HC{\equiv}C)_3SiOSi(C{\equiv}CH)_3$, polymerizes through the unsaturated groups because it is a yellowish powder[9] melting at 20°. No information is available on the possible polymerization of allyltriethoxysilane.[11]

The diallyldichlorosilane, methylallyldichlorosilane, divinyldichlorosilane, and methylvinyldichlorosilane which were described in the preceding chapter may be hydrolyzed to the corresponding siloxanes and then polymerized through the unsaturated groups by heating the products in air or with benzoyl peroxide as catalyst. In this way a combination of silicon–oxygen and silicon–carbon polymeric linkage may be obtained.[12]

A further extension of the principle of polymerization through ethylenic unsaturation allows copolymers to be made with the chemically similar organic substances. For example, methylallyldichlorosilane may be hydrolyzed to the corresponding diol and mixed with monomeric methyl methacrylate, and the mixture polymerized to a homogeneous solid by heating with benzoyl peroxide as a catalyst.

SILOXANE CHAINS

An entirely different approach to the synthesis of organosilicon polymers makes use of the silicon–oxygen network of the siloxanes and silicon dioxide as a basis for the polymeric structure. In this method various reactions are directed toward attaching organic groups to the silicon atoms which are linked one to another through oxygen, rather than toward the placement of silicon atoms within the carbon network of an organic compound. The result is variously described as an *organosiloxane*, a *silicone polymer*, or an *organosilicon oxide*, but all these terms convey essentially the same meaning; all refer to an arrangement of alternate silicon and oxygen atoms in which the silicon atoms bear organic substituents.

The siloxane chains which form the structural basis for these organosilicon oxides have been treated in the discussion of siloxanes in

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[9] Ushakov and Itenberg, *J. Gen. Chem. USSR* **7**, 2495 (1937).

[10] Volnov and Reutt, *J. Gen. Chem. USSR* **10**, 1600 (1940).

[11] Andrianov and Kamenskaya, *J. Gen. Chem. USSR* **7**, 2495 (1937); *ibid.* **8**, 969 (1938).

[12] Hurd, *J. Am. Chem. Soc.* **67**, 1813 (1945).

Chapter 1.   The general formula of the linear siloxanes may be represented as

$$H_3SiO(H_2SiO)_xSiH_3$$

where x has a value of zero (in disiloxane) or a small integer (in trisiloxane, tetrasiloxane, and so on).   A still simpler formula

$$(H_2SiO)_x$$

represents the cyclic types which are formed by prosiloxane,* in which x may vary from six to some larger but undetermined value. The linear siloxanes are characterized by physical properties close to those of the silanes,† but the chemical properties are decidedly different from those of a silicon–silicon chain.‡

For our purpose it will suffice to consider the structure

$$\begin{array}{ccc} H & H & H \\ -Si-O-Si-O-Si-O- \\ H & H & H \end{array}$$
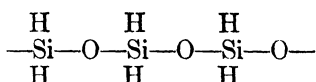
extracted from a cyclic siloxane or from the center portion of a linear siloxane of five or more silicon atoms. If monovalent hydrocarbon radicals were to be attached to silicon in place of hydrogen, the result would be an organosiloxane structure

$$\begin{array}{ccc} R & R & R \\ -Si-O-Si-O-Si-O- \\ R & R & R \end{array}$$
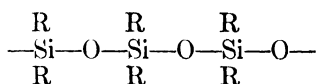
in which two of the bonds of each silicon atom are occupied by organic groups and two are linked to separate oxygen atoms of the polymeric chain. Since the chain itself is a stable oxidized structure common to silica and the silicate minerals as well as to the siloxanes, and since certain R—Si linkages have been shown to be exceedingly inert and resistant to oxidation, it follows that the combination should provide thermal stability and resistance to some types of reagents to an extent not found in any of the organic polymers. The properties of any *particular* configuration in turn may be expected to depend upon the size of the molecule and the type of R group attached to the silicon atoms.
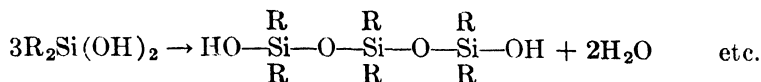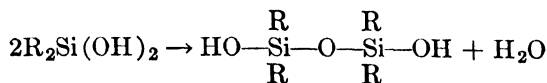
* See Chapter 1. The benzene-soluble cyclic hexamer $(H_2SiO)_6$ is formed by the hydrolysis of H_2SiCl_2 in benzene; a variety of other liquid and solid polymers results from the oxidation of SiH_4 or the hydrolysis of H_2SiCl_2 without solvents.

† Disilane boils at $-14.5°$ and disiloxane at $-15.2°$; Si_2Cl_6 boils at $147°$ and Si_2OCl_6 at $137°$.

‡ The siloxane chain is not cleaved by alkalies with the evolution of hydrogen; neither do the siloxanes take fire in air as do the silanes. ·

Such organosiloxanes commonly are formed from the corresponding organosilanediols by a process of intermolecular condensation, as has been described in the discussion of the silicols:

$$2R_2Si(OH)_2 \rightarrow HO-\underset{\underset{R}{|}}{\overset{\overset{R}{|}}{Si}}-O-\underset{\underset{R}{|}}{\overset{\overset{R}{|}}{Si}}-OH + H_2O$$

$$3R_2Si(OH)_2 \rightarrow HO-\underset{\underset{R}{|}}{\overset{\overset{R}{|}}{Si}}-O-\underset{\underset{R}{|}}{\overset{\overset{R}{|}}{Si}}-O-\underset{\underset{R}{|}}{\overset{\overset{R}{|}}{Si}}-OH + 2H_2O \qquad \text{etc.}$$

Kipping has observed these stepwise condensation reactions in his study of the phenyl compounds, and he has isolated the phenylsiloxanediols of the type previously shown (see compound index at the end of this chapter). Although the progress of the reaction has not been followed with other organosilanediols, it is assumed that they behave the same way.
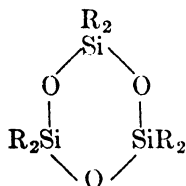
In such a condensation between bifunctional molecules, the chains may grow by adding units of monomer or by condensing with other chains. It has been found in connection with polycondensation reactions of organic compounds that a hydroxyl group on the end of a long chain is fully as reactive as one on the monomer, and that the increasing viscosity of the mixture does not alter this relation.[13] The condensation therefore proceeds at a rate which depends only on the number of hydroxyl groups remaining in the mixture. A wide variety of molecular species is formed, with the number of molecules of monomer always greater than the number of molecules of any other given size. The laws which govern the increase in molecular weight by such a progressive condensation are fully treated[13] in connection with organic-condensation polymers and need not be discussed here. It should be pointed out, however, that the condensation of some organosilanediols proceeds with a reaction velocity far greater than that usually encountered in organic condensations; the condensation of dimethylsilanediol, for example, is so rapid even at 0° as to prevent the isolation of the monomer. There may be other differences which make it inadvisable to depend too much on laws derived from observations on organic systems.

As the organosiloxane polymers grow by the process of condensation, the number of hydroxyl groups falls off rapidly, and effective collisions become much less frequent. Heat then must be applied to
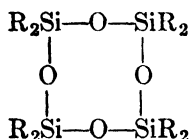
[13] Powers, Synthetic Resins and Rubbers, pp. 25–33 (1943, John Wiley & Sons, Inc.); Flory, *J. Am. Chem. Soc.* **58**, 1877 (1936); *ibid.* **61**, 3334 (1939); Carothers, *Trans. Faraday Soc.* **32**, 39 (1936).

increase the number of collisions per second and to drive off the water of condensation. Alternatively, dehydrating agents or catalysts[14] may be employed to hasten the process, or a combination of heat and catalyst may be necessary to "cure" the polymeric mass to the required degree. The extent to which heat and catalysts must be employed to attain a siloxane molecule of given size is found to increase as the size of the R group is increased; diphenylsilanediol requires heating to approximately 100° C. in order for its condensation even to start. Various alkyl and aryl groups attached to silicon not only exert a characteristic effect upon the rate of condensation of the hydroxyl groups attached to that silicon atom but also influence the type of condensation product and its behavior toward reagents.[15]

The condensation of an organosilanediol produces cyclic structures as well as linear ones. Thus the cyclic trimer

$$
\begin{array}{c}
R_2 \\
Si \\
\diagup \quad \diagdown \\
O \qquad O \\
| \qquad\quad | \\
R_2Si \qquad SiR_2 \\
\diagdown \quad\; O \quad \diagup
\end{array}
$$

and the cyclic tetramer

$$
\begin{array}{c}
R_2Si\!-\!O\!-\!SiR_2 \\
| \qquad\quad | \\
O \qquad\quad O \\
| \qquad\quad | \\
R_2Si\!-\!O\!-\!SiR_2
\end{array}
$$

were among the first molecular types to be isolated from the mixed condensation products of diphenylsilanediol.[16] Other cyclic forms continue through the pentamer and hexamer (analogous to the hexamer of prosiloxane*) up to rings with 18 or more members. Undoubtedly the larger size of the silicon atom and the greater valence angle of oxygen allow rings very much larger than are encountered in carbon chemistry.

[14] U. S. patent 2 371 068 to E. G. Rochow; Dilthey [*Ber.* **37**, 1139 (1904), and **38**, 4143 (1905)] and Kipping [*J. Chem. Soc.* **101**, 2121–42 (1912), and **105**, 484 (1914)] both observed that alkalies and acids exert a considerable effect upon the type of product obtained by the condensation of diphenylsilanediol.

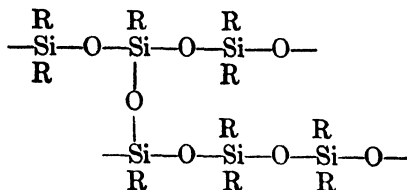[15] Hyde and DeLong, *J. Am. Chem. Soc.* **63**, 1194 (1941).

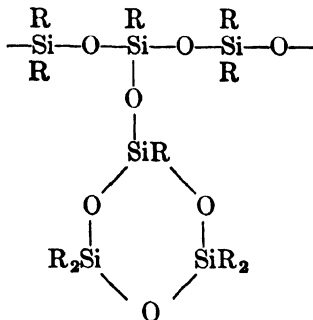[16] Kipping, *J. Chem. Soc.* **101**, 2125 (1912).

* See Chapter 1.

SILOXANE NETWORKS

Whether in cyclic form or in straight chains terminated by hydroxyl or trimethylsilyl groups, the organosiloxane polymers so far considered have consisted principally of repetitions of the unit —R_2SiO—. Now it is necessary to consider another concept, that of the cross linking of siloxane chains and rings. Cross linking is a means of further increasing the average molecular weight of the polymer, and at the same time it also serves to establish a three-dimensional network of increased rigidity and decreased solubility.

One way to obtain cross links consists in introducing trifunctional silicon atoms at intervals along the siloxane chains and then establishing oxygen bridges between such monosubstituted trifunctional atoms:
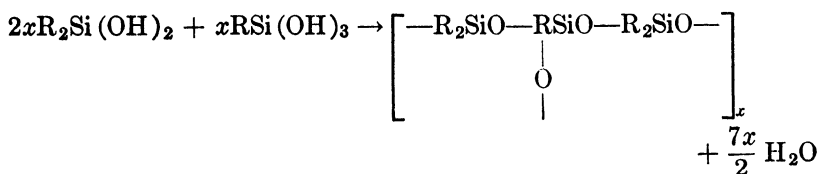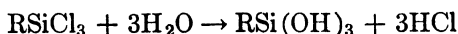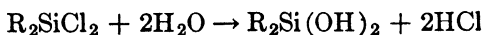
$$\begin{array}{c}
\quad R \qquad R \qquad R \\
-Si-O-Si-O-Si-O- \\
\quad R \qquad | \qquad R \\
\qquad\quad O \\
\qquad\quad | \qquad R \qquad R \\
\quad -Si-O-Si-O-Si-O- \\
\qquad R \qquad R \qquad R
\end{array}$$

Likewise rings may be incorporated into chains:

$$\begin{array}{c}
\quad R \qquad R \qquad R \\
-Si-O-Si-O-Si-O- \\
\quad R \qquad | \qquad R \\
\qquad\quad O \\
\qquad\quad | \\
\qquad\quad SiR \\
\qquad O \qquad\quad O \\
\qquad | \qquad\qquad | \\
R_2Si \qquad\quad SiR_2 \\
\qquad\quad O
\end{array}$$

In either instance the cross link is associated with a condition of less than two organic substituents per silicon atom, so that in the entire polymer the average R/Si ratio becomes something less than two. Hence the R/Si ratio becomes a convenient measure of the degree of cross linking. If R/Si = 1.5, every other silicon atom (on the average) is cross-linked to another ring or chain; if R/Si = 1.0, every silicon atom is trifunctional and is bound into a completely cross-linked rigid structure.
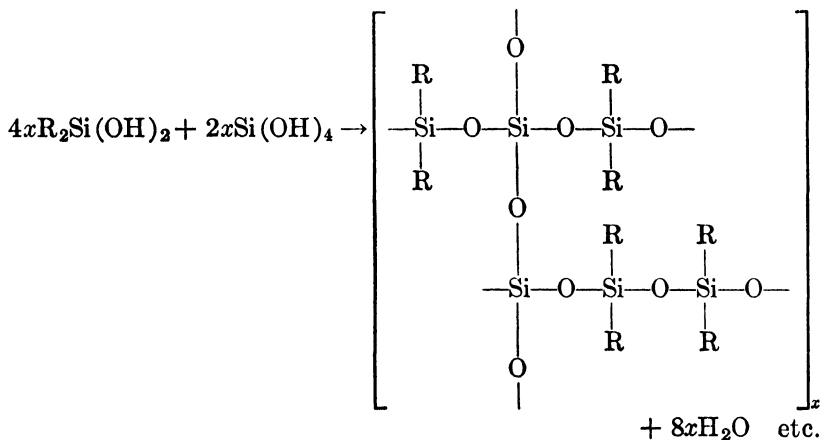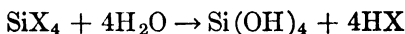
There are two methods available for inserting the trifunctional groups to obtain such cross-linked structures. In one method a composition of R/Si = 2 is first prepared, and then R groups are removed

by processes of oxidation or hydrolysis[15,17] and are replaced by oxygen bridges. The other method makes use of the hydrolysis of mixed mono- and disubstituted silicon halides or esters, and cocondensation of the silanetriols and silanediols so formed:[18]

$$R_2SiCl_2 + 2H_2O \rightarrow R_2Si(OH)_2 + 2HCl$$

$$RSiCl_3 + 3H_2O \rightarrow RSi(OH)_3 + 3HCl$$

$$2xR_2Si(OH)_2 + xRSi(OH)_3 \rightarrow \begin{bmatrix} -R_2SiO-RSiO-R_2SiO- \\ | \\ O \\ | \end{bmatrix}_x$$
$$+ \frac{7x}{2} H_2O$$

In these reactions the composition of the final product is controlled by suitable proportioning of the intermediate organosilicon halides, the R/Si ratio in the mixture of intermediates being substantially the same as that in the product.

It follows that in this method of cocondensation one may employ even an unsubstituted silicon tetrahalide or orthoester in the mixture as a source of *tetra*functional groups. The unsubstituted SiX_4 (where X is a halogen or ester group) hydrolyzes to the hypothetical ortho-silicic acid, $Si(OH)_4$, and this cocondenses with the equally hypothetical organosilanediol to incorporate the *silica* unit within the polymeric structure:

$$SiX_4 + 4H_2O \rightarrow Si(OH)_4 + 4HX$$

$$4xR_2Si(OH)_2 + 2xSi(OH)_4 \rightarrow \begin{bmatrix} & & O & & \\ R & & | & R & \\ | & & | & | & \\ -Si-O-Si-O-Si-O- \\ | & & | & | & \\ R & & | & R & \\ & & O & & \\ & & | & R & R \\ & & | & | & | \\ & & -Si-O-Si-O-Si-O- \\ & & | & | & | \\ & & | & R & R \\ & & O & & \\ & & | & & \end{bmatrix}_x$$
$$+ 8xH_2O \quad \text{etc.}$$

[17] U. S. patent 2 371 050 to J. F. Hyde.
[18] Rochow and Gilliam, *J. Am. Chem. Soc.* **63**, 798 (1941).

It is necessary that the silicol condense at a rate comparable to that for orthosilicic acid, since otherwise the latter will condense only with itself and will precipitate as silica before it can be included within the siloxane network. It also is found by experiment that only a rather small proportion of SiX_4 may be included in the mixture of intermediates if the precipitation of silica is to be avoided. However, the mere fact that appreciable amounts of silica *can* be combined chemically within the polysiloxane structure is strong evidence in support of the theory of intermolecular condensation as given here, and at the same time it illustrates the close chemical similarity between silica and the organosiloxanes.

At this point it would be well to pursue further the similarity of siloxane polymers to silicon dioxide, for all of the silicone or organosiloxane polymers are essentially organosubstituted silicon oxides, and their behavior is best understood if that fact is kept in mind. Silica is found to exist in many forms, hydrated and unhydrated, crystalline and vitreous, but the basic relationship of silicon and oxygen atoms remains much the same in all. In the structure of β-quartz, for example, each silicon atom is linked to four separate oxygen atoms and each oxygen is linked in turn to two separate silicon atoms. This structural tetrahedron composed of silicon and four oxygens is repeated in a characteristic spiral pattern in certain directions through the crystal of β-quartz, and this spiral appears also in the other crystalline and vitreous forms of silica. Fused silica differs in structure from crystalline silica only in the lack of regular repetition beyond the fourth or fifth neighboring unit.

In terms of the chemistry of high polymers, then, silica is a completely cross-linked rigid network of tetrafunctional groups. In some silicate minerals there are rows or layers of metal ions which satisfy some of the oxygen bonds and thus interfere with complete cross linking of the siloxane chains, resulting in a laminar structure (as in mica) or a fibrous structure (as in the asbestos minerals). An organosiloxane may be likened roughly to such a silicate mineral, with the organic groups performing much the same function as metal ions. Instead of acquiring properties associated with metallic ions, however, the organosiloxane polymer acquires some properties usually associated with hydrocarbon compounds, such as solubility in specified organic solvents and a marked water-repellent character of the surface.

It is interesting to note that silicon disulfide, SiS_2, is even more closely analogous to the flexible organosiloxane chain polymers than is the oxide. In the crystal structure of the sulfide as determined by X-ray analysis, the silicon atoms are linked to two pairs of sulfur

atoms, and each pair is turned 90° from the last, giving a spiral-chain molecule. The sulfur atoms are bonded only to neighboring silicon atoms in the same chain, instead of to other chains. The result is a linear rather than a three-dimensional structure, and this difference is reflected in the properties of the crystal.[19] If pressure is applied to the crystal it cleaves lengthwise, thereby splitting into finer and finer fibers. These fibers are flexible and have a high tensile strength. Unfortunately they have not been put to use, because silicon disulfide hydrolyzes readily in moist air to silica and hydrogen sulfide.

It is impossible to tell at this time whether the spacings and configuration of the polyorganosiloxanes follow those of silicon dioxide or silicon disulfide, or neither of them. Such comparisons must await X-ray analysis of the polymeric structure. Once the interatomic distances and the approximate bond angles are known for several organosiloxane chains, it may become possible to plan stronger and better polymeric structures instead of continuing to seek them on a purely empirical basis.

Although this general discussion of organosiloxane networks has centered around the condensation reactions of the silicols, and certain analogies were drawn to the polycondensation reactions of organic compounds, it should not be inferred that the polyorganosiloxanes can be made only by a process of condensation. As has been pointed out, polymers of prosiloxane are formed by the oxidation of monosilane as well as by the hydrolysis of dichlorosilane. Similarly, ethyl silicone in the form of a syrupy polymer also has been made by the partial oxidation of silicon tetraethyl.[20] Solid polymeric silica not only is precipitated by condensation of silicic acid, but also is formed by burning silicon in dry oxygen, a process in which no hydroxyl groups can play a part. It must be concluded, then, that silicon dioxide and the silicones are polymeric because the size and nuclear charge of the silicon atoms require it, and not just because a condensation reaction has been induced. The same consideration holds for related compounds like the silazines, which have polymeric chains of the type —Si—NH—Si—NH—.[21] It might also be expected to hold for other combinations of organosilicon groups with negative elements such as sulfur.

Of these various types of organosilicon polymeric structures, only

[19] Zintl and Loosen, Z. physik. Chem. A174, 301 (1935).

[20] Friedel and Crafts, Ann. chim. phys. [4] 9, 5 (1866).

[21] Sauer, J. Am. Chem. Soc. 66, 1708 (1944), describes the preparation of $(CH_3)_3Si—NH—Si(CH_3)_3$ from trimethylchlorosilane by a process exactly analogous to the formation of hexamethyldisiloxane by hydrolysis.

the organosiloxanes have been studied in any great detail, but here alone there is sufficient material to occupy the attention of many investigators over a long period to come. With an almost endless variety of usable organic groups available for attachment to the siloxane chain, and with wide variation of the R/Si ratio possible in the case of each type of organic group, it is evident that the field of organosiloxane polymers is extremely broad, fully as broad as that of all organic polymers together.

Our knowledge of the field is not correspondingly broad, but rather centers around the polymers deri ed from the substitution of a relatively few specific organic groups in the siloxane structure. The next chapter considers these known polymers in an order which is based on the type of organic group they bear. All may be considered examples of the general principles outlined in the latter part of this chapter, although actually the "examples" were studied first and the generalizations contained herein were drawn from the observed facts.

INDEX OF REPRESENTATIVE COMPOUNDS AND THEIR PROPERTIES

Compound	Formula	M.P., °C.	B.P., °C.	Density at 20° C.
Hexamethyldisilane	$(CH_3)_6Si_2$	12	112	0.723
Hexaethyldisilane	$(C_2H_5)_6Si_2$		255	0.8403
Hexa-n-propyldisilane	$(C_3H_7)_6Si_2$		114/3 mm.	0.869
Diethyldipropyldiphenyldisilane	$(C_2H_5)_2(C_3H_7)_2(C_6H_5)_2Si_2$		270/100 mm.	
Diethyldipropyldibenzyldisilane	$(C_2H_5)_2(C_3H_7)_2(C_7H_7)_2Si_2$		244/20 mm.	
Hexaphenyldisilane	$(C_6H_5)_6Si_2$	355		
Hexa-p-tolyldisilane	$(C_7H_7)_6Si_2$	345		
Hexabenzyldisilane	$(C_7H_7)_6Si_2$	194		
Octaphenyltetrasilane	$—(C_6H_5)_8Si_4—$	335		
Cyclooctaphenyltetrasilane	$[(C_6H_5)_2Si]_4$	400		
Octa-p-tolyltetrasilane	$—(C_7H_7)_8Si_4—$	293		
Cycloocta-p-tolyltetrasilane	$[(p-C_7H_7)_2Si]_4$	310		
Diethyloctaphenyltetrasilane	$(C_2H_5)_2(C_6H_5)_8Si_4$	254		
Diphenoxyoctaphenyltetrasilane	$(C_6H_5O)_2(C_6H_5)_8Si_4$	216		
Cyclooctaphenyltetrasilane oxide	$(C_6H_5)_8Si_4O$	ca. 240		
Cyclooctaphenyltetrasilane dioxide	$(C_6H_5)_8Si_4O_2$	222		
Cycloocta-p-tolyltetrasilane oxide	$(C_7H_7)_8Si_4O$	229		
Hexamethyldisiloxane	$(CH_3)_6Si_2O$		100	0.7619
Hexamethyldisilazine	$(CH_3)_6Si_2NH$		125	0.7742
Hexaethyldisiloxane	$(C_2H_5)_6Si_2O$		231	0.859/0°
Hexapropyldisiloxane	$(C_3H_7)_6Si_2O$		ca. 285	

INDEX OF REPRESENTATIVE COMPOUNDS AND THEIR PROPERTIES

Compound	Formula	M.P., °C.	B.P., °C.	Density at 20° C.
Hexaisoamyldisiloxane	$(C_5H_{11})_6Si_2O$	221	ca. 365	
Hexaphenyldisiloxane	$(C_6H_5)_6Si_2O$	224		
Hexa-p-tolyldisiloxane	$(C_7H_7)_6Si_2O$			
Dimethyltetraphenyldisiloxane	$(CH_3)_2(C_6H_5)_4Si_2O$	52		
Diethyltetraphenyldisiloxane	$(C_2H_5)_2(C_6H_5)_4Si_2O$	66		
Diethyldipropyldibenzyldisiloxane	$(C_2H_5)_2(n\text{-}C_3H_7)_2(C_7H_7)_2Si_2O$		272/50 mm.	
Diethyldibutyldibenzyldisiloxane	$(C_2H_5)_2(i\text{-}C_4H_9)_2(C_7H_7)_2Si_2O$		252/20 mm.	
Tetraphenyldisiloxane-1,3-diol	$(C_6H_5)_4Si_2O(OH)_2$	113		
Hexaphenyltrisiloxane-1,5-diol	$(C_6H_5)_6Si_3O_2(OH)_2$	111		
Diethyldiphenyldisiloxane-1,3-diol	$(C_2H_5)_2(C_6H_5)_2Si_2O(OH)_2$	87.5		
Tetrabenzyldisiloxane-1,3-diol	$(C_7H_7)_4Si_2O(OH)_2$	76		
Hexabenzyltrisiloxane-1,5-diol	$(C_7H_7)_4Si_3O_2(OH)_2$	82		
Hexamethylcyclotrisiloxane	$(Me_2SiO)_3$	48		
Hexaethylcyclotrisiloxane	$(Et_2SiO)_3$		144/17 mm.	
Hexaphenylcyclotrisiloxane	$(C_6H_5)_6Si_3O_3$	190	295/1 mm.	
Octaphenylcyclotetrasiloxane	$(C_6H_5)_8Si_4O_4$	202	335/1 mm.	
Hexabenzylcyclotrisiloxane	$(C_7H_7)_6Si_3O_3$	98		
Triethyltribenzylcyclotrisiloxane	$(EtBzSiO)_3$		310/22 mm.	

PROPERTIES OF THE SPECIFIC SILICONE POLYMERS

Most of what was known about the polymeric organosiloxanes up to about 1940 was the result of the researches conducted by Frederick Stanley Kipping and his coworkers at University College, Nottingham, England. Over a period of 45 years Professor Kipping published a series of 51 papers[1] on organosilicon chemistry, and these papers have become the classics in this field. The work began with the preparation of asymmetric compounds of tetrasubstituted silicon for the study of optical rotation, and received great impetus in 1904 with the discovery of the reaction of Grignard reagents with silicon halides. This new method of synthesis then was applied widely to the preparation of many new compounds, which were isolated, identified, and reported in the now famous series of publications. In the midst of this work

[1] Actually there are at least 57, for there are four or more outside the numbered series and two within the series which bear supplementary numbers (*37a* and *45a*). The entire numbered series (*1* to *51*) appears in the *Journal of the Chemical Society*, and for convenience the papers are listed below by reference to volume and page of that journal. References to specific investigations by Professor Kipping also have been made at the appropriate places in the text.

1.	79,	449	(1901)	*19.*	101,	2156	(1912)	*36.* 1928, 1427
2.	91,	209	(1907)	*20.*	105,	40	(1914)	*37.* 1928, 1431
3.	91,	717	(1907)	*21.*	105,	484	(1914)	*37a.* 1929, 357
4.	93,	198	(1908)	*22.*	105,	679	(1914)	*38.* 1929, 360
5.	93,	439	(1908)	*23.*	107,	459	(1915)	*39.* 1929, 1176
6.	93,	457	(1908)	*24.*	119,	647	(1921)	*40.* 1929, 1180
7.	93,	2004	(1908)	*25.*	119,	830	(1921)	*41.* 1929, 2545
8.	93,	2090	(1908)	*26.*	119,	848	(1921)	*42.* 1930, 1020
9.	95,	69	(1909)	*27.*	123,	2590	(1923)	*43.* 1930, 1029
10.	95,	302	(1909)	*28.*	123,	2598	(1923)	*44.* 1931, 1290
11.	95,	489	(1909)	*29.*	123,	2830	(1923)	*45.* 1931, 2774
12.	97,	142	(1910)	*30.*	125,	2291	(1924)	*45a.* 1931, 2830
13.	97,	755	(1910)	*31.*	125,	2616	(1924)	*46.* 1932, 2200
14.	99,	138	(1911)	*32.*	1927,	104		*47.* 1932, 2205
15.	101,	2106	(1912)	*33.*	1927,	2719		*48.* 1933, 1040
16.	101,	2108	(1912)	*34.*	1927,	2728		*49.* 1935, 1085
17.	101,	2125	(1912)	*35.*	1927,	2734		*50.* 1935, 1088
18.	101,	2142	(1912)					*51.* 1944, 81

Also *Proc. Chem. Soc.* 15, 174 (1899); *Proc. Chem. Soc.* 20, 15 (1904); *Proc. Chem. Soc.* 28, 243 (1912); *Proc. Roy. Soc. London*, A159, 139 (1937).

Kipping discovered the principle of intermolecular condensation of the silanediols, which he then extended to the silanetriols by proving that they too condensed to polyorganosiloxanes instead of to " siliconic acids," RSiOOH, as had been thought. In this and in several other major aspects, Kipping decided that the chemistry of organosilicon compounds seemed clearly set apart from classical organic chemistry. In the Bakerian Lecture, delivered in 1937, he stated in part:

Even after a very short experience. it was evident that corresponding dorivatives of the two elements in question showed very considerable differences in their chemical properties; it may now be said that the principal if not the only case in which they exhibit a really close resemblance is that of the paraffins and those particular silicohydrocarbons, containing a silicon atom directly united to four alkyl radicals.[2]

Oddly enough, Kipping had not been concerned primarily with the organosilicon polymers for which his work may best be remembered. He and his students had been interested principally in the preparation and characterization of new compounds, and in the study of their reactions. From such reactions they strove to isolate pure compounds as products, but in certain hydrolytic reactions they constantly were troubled by the appearance of oily or " gluelike " substances which could not be crystallized and which acted like very complex mixtures when subjected to fractionation procedures. It now seems surprising that they were able to isolate as many of the simpler cyclic and linear polymers as they did, considering the annoying qualities of the resinous masses.

The compounds of the empirical composition R_2SiO which were isolated with so much difficulty from the hydrolysis products of the disubstituted silicon chlorides were designated *silicones* by Kipping,[3] because he at first considered them analogous to the ketones, R_2CO. The analogy is a purely formal one, however, and is not particularly helpful (as Kipping later admitted), because the siloxane bond bears no chemical resemblance to the carbonyl group of organic chemistry. No $Si{=}O$ structure, or even $Si{=}C$, has ever been demonstrated conclusively in silicon chemistry.[4]

Nothing in his writings indicates that Kipping foresaw any usefulness in the resinous silicone polymers with which he worked so long. Certainly he made no attempt to develop or apply them. Indeed, his

[2] Kipping, *Proc. Roy. Soc. London*, A159, 139 (1937).
[3] Kipping, *Proc. Chem. Soc.* 28, 243 (1912); *J. Chem. Soc.* 101, 2106 (1912).
[4] Schlenk and Renning, *Ann.* 394, 221 (1912); Kipping, *J. Chem. Soc.* 1927, 104; Post and Hofrichter, *J. Org. Chem.* 5, 572 (1940).

opinion of the potentialities of organosilicon chemistry remained very modest, for he concluded his Bakerian Lecture with these words:

We have considered all the known types of organic derivatives of silicon and we see how few is their number in comparison with the purely organic compounds. Since the few which are known are very limited in their reactions, the prospect of any immediate and important advance in this section of chemistry does not seem very hopeful.

Present-day silicone chemistry has taken up where the " not very hopeful " researches of Kipping left off and has centered on the production, the study, and the application of the liquid and solid organosiloxane polymers. Some silicones or classes of silicones were known to Kipping but have now been studied in much greater detail; others are entirely new. In the following discussion no attempt will be made to separate the old from the new or to describe separately the preparations by Kipping. Instead, each group of substances is discussed in the light of all the published and patented information; it is hoped that much more such information will soon be forthcoming.

ALKYL SILICONES

The newest and simplest polyorganosiloxane, and possibly the most important, is *methyl silicone*. Kipping did not investigate this substance, nor was there any other full-scale study of its properties before it was taken up as a material of potential usefulness. As was pointed out in Chapter 1, Stock and Somieski[5] came across dimethylsiloxane during their study of the chlorination and methylation of monosilane when they acidified an alkaline solution of dimethylsilane, $(CH_3)_2SiH_2$, but, as they started their " micropreparation " with only 1,300 cc. of SiH_4 *as gas*, and isolated and identified five new silane derivatives, they obtained only a trace of dimethyl silicone, not enough for an investigation of its properties or even for a chemical analysis.

The more recent interest in methyl silicone which has led to extensive investigation of its chain and network polymers arises from the theoretical and practical advantages of the material. It is unique because it contains absolutely no carbon-to-carbon bonds, being composed entirely of siloxane chains with methyl groups attached to the silicon atoms. Such a structure makes fullest use of the inorganic character of the siloxane network, for it contains a minimum of organic substituent. Carbon and hydrogen constitute only 40.5 per cent by weight of dimethyl silicone, $[(CH_3)_2SiO]_x$, and only 22.4 per cent by weight of the cross-linked polymethylsiloxane, $[CH_3SiO_{1.5}]_x$.

[5] *Ber.* **52,** 695 (1919).

Methyl silicone actually is a generic name for a large number of materials, including oils, resins, and elastomers. The various physical forms which it assumes reflect the different molecular complexities of the polymers, for the oils are composed of linear molecules of finite length, the resins are cross-linked aggregates of cyclic and linear structures, and the elastomers are superpolymers of much higher molecular weight and of unknown configuration. All of these materials are derived from the same intermediates by different methods of treatment.

When dimethyldichlorosilane is hydrolyzed simply by stirring with a large excess of water, there is formed a colorless oil containing a large variety of molecular species. About one half of the oil consists of cyclic polymers of dimethylsiloxane of the type

$$[(CH_3)_2SiO]_x$$
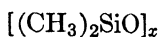
where x is an integer greater than two;[6] these may be distilled from the oil at temperatures up to 200° C. and pressures as low as 1 mm. Of these cyclosiloxanes, the cyclic tetramer is found to distill in the largest quantity, the proportions of products in one experiment[6] being approximately 0.5 per cent hexamethylcyclotrisiloxane, 42 per cent octamethylcyclotetrasiloxane, 7 per cent decamethylcyclopentasiloxane, 1.6 per cent dodecamethylcyclohexasiloxane, about 1 per cent of higher cyclic polymers, and 48 per cent of nonvolatile residual oil. Cyclic dimethylsiloxanes as large as the nonomer, $[(CH_3)_2SiO]_9$, have been isolated, and still larger ones probably are present although their small proportions and high boiling points make their isolation difficult. Neither a monomeric CH_3SiO nor a dimeric $[(CH_3)_2SiO]_2$ ever has been found.

The nonvolatile portion of the hydrolysis product consists of high-molecular-weight diols of the type

$$HO[Si(CH_3)_2O]_xSi(CH_3)_2OH$$
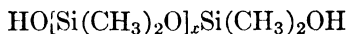
where x is a large integer. The simplest diol, $(CH_3)_2Si(OH)_2$, has not been found, nor have the short-chain α-ω diols. All of the complex high-molecular-weight material may be converted to volatile cyclic dimethylsiloxanes by a process of thermal rearrangement or pyrolysis,[7] in which the siloxane bonds are opened by severe heating (400° to 600° C.) in the absence of oxygen. At 400° in a current of nitrogen, the conversion proceeds steadily and yields a distillate containing about one half by volume of hexamethylcyclotrisiloxane, about one

[6] Patnode, *J. Am. Chem. Soc.* **68**, 358 (1946).
[7] Patnode, *J. Am. Chem. Soc.* **68**, 360 (1946).

fourth of octamethylcyclotetrasiloxane, and the rest a mixture of the higher cyclic polymers. It is remarkable that the methyl-to-silicon bond resists both the hydrolytic reagents and the high temperature of such thermal rearrangement without splitting off methyl groups or degrading in any other way.

When dimethyldichlorosilane is hydrolyzed by stirring with water in a mutual solvent the proportion of volatile dimethylpolysiloxanes is increased, and it appears that hydrolysis in strong acids also increases the tendency toward the formation of lower cyclic forms. Hydrolysis in ammonium hydroxide solution decreases the proportion of volatile cyclic material.[6] If insufficient water for complete hydrolysis is supplied, and particularly in a mutual solvent such as ether, there is formed a series of complex dichlorosilanes of the type

$$Cl[Si(CH_3)_2O]_xSi(CH_3)_2Cl$$
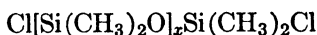
where x is unity or a small integer. These α-ω dichlorosilanes may be hydrolyzed as usual, but seldom yield the corresponding diols, because the latter compounds condense to form high-molecular-weight dimethylsiloxanes. The physical properties of some of the cyclic dimethylsiloxanes and the linear α, ω dichlorodimethylsiloxanes are given in Table 1, which is taken from reference 6.

TABLE 1

| Compound | B.P. in °C. | | M.P., | Density at 20° C., | η_{20}^D |
	760 mm.	20 mm.	°C.	g. per cc.	
[(CH₃)₂SiO]₃	134	...	64	...	...
]₄	175	74	17.5	0.9558	1.3968
]₅	210	101	−38	0.9593	1.3982
]₆	245	128	−3	0.9672	1.4015
]₇	...	154	−26	0.9730	1.4040
]₈	...	175	ca. 30	...	1.4060
]₉	...	ca. 188	...	...	1.4070
Cl[(CH₃)₂SiO]₁Si(CH₃)₂Cl	138	41	−37	1.038	...
]₂	184	79	−53	1.018	...
]₃	222	111	−62	1.011	...
]₄	...	138	ca. −80	1.005	...
]₅	...	161	ca. −80	1.003	...

METHYL SILICONE OIL

The hydrolysis of trimethylchlorosilane alone yields principally hexamethyldisiloxane, $(CH_3)_3SiOSi(CH_3)_3$,[8] but if a mixture of dimethyldichlorosilane and trimethylchlorosilane is hydrolyzed there

[8] Sauer, *J. Am. Chem. Soc.* **66**, 1707 (1944).

is obtained a mixture of hexamethyldisiloxane, cyclic dimethylsiloxanes, and some cocondensation products of the type

$$CH_3[(CH_3)_2SiO]_xSi(CH_3)_3$$

in which chains of dimethylsiloxane units are terminated by the monofunctional trimethylsilyl units.[6] These might be called copolymers of —$(CH_3)_2SiO$— and $(CH_3)_3Si$— units. The lower compounds of the series, for which x has values from two to five, have been isolated[6] from a hydrolyzed mixture and are found to have the properties listed in the first four lines of Table 2. Larger molecules of the same type, in which x is greater than five, undoubtedly are formed during the same cohydrolysis and also may be prepared by another method soon to be described. Those with chains of 7 to 11 silicon atoms have been isolated by fractional distillation at low pressure from a mixture prepared by the second method and are characterized by the properties given in the next five lines of Table 2.[9] The densities will be seen to

TABLE 2

Compound	B.P., °C.	M.P., °C.	Density at 20°C., g. per cc.	n_{20}^D
$CH_3[(CH_3)_2SiO]_2Si(CH_3)_3$	153 /760 mm.	ca. −80	0.8200	1.3848
]₃	194 /760 mm.	ca. −70	0.8536	1.3895
]₄	229 /710 mm.	ca. −80	0.8755	1.3925
]₅	142 /20 mm.	< −100	0.8910	1.3948
]₆	165 /20 mm.	. .	0.911	1.3965
]₇	153 / 5.1 mm.	. .	0.913	1.3970
]₈	173 / 4.9 mm.	. .	0.918	1.3980
]₉	183 / 4.1 mm.	. . .	0.925	1.3988
]₁₀	201 / 4.7 mm.	.	0.930	1.3994

approach those of the polymeric dimethylcyclosiloxanes listed in Table 1, for as the chain grows longer and longer through addition of $(CH_3)_2SiO$ units the effect of the terminal $(CH_3)_3Si$— groups becomes less and less important, and the molecule approaches a linear polymer of dimethylsiloxane in composition and in properties. The average length of the chain in a mixture of such linear polymers will be seen to depend principally upon the proportion of dimethyldichlorosilane to trimethylchlorosilane employed at the beginning, for the former gives rise to chain-building difunctional units, whereas the latter forms chain-blocking monofunctional units.

If we consider the increasing boiling points and the low melting

[9] These latter data are from a paper by Wilcock, *J. Am. Chem. Soc.* **68**, 691 (1946).

points of the compounds in Table 2 and extrapolate the values for chains of still greater length, we find we have a series of methylpolysiloxanes of very wide liquid range. Since the compounds are " chain-stoppered " and are incapable of further condensation, they are chemically stable and should be unaffected by high temperatures or most chemical reagents. Such linear methylpolysiloxanes are in fact the basis for *silicone oils* or *fluids* designed to withstand extremes of temperature and to be inert to metals and to most chemical reagents. The development of these improved silicone oils is in itself an exemplary research on new polymeric forms of methyl silicone and the means of making them.

The first requirement in the preparation of a silicone oil of desired characteristics is a method for preparing a single compound or a narrow range of compounds of the type

$$CH_3[(CH_3)_2SiO]_xSi(CH_3)_3$$

having the desired maximum vapor pressure and the desired viscosity (for viscosity is found likewise to depend principally upon molecular size). Although cohydrolysis of dimethyldichlorosilane and trimethylchlorosilane produces the desired compounds, it also produces hexamethyldisiloxane and the volatile cyclic dimethylsiloxanes.[6] A more satisfactory method of obtaining the " tailor-made " molecules of the desired size alone involves a catalytic rearrangement of monofunctional and difunctional siloxane units.[10] Hydrolyzed dimethyldichlorosilane (or any other source of dimethylsiloxane units, such as octamethylcyclotetrasiloxane) is mixed with the proper proportion of hexamethyldisiloxane to give the desired average chain length, and about 4 per cent by volume of concentrated sulfuric acid is added. This mixture then is agitated at room temperature. The sulfuric acid appears to react with the siloxane bonds to form sulfate esters and water; the sulfate esters then hydrolyze, and the regenerated sulfuric acid attacks another siloxane bond. In this way, siloxane bonds are opened and closed at random until an equilibrium distribution of chain lengths is obtained. The distribution is found to be rather narrow, and the average chain length is determined closely by the proportions of reagents. After equilibrium is established about 20 per cent by volume of water is added and the shaking is continued, thereby hydrolyzing the remaining sulfate esters. The aqueous acid then is separated, and the " equilibrated " oil is neutralized and dried. If desired, the more volatile constituents of the equilibrium mixture may be distilled off

[10] Patnode and Wilcock, *J. Am. Chem. Soc.* **68**, 362 (1946).

under reduced pressure, thereby still further narrowing the range of linear polymers remaining in the oil.

This method for preparing methylpolysiloxane liquids of predetermined molecular size permits the design of silicone oils from data obtained on pure molecular species. The properties of the pure compounds therefore have been studied carefully, with particular attention to the relations that exist between compounds in a series. The vapor pressures at several temperatures have been measured for the linear polymers with chains of 2 to 11 silicon atoms,[11] and the heats of vaporization have been found to fit the equation,

$$\Delta H_{\text{vap}} \text{ linear} = 4.70 + 1.65x \text{ kcal.}$$

where x is the number of silicon atoms in the chain. The same information gained from a study of the *cyclic* polymers of dimethylsiloxane, from the tetramer to the octamer, gives heats of vaporization which fit the formula

$$\Delta H_{\text{vap}} \text{ cyclic} = 5.45 + 1.35x \text{ kcal.}$$

where x again is the number of silicon-containing units. At a given temperature, a cyclic polymer always has a higher vapor pressure than a linear polymer of the same number of silicon atoms.[11]

The viscosities of the same two series of methylpolysiloxanes have been measured at several temperatures,[11] and the logarithm of the absolute viscosity at any one temperature has been found to be a linear function of the logarithm of the number of units in either series. The activation energy of viscous flow may be expressed by an equation very similar to those just given for heat of vaporization:

$$E_{\text{vis}} \text{ linear} = 1.74 + 1.49 \log x \text{ kcal.}$$

and $$E_{\text{vis}} \text{ cyclic} = 0.98 + 3.96 \log x \text{ kcal.}$$

where x again is the number of silicon-containing units. The cyclic polymers always have a higher viscosity than the linear polymers of the same number of units at the same temperature. The cyclic forms also change their viscosities more rapidly with temperature.* The remarkably small change of viscosity with temperature shown by the linear methylpolysiloxanes sets them apart from hydrocarbon liquids and from other siloxane polymers and makes them of unique interest as lubricants and hydraulic fluids.

[11] Wilcock, *J. Am. Chem. Soc.* **68**, 692 (1946). See also Charles B. Hurd, *ibid.*, **68**, 364 (1946).
* The reader who is interested in pursuing further the relative relationships between the two series of polymers will find an excellent set of curves in the Wilcock reference 11.

The activation energy of viscous flow for methylpolysiloxanes is a definite fraction of the energy of vaporization at the normal boiling point, the ratio E_{vap}/E_{vis} being 2.34 for the cyclic polymers and from 2.14 to 3.76 for the linear polymers (increasing with chain length). The ratio developed by Eyring for several series of organic compounds[11] is approximately three for nearly spherical molecules and four for long molecules, which gives some indication of the shape of the methyl-polysiloxane molecules. In very long polymers the chain seems to flow in segments, and the size of the segment (or " unit of flow ") is found to be about seven siloxane units long. This is approximately the same length as the unit of flow in hydrocarbons, although the hydrocarbon unit contains about 20 carbon atoms. Since the activation energy for viscous flow of the hydrocarbons is about 70 per cent greater than that for the linear methylpolysiloxanes, and the mobile unit is about the same size, it is concluded that the siloxane chains move about more readily and therefore must have lower forces of attraction between chains than are observed in hydrocarbons of comparable molecular weight.

One of the fundamental advantages of a methyl silicone oil, therefore, is its small temperature coefficient of viscosity.[12] Other advantages are the chemical inertness, wide liquid range, and low freezing point. Whereas the chemical properties derive from the nature of the siloxane bond and the methyl-to-silicon links and do not vary much with changes in polymer size, the freezing points depend upon the molecular size and configuration. Therefore, it becomes important to know how chain branching and variation of molecular shape affect the physical properties. One method of studying these effects is to prepare equilibrated oils from trifunctional, difunctional, and monofunctional units[13] by choosing proportions of methyltrichlorosilane, dimethyldichlorosilane, and trimethylchlorosilane such that there is an extra trimethylsilyl group for every molecule of trichlorosilane introduced. After random catalytic rearrangement[10] the siloxane chains will be branched to a degree depending on the proportion of trifunctional units introduced, and each branch will be terminated by a $(CH_3)_3Si-$ unit so that the chemical stability is preserved. It is

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[12] " Viscosity index," the customary basis for comparison of change of viscosity in hydrocarbon oils, becomes less satisfactory when applied to silicone oils, because the viscosity index varies with viscosity as well as with the temperature coefficient. In silicone oils the variation of viscosity with temperature is too small in relation to the viscosity itself. A true viscosity–temperature coefficient (VTC) has been proposed as a more satisfactory criterion [see Wilcock, *Mechanical Engineering* **66**, 739 (1944)].

[13] Wilcock, papers in publication.

found[13] that the branched-chain polymers have a lower viscosity and a lower freezing point than the straight chains of the same weight. Branching also increases the viscosity–temperature coefficient somewhat but does not change the density. It could be argued that the decrease in viscosity is due to the greater compactness that accompanies branching, but the same reasoning would require still lower viscosities for cyclic dimethylsiloxanes, a conclusion contrary to observation.

Branched methylsiloxane chains in an oil also seem to affect the results of equilibration with sulfuric acid.[13] There is a broadening of the molecular-size distribution when some of the chains are branched, and hence there is more volatile material to be distilled off if a low vapor pressure is desired. Some of the changes in properties can be explained only by assuming the formation of cyclic structures in the components of higher molecular weight. Such cyclization does not affect materially the usefulness of the oil, however, for the viscosity–temperature coefficients for branched oils do not go above 0.67, whereas those of petroleum oils are in the range of 0.8 to 0.9. In addition the branched oils have a substantially lower freezing point, some remaining liquid as low as $-89°$ C.[13]

It may be helpful to express the change of viscosity of a silicone oil in a different manner. If we compare a typical silicone oil with a standard hydrocarbon oil of viscosity index 100, the two having the same viscosity at 100° F., we find that after cooling to $-35°$ F. the silicone oil has seven times the viscosity it had, whereas the hydrocarbon oil has increased 1,800-fold in viscosity. This relative constancy of viscosity of the silicone oil makes it particularly suitable for use as a fluid in hydraulic systems for the transmission of power. Silicone oils do not react with the common metals of construction, and they are so inert that even at 300° F. they do not discolor or become acid or form sludge. They are satisfactory lubricants in hydraulic pumps and in any other device where conditions of hydrodynamic lubrication prevail. When used as lubricants, methyl silicone oils do not suffer loss of viscosity through shear breakdown under continuous load at high speed.

Although the methyl silicone oils are soluble in benzene and in the lighter hydrocarbons, they are only partially soluble in alcohol and in the heavy hydrocarbons. The relative insolubility in petroleum lubricating oil may be the reason for the success of silicone oils in suppressing foam in certain engine oils; at the limit of solubility the silicone may set up a high local concentration at the oil–air interface and so exercise a surface-active effect. Whatever the mechanism, a very

small proportion of the silicone oil greatly reduces the tendency of the lubricating oil to foam.[14]

The methyl silicone oils also are insoluble in natural and synthetic rubber and hence do not swell rubber compositions. Electrically, they are found to have very low dielectric losses; the power factor of a typical sample was found to be about 0.0001 at 12 megacycles and to be quite constant with frequency and with temperature. Some related methyl phenyl, ethyl phenyl, and ethylsiloxane liquid polymers are recommended as dielectric media for transformers and capacitors.[15]

METHYL SILICONE RESINS

In the strict sense, the methyl silicone resins are not silicones at all, because they require cross linking in order to attain resinous properties and hence the R/Si ratio is always less than two. However, it has become customary to extend the term silicone to include compositions related to or derived from the original R_2SiO composition for which the term was coined. Confusing as this extension of meaning may be, it now seems too firmly established to be altered at this time. The suggested rules of nomenclature (reference 6, Chapter 1) accept the generalization and avoid ambiguity by naming the pure chemical compounds as specific siloxanes.

Three methods are available for preparing the cross-linked resins:

1. Dimethyl silicone may be prepared by hydrolyzing dimethyldichlorosilane or its esters, and then oxidized with air and a catalyst[16] to attain the desired CH_3/Si ratio.

2. Dimethyldichlorosilane may be mixed with methyltrichlorosilane or silicon tetrachloride and then hydrolyzed and the products cocondensed.[17]

3. Silicon tetrachloride may be partially methylated (as with methyl magnesium chloride) to the desired CH_3/Si ratio and the reaction mixture hydrolyzed directly.[18]

The first method has the advantage of direct control of the final viscosity by " bodying " the resin in a solvent, and it might be combined with method 3 by hydrolyzing the reaction product from two equivalents of Grignard reagent per mole of silicon tetrachloride and then proceeding with the oxidation. The second method requires that the hydrolysis be carried out in a solvent capable of dissolving both the chlorosilanes and water in order that the resin may remain soluble;

[14] U. S. patent 2 375 007 to R. G. Larsen and Hyman Diamond.
[15] U. S. patent 2 377 689 to J. F. Hyde.
[16] Hyde and DeLong, *J. Am. Chem. Soc.* **63**, 1194 (1941).
[17] Rochow and Gilliam, *J. Am. Chem. Soc.* **63**, 798 (1941).
[18] U. S. patent 2 258 218 to E. G. Rochow.

in the absence of a solvent or in one of low water tolerance there are high local concentrations of hydrochloric acid which may gel the resin. Since no elevated temperature is required, however, the method is particularly well adapted to the preparation of rapidly curing resins of low CH_3/Si ratio, which must be handled in cold dilute solution to prevent gelation. The method is more economical of methyl groups than method 1 and offers direct control of composition, but requires preliminary separation of the intermediate chlorosilanes. The third method is simpler, for the ethyl ether used as solvent for the Grignard reaction also serves as a homogeneous medium for hydrolysis, but control of composition is more remote, and the ether is seldom a satisfactory solvent for application of the resin.

Resins of the same CH_3/Si ratio prepared by the first and second methods undoubtedly are different in their properties, for the polymeric structures are built up under different conditions of condensation. Methyl silicone polymers with CH_3/Si ratios of 1.2, 1.3, 1.4, and 1.5 prepared by the second method are described[17] as colorless solids with densities decreasing from 1.20 to 1.06; the time required to harden them at 100° C. increases from 2 to 24 hours in the series, and the refractive indexes bear an interesting linear relation to the methyl content.[17] Below 1.2 methyl groups per silicon atom the resins are sticky syrups which cure at room temperature (or with moderate heating) to hard brittle glassy masses; above a ratio of 1.5, and particularly above 1.7, the products are oily and quite volatile but set to a soft gel after several days or weeks at 200°. Resins prepared by the third method have been shown to be substantially similar to those of the second method[17] at low CH_3/Si ratios; at higher ratios they cure more slowly and suffer more evaporation loss because the unseparated trimethylchlorosilane from the methylation reaction shortens the chains.[18]

As a group, the methyl silicone resins are characterized by excellent thermal stability and good resistance to oxidation. Samples have been heated to 550° *in vacuo* and to 500° in hydrogen without disintegration, decomposition, or melting; a transparent piece heated in air to 200° C. for one year looks the same as another piece of the same disk kept at room temperature.[18] Above 300° C. the resins will oxidize slowly if they have free access to air, but for analytical combustions it has been found necessary to heat the samples to 550° C. or more in pure oxygen. The residue from oxidation under these conditions is a white mass of silica.

The fact that methyl silicone does not decompose to a carbonaceous residue makes it particularly well suited for use as electrical insulation,

where its superior thermal stability allows it to be operated at temperatures well above those which can be endured by conventional organic insulation.   Such elevated temperatures may be encountered, for example, in aircraft equipment where high output from machines of small size and low weight requires that higher temperature differentials be used to dissipate the heat from iron and copper losses.[19]   If such service temperatures should exceed the recommended values for methyl silicone insulation, the material does not char as would a substance with a carbon-to-carbon structure; it simply oxidizes superficially to silica.

Of much greater importance to the every-day use of methyl silicone resins for insulation is their behavior under electrical stress.   Following approved engineering practice,[20] their performance in this respect can best be evaluated in terms of three quantities: the dielectric constant (the capacitance of the system referred to vacuum or air as 1.00, and hence a measure of the recoverable energy stored within the dielectric material), the loss factor (proportional to conductance per cycle, and hence a measure of the total energy dissipated as heat per unit volume of the dielectric), and the power factor (cosine of the angle whose tangent is the ratio of loss factor to dielectric constant, and hence a measure of both stored and dissipated energy).   For a cast disk of methyl silicone resin prepared by partial methylation of silicon tetrachloride and direct hydrolysis, for example, the dielectric constant was 3.7 at 26° C. and 3.6 at 56°, and the power factor was 0.008 at 26° and 0.0045 at 56° (all measured at 60 cycles per second).

SILICONE RUBBER

Methyl silicone rubber is a development based on principles entirely different from those of the resins.   An elastomeric gum is first prepared by treating the hydrolysis product of very pure dimethyldichlorosilane with one or more reagents which are effective in increasing the molecular weight without resorting to cross linking.   This process brings about a complete reshuffling or equilibration of structural units, as is done in the preparation of silicone oil; the reagents chosen are those which have the power to open a few silicon–oxygen bonds and thereby to rearrange the polymers in a manner that could not be achieved by the process of condensation alone.   With dimethyl silicone, if the presence of trifunctional groups has been avoided carefully, it becomes possible to build up aggregates composed of two thousand

[19] Kiltie, *Trans. AIEE* **62,** 899 (1943).
[20] Race, *Elec. Eng.* **61,** 105 (1942).

or more $(CH_3)_2SiO$ units[21] without forming an insoluble gel. The elastomer is then milled with inorganic fillers on the mixing rolls, just as is done with natural or synthetic rubber. A curing catalyst is added during the mixing, and then the plastic mass is molded to the desired shape and is cured to an insoluble infusible elastic material.

This compounded cured elastomer or " rubber " shares with all the other methyl silicone products the common characteristic of exceptional thermal stability. The material does not melt when heated in air at 300° C., which is far above the decomposition temperature of natural rubber or of any of the synthetic organic elastomers. Service over long periods of time at 150° C. does not destroy its elasticity.

As with silicone oil, the properties of silicone rubber change slowly with temperature; the elasticity persists down to −55° C. Although the mechanical properties require improvement before the material can be recommended for usage under severe stress or abrasion, it is well suited to other applications where thermal stability and resistance to chemical reagents are more important than tensile strength or tear resistance.

Methyl silicone rubber also shares the excellent electrical properties of the resins and oil. A molded sample with silica filler had a dielectric constant of 3.0 at room temperature over a range of 60 to 10^{10} cycles. The loss factor remains at 0.004 from 60 to 10^7 cycles and then rises rapidly to 0.037 at 10^9 cycles and 0.055 at 10^{10} cycles. At 102° C. the values remain the same except for a small decrease in dielectric constant (caused by a decrease in density) and a slight indication of enhanced d-c conductivity. The rubber does not seem to be affected by ozone.

ETHYL SILICONE RESINS

The colorless rather viscous oily ethyl silicone which forms when diethyldichlorosilane or the diethyldialkoxysilanes are hydrolyzed was one of the first silicone polymers to be prepared.[22] Since it distilled over a range of temperatures above 300° C., at first it was considered an anomalous and puzzling form of organic compound; Ladenburg considered it as valid proof against the newly introduced periodic system when he wrote that the diethyl silicon oxide " differs from the ketones by its oddly high boiling point, and so constitutes a striking

[21] D. W. Scott, work in publication.
[22] Ladenburg, *Ann.* **164**, 311 (1872). See also preparation by oxidation of $(C_2H_5)_4Si$: Friedel and Crafts, *Ann. chim. phys.* [4] **9**, 5 (1866).

example of the incorrectness of Mendeleef's Law,[23] by which silicon compounds should boil at a lower temperature than the corresponding carbon compounds." Kipping later interpreted the structure of the liquid differently and considered it to be a mixture of high-molecular-weight substances formed by a process of condensation, a view which remains unchanged today.[24]

The ethyl group attached to silicon in a polymeric siloxane chain renders the composition softer, more soluble, and slower to cure than would a methyl group, so that, for a given hardness and degree of infusibility and insolubility, fewer ethyl than methyl groups are required. For this reason a preferred range of composition for ethyl silicone resins is from 0.5 to 1.5 ethyl groups per silicon atom.[25] Below an Et/Si ratio of 0.5 the compositions are brittle masses which shrink and crack as they condense; being so highly cross-linked, they become insoluble at an early stage in the condensation and so are difficult to store or apply. The excessive shrinkage, which is due to the splitting out of relatively large quantities of water during condensation, sets up internal strains which leave the mass weak and friable. Above an Et/Si ratio of 0.5 the condensation products become more resinous and less vitreous, increasing in flexibility and softness as the ratio increases. With an average of about one ethyl group per silicon atom the products are suitable as coating compositions, since they form films of good adhesiveness and fair flexibility. Higher Et/Si ratios bring increased flexibility and plasticity required in a polymer to be used in thicker sections, but above a ratio of 1.5 the ethyl silicones become difficult to condense to the solid state. The evaporation losses increase rapidly as the degree of cross linking diminishes, and, since the simple diethylsiloxane polymers evaporate selectively and leave the larger cross-linked aggregates in the polymer, the end result of curing a high-ratio resin by heat alone is to lower the ethyl content to a value that could have been chosen as well initially. With two ethyl groups per silicon atom the polymers are oils which remain liquid despite attempts to convert them to gels or elastomers.[26]

OTHER ALKYL SILICONE RESINS

Propyl, butyl, and amyl silicones of the type $(R_2SiO)_x$ are colorless oily liquids which resemble ethyl silicone in appearance. The cor-

[23] Mendeleef, *Ann.*, Supplement 8, 220 (1869).
[24] Robison and Kipping, *J. Chem. Soc.* 93, 439 (1908); Martin and Kipping, *J. Chem. Soc.* 95, 313 (1909).
[25] U. S. patent 2 258 220 to E. G. Rochow.
[26] Martin and Kipping, *J. Chem. Soc.* 95, 313 (1909), report that in one case a soft gel was obtained from diethyl silicone oil, but that the result could not be repeated.

responding polyalkylsiloxanes of the type $(RSiO_{1.5})_x$, which are obtained by the hydrolysis of alkyltrichlorosilanes or their esters, are solid infusible or glassy polymers.[27] Of these, the n-propyl compound is an insoluble powdery white solid like the corresponding methyl and ethyl members of the series, but the amyl compound is resinous and soluble in ether and benzene. The alkyltriethoxysilanes have been hydrolyzed with insufficient water and found to produce linear polymers of the type $RSi(OEt)_2$—O—$(RSiOEt)_x$—O—$RSi(OEt)_2$, but complete hydrolysis gave stable polymeric products which might be used as varnishes.[28] The condensation polymers of the phenyl, benzyl, and naphthyl silanediols and silanetriols were found to have high thermal stability and low electrical losses, but to be vitreous and fragile in nature.[29]

Little is known about the resins of intermediate R/Si ratio which may be derived from mixture of the higher alkyl- and dialkylchlorosilanes, except that the larger alkyl groups cause the resin to cure more slowly and to remain softer in consistency. As the larger groups are used, fewer are required to produce a resinous polymer of given flexibility and curing characteristics, so that a butyl silicone roughly comparable to a methyl silicone in physical properties does not necessarily contain four times as much carbon. The compensation is only partial, however; the higher alkyl silicones are necessarily higher in organic content than a comparable methyl silicone and are dominated to a correspondingly lesser extent by the siloxane network which is their basis.

The higher alkyl silicones also oxidize more readily than do the lower members of the series. The ease with which an alkyl group may be removed from the siloxane chain by oxidation can best be measured by the time the polymer takes to crumble and disintegrate when heated in air at a given temperature. Methyl silicone may have a life equivalent to some 10 years of service at 200° C., whereas amyl silicone cracks and checks after a day at 200°.

Although it contains an aromatic nucleus, benzyl silicone is correctly classed as an alkyl silicone, because the phenyl group is attached through a —CH_2— group to the silicon. Moreover, benzyl silicone resembles all the previously described alkyl silicones in that the complex polymeric mixture from the condensation of dibenzylsilanediol is an oil[30] and not a resin. Chemically, the benzyl group

[27] Meads and Kipping, *J. Chem. Soc.* **105**, 679 (1914); *ibid.* **107**, 459 (1915).
[28] Andrianov, *J. Gen. Chem. USSR* **8**, 1255 (1938); Andrianov, *Org. Chem. Ind. USSR* **6**, 203 (1939).
[29] Koton, *J. Applied Chem. USSR* **12**, 1439 (1939).
[30] Robison and Kipping, *J. Chem. Soc.* **93**, 448, 552 (1908); *ibid.* **101**, 2148 (1912).

is quite readily removed from silicon by oxidation, as is true of butyl and amyl silicones, and it also is removed in the form of toluene by solutions of sodium hydroxide.[31]   It is not removed under acid conditions of hydrolysis which serve to remove phenyl groups.

The large size of the benzyl group, rather than the presence of a phenyl radical, probably is responsible for the fact that dibenzyl-silanediol may be isolated, and may be converted into hexabenzyl-cyclotrisiloxane[32] and other well-defined crystalline substances.   Poly-benzylsiloxane derived from the hydrolysis of benzyltrichlorosilane[33] is a sticky soluble resin which upon standing gradually condenses further to an insoluble resin.   The hydrolysis of the trichlorosilane with steam gives a similar hard brittle soluble resin.   All such compositions are soluble in alcoholic alkalies to form the water-soluble salts, from which the resin may be recovered by the addition of acids.

Cyclohexyl silicone resembles benzyl silicone quite closely.   Compositions of the type $(C_6H_{11}SiO_{1.5})_x$ are gluelike in consistency, as Kipping described them, and they may be converted to ether-insoluble resins.[34]   Almost all chemical manipulations of the lower polymeric forms result in conversion of these into more of the gluelike higher polymers.

The siloxanes which contain unsaturated alkyl groups form a special class of polymers, because they may be linked through their organic components as well as through their siloxane groups. As was noted in Chapter 2, the vinyl- and allylsiloxanes polymerize through their unsaturated groups when they are heated in air or with peroxide catalysts, and they also form copolymers with some organic allyl and vinyl compounds.[35]   Unsaturated groups attached to silicon seem to be particularly easily oxidized, and this may limit the use at elevated temperatures of polymers containing such groups. A more extreme example of labile behavior by unsaturated groups linked to silicon is furnished by hexaethynyldisiloxane, which decomposes in cold water to acetylene and silica:[36]

$$(CH{\equiv}C)_3SiOSi(C{\equiv}CH)_3 + 3H_2O \rightarrow 6CH{\equiv}CH + 2SiO_2$$
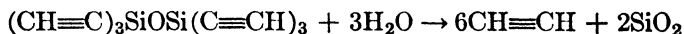
This observation led to the conclusion that a triple bond next to a

[31] Kipping, *Proc. Roy. Soc.* A159, 142 (1937).
[32] Dilthey and Eduardoff, *Ber.* 38, 4132 (1905); Robison and Kipping, *J. Chem. Soc.* 105, 40 (1914).
[33] Melzer, *Ber.* 41, 3393 (1908); Martin and Kipping, *J. Chem. Soc.* 95, 307 (1909); Martin, Kipping, and Meads, *J. Chem. Soc.* 107, 463 (1915).
[34] Palmer and Kipping, *J. Chem. Soc.* 1930, 1020.
[35] Hurd, *J. Am. Chem. Soc.* 67, 1813 (1945).
[36] Volnov and Reutt, *J. Gen. Chem. USSR* 10, 1600 (1940).

silicon atom weakens the carbon–silicon bond enormously and thus " disproves the generally accepted view regarding the stability of carbon–silicon bonds."[36]

ARYL SILICONES

The aryl silicones in general are decidedly different from the alkyl silicones, and nowhere is the difference so marked as in the comparison of *phenyl silicone* with methyl silicone. The hydrolysis of diphenyldichlorosilane yields products which in no way could have been predicted from the behavior of dimethyldichlorosilane upon hydrolysis. Indeed, no better example need be given of the inadvisability of transferring information gained with one organosiloxane to another series of organosiloxanes bearing widely different organic groups. Although the hydrolysis of dimethyldichlorosilane yields a wide assortment of siloxane polymers from which a few pure chemical individuals can be separated laboriously, the hydrolysis of diphenyldichlorosilane in cold water and solvent yields an almost theoretical equivalent of diphenylsilanediol, $(C_6H_5)_2Si(OH)_2$,[37] which can be recrystallized and obtained in a pure form melting at 148° C. If the crystals are dissolved in ether and warmed with a little concentrated hydrochloric acid, there is obtained a high yield of a single molecular species, hexaphenylcyclotrisiloxane, $[(C_6H_5)_2SiO]_3$. The corresponding cyclic trimer of methyl silicone, it will be remembered, can be obtained in appreciable yields only by thermal " cracking " of large polymers.

Another striking conversion in the phenyl series of siloxanes is that which produces the cyclic tetramer. Diphenylsilanediol is dissolved in boiling alcohol, and a few drops of aqueous caustic are added. Upon cooling, the distinctive crystals of octaphenylcyclotetrasiloxane separate.[37] Apparently strong bases bring about the condensation of diol to tetramer almost exclusively, whereas strong acids favor the formation of almost all trimer. Since both condensation reactions proceed at very moderate temperatures it cannot be said that the molecular form assumed by the product is determined by the temperature.

Octaphenylcyclotetrasiloxane is one of the products isolated by Kipping[38] from the mixed hydrolysis products obtained by boiling diphenyldichlorosilane with water. There was some evidence of polymorphism, but Kipping believed from cryoscopic data that the crystals melting at 200° to 201° were the tetramer. Other determina-

[37] Burkhard, *J. Am. Chem. Soc.* 67, 2173 (1945).
[38] Kipping, *J. Chem. Soc.* 101, 2138 (1912); Kipping and Robison, *ibid.* 105, 499 (1914).

tions of molecular weight[39] indicated that the compound might have been the trimer, but an extensive X-ray investigation of the structure of crystals melting at 201° to 202° C. has indicated a monoclinic crystal structure in which the unit cell contains four molecules of tetramer, or 16 $(C_6H_5)_2SiO$ units.[40] The cyclic trimer is excluded as a structure capable of building this crystal, because the presence of glide planes of symmetry requires an even number of atoms of each kind, in this case 16 silicon atoms, 16 oxygen atoms, and so on. Since 16 is a multiple of 4 and not of 3, the substance must be a crystal form of the cyclic tetramer.

If diphenyldichlorosilane is hydrolyzed incompletely, as by using only one-fourth the water required for the diol, there is formed a series of α-ω dichloropolysiloxanes. Of these, tetraphenyl-1,3-di-chlorodisiloxane and hexaphenyl-1,5-dichlorotrisiloxane have been isolated as crystalline solids.[37] These substances hydrolyze very slowly when dissolved in a hydrocarbon–alcohol mixture and stirred with cold water, yielding the corresponding α-ω diols.

From these investigations it is evident that the first product of hydrolysis of diphenyldichlorosilane is diphenylsilanediol, and that this begins to condense if the temperature is above 20 or 30° C. The cyclic trimer and tetramer of diphenylsiloxane are formed, and probably other higher cyclic condensation products. At the same time, linear polysiloxanediols are formed. At 100° the latter diols condense further, and by heating the hydrolysis product to 200° or more the condensation is made to proceed more rapidly. Phenyl silicone prepared in this way no longer develops crystals of the cyclic trimer or tetramer on standing, and takes on a more resinous character. It remains weak and brittle when cold, however, and still softens at a moderate temperature. It burns readily with a sooty flame, depositing carbon and silica, but it is remarkably resistant to oxidation. The phenyl groups seem to stand 400° or even 500° in air for several hours without splitting off the silicon, but they are removed quite readily by heating the polymer with aqueous acids[41] or with bromine water in a sealed tube.[42]

The initial hydrolysis product of phenyltrichlorosilane is also a brittle resin, but it is fusible even though it is so highly cross-linked.[29]

[39] Hyde and DeLong, *J. Am. Chem. Soc.* **63**, 1194 (1941).

[40] Burkhard, Decker, and Harker, *J. Am. Chem. Soc.* **67**, 2174 (1945).

[41] Hyde and DeLong, *J. Am. Chem. Soc.* **63**, 1196 (1941); U. S. patent 2 371 050 to J. F. Hyde.

[42] Kipping and Blackburn, *J. Chem. Soc.* **1932**, 2200; Vorlander, *Ber.* **58**, 1900 (1925).

It seems likely that the solubility and fusibility of this polyphenyl-siloxane are consequences of incomplete condensation, however, for its melting point (given as 92°) rises with continued heating. If the resin is heated long enough, it eventually goes over to an infusible condition. In both stages, this material resembles diphenyl silicone in being weak and brittle, and resistant to oxidation, but capable of burning in air. Similar properties result from the cocondensation of phenylsilanetriol and diphenylsilanediol to make resins with phenyl-to-silicon ratios between one and two.

Modification of the properties of the phenyl silicones is possible through chlorination of the aromatic nucleus.[43] One or more chlorine atoms may be substituted for hydrogen in each ring, as by chlorination of the phenylchlorosilane with iron powder as a carrier. The chloro-phenylchlorosilane is then hydrolyzed, and the resulting silicols are condensed by heat, just as is done with unsubstituted phenylchloro-silanes. The product is a brittle fusible resin, but it melts at a higher temperature than phenyl silicone and is less flammable. If an average of three chlorine atoms has been introduced into each phenyl nucleus, the product will not burn at all.

Such chlorinated phenyl silicones are highly resistant to oxidation and are thermally stable up to at least 450° C. They are soluble in chlorinated hydrocarbons and in various other organic solvents, but their solubility and fusibility again depend upon the degree of cross linking and the degree of condensation. The electrical losses remain low at elevated temperatures; a typical trichlorophenyl silicone had a specific conduction below 10^{-9} reciprocal ohm per cc. at 320° C., which is less than that of some common glasses at that temperature. The dielectric constant increases with chlorine content, reaching 3.5 for trichlorophenyl silicone at 25°.

In the same manner, it is possible to incorporate fluorine, bromine, or iodine atoms within an aromatic nucleus to modify its properties. The fluorophenyl silicones are particularly interesting as stable flame-proof resins for service at elevated temperatures.

A halogenated aryl group also may be used in conjunction with an alkyl group, as in methyl chlorophenyl silicone. If the aryl group contains chlorine in sufficient proportion, it can suppress the flammability of the alkyl group so that the entire composition is flame-proof.

Other *aryl silicones* have been prepared in considerable variety, and they all resemble phenyl silicone rather than the higher alkyl

[43] U. S. patent 2 258 219 to E. G. Rochow.

silicones.   Thus xylyl- and naphthylsiloxanes of the type $(RSiO_{1.5})_x$ are soluble glassy brittle substances of polymeric character.[44]   Ditolyl silicone prepared from ditolyldichlorosilane[45] is a low-melting sticky resin which is readily soluble in acetone and hydrocarbons and is brittle when cold.   The cross-linked condensation product of p-tolylsilanetriol likewise is brittle and soluble, but it does not melt at 360°.

Phenoxyphenyl silicone is a particularly resinous composition which may be prepared from p-bromodiphenyl ether[46] through the Grignard reaction.   The large size of the phenoxyphenyl group causes the corresponding silicols to condense very slowly, so that extreme heat is required to convert the rather pasty crystalline masses to cross-linked siloxanes.   A polymer containing an average of 1.1 such groups per silicon atom is a hard brown brittle resin of high thermal stability and good electrical properties.   By chlorination of one or both of the phenyl nuclei the resin may be made flameproof.

ALKYL–ARYL SILICONES

It has been pointed out that the alkyl silicones of high R/Si ratio are oily liquids or weak gels when polymerized by heat alone, and that in order to get resinous and adhesive properties the R/Si ratio must be brought down to about 1.5 for a methyl silicone and about 1.0 for a butyl or benzyl silicone.

At the same time, the aryl silicones of high R/Si ratio are brittle vitreous soluble fusible solids, which actually are supercooled liquids. By themselves they are too brittle and weak for coating or impregnation.

It has been found possible to alter the properties of either class of resin by inclusion of the other.   This is accomplished not by mere admixture (which often is impossible because of immiscibility), but by attaching both alkyl and aryl groups to the same silicon atom in the intermediate or by cocondensing alkyl and aryl silicols to make a copolymer.   The copolymer method has the advantage of flexibility, for it permits various combinations of alkyl and aryl groups to be used in different proportions within a single polymeric structure.   A wide range of properties thus becomes possible.   Resins may be designed to have a desired balance of flexibility, thermoplasticity, and mechanical strength.

[44] Kipping and Meads, *J. Chem. Soc.* **105**, 679 (1914); *ibid.* **107**, 459 (1915); Steele and Kipping, *J. Chem. Soc.* **1929**, 357; Ladenburg, *Ann.* **173**, 151, 165 (1874); Melzer, *Ber.* **41**, 3390 (1908); Martin and Kipping, *J. Chem. Soc.* **95**, 307 (1909); *ibid.* **107**, 463 (1915).

[45] Steele and Kipping, *J. Chem. Soc.* **1929**, 2545.

[46] U. S. patent 2 258 221 to E. G. Rochow.

Fortunately, it is found that some alkyl–aryl copolymers have mechanical strength and toughness exceeding those of the pure alkyl or aryl silicones, so that it becomes possible to improve upon the pure types in this respect. Such improvement in strength is obtained without sacrifice of other desirable properties, and therefore the alkyl–aryl copolymers often are more useful wherever strength and toughness are important.

Methyl phenyl silicone is an interesting example of such an alkyl–aryl copolymer. It develops a good balance of flexibility, strength, and infusibility (in the cured condition) when the molar proportions of methyl and phenyl groups are almost equal and the total R/Si ratio is about 1.8. Compositions higher in proportion of methyl groups are preferred to those higher in phenyl groups,[47] in order to avoid brittleness. A resin having an average of 1.00 methyl group and 0.80 phenyl group per silicon atom, in the form of a film cured on glass fiber cloth, had a 60-cycle power factor of 0.001 and a dielectric strength of about 800 volts per mil at 100° C. The same methyl phenyl silicone, as a cast disk without the glass fiber as filler, had a power factor one half as high at the same temperature.

A similar methyl phenyl silicone was used to impregnate and coat glass cloth which was then aged at 300° C. in air to determine how well the composite insulation would maintain its dielectric strength at this temperature. For 300 hours the dielectric strength (measured at room temperature and 60 cycles) stayed near an average of 1,000 volts per mil (for a thickness of 5 mils), and then dropped slowly to 500 volts per mil, where it remained for 340 hours more. Only after 640 hours at 300° C. did the dielectric strength drop to values approximating those of an air gap, indicating cracks in the resin film. The cracks still could not be seen with the unaided eye, and the test probably was more severe than ordinary service at the same temperature, because the samples constantly were being flexed by the circulating air in the oven and were cooled rapidly each time they were taken from the oven for test. Thus the dielectric properties of methyl phenyl silicone appear to be somewhat better than those of the methyl silicone resins, and the resistance to abrasion is somewhat higher.

Ethyl phenyl silicone is another alkyl–aryl silicone which may be made either from ethylphenyldichlorosilane[41] or by cocondensation of mixed ethyl and phenyl chlorosilanes. The cross-linked ethyl phenyl silicone resins have good dielectric and mechanical properties, but their maximum service temperatures in air are somewhat lower than those for methyl phenyl silicone, being limited to about 250° C. for

[47] U. S. patent 2 258 222 to E. G. Rochow.

short periods or 175° C. for continuous operation.   Apparently oxidation of the ethyl group sets in at higher temperatures.

Many other alkyl–aryl silicones are possible, and some may prove to have mechanical properties superior to those of the two copolymers which have been described.   What is needed is a theory of structure of such copolymers which will explain the development of mechanical properties not present in the alkyl or aryl polysiloxanes separately and which thereby will serve as a guide to the formulation of more useful compositions.

WATER-REPELLENT FILMS FROM ORGANOSILICON MATERIALS

REACTION OF METHYLCHLOROSILANES

The discovery that the methylchlorosilanes in the vapor phase will react with many types of surfaces to produce water-repellent films[1] has led to one of the most important developments in the organosilicon field. The effect was an entirely unexpected outcome of the preparation and handling of large volumes of methylchlorosilanes intended for methyl silicone and serves as an excellent illustration of how the availability of new or of previously scarce intermediates may lead to valuable developments which are entirely unrelated to the original purpose of the investigation.

In its simplest form, the water-repellent treatment consists of the rapid reaction of methylchlorosilane vapor with the hydroxyl groups or adsorbed water on a surface to deposit a very thin film of methylpolysiloxane, thereby changing the contact angle of that surface to liquid water. Thus a piece of ordinary filter paper, when exposed for one second or so to air which is saturated with the vapors of a mixture of the methylchlorosilanes, becomes water-repellent wherever the vapor has reached it. Water then rolls off the paper, leaving it dry, or stands in small droplets with a high contact angle. Hydrocarbon solvents will wet the treated paper readily, but they do not dissolve off the film. Only strong reagents (such as hydrofluoric acid) which are capable of dissolving the solid silicone resins are capable of removing the water-repellent film.

The same reaction is found to occur with cotton cloth and with wood, and in a less pronounced way with wool, silk, leather, and many other materials. Glass and other ceramic surfaces also react readily with the methylchlorosilane vapor to give very effective water-repellent films,[2] but only if the surface had upon it an adsorbed film of water. Completely dry glass, baked out under vacuum, does not become distinctly water-repellent upon treatment. Glass which has stood at ordinary room conditions usually has on its surface a film of

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[1] U. S. patent 2 306 222 to W. I. Patnode.
[2] Norton, *Gen. Elec. Rev.* 47, No. 8, p. 6 (1944).

water up to 100 molecules thick, the actual thickness depending upon the relative humidity of the surrounding air.[2] The methylchlorosilanes appear to react with this strongly bound water film to liberate hydrogen chloride and attach methyl-bearing silicon atoms to the surface, thereby rendering the surface water-repellent. Again the organosilicon film is not removed by neutral solvents or by detergents and is taken off only by severe abrasion or by destructive reagents such as hydrofluoric acid or an alcoholic solution of potassium hydroxide. Solutions of wetting agents will wet the surface and allow it to be cleaned, but when the solution is rinsed off the surface again is water-repellent.

These experimental facts point toward a hydrolytic reaction of methylchlorosilane vapor at the surface of the object being treated, depositing a thin film of methylpolysiloxane which becomes the water-repellent agent. Insofar as the end result is concerned, it matters little whether the reaction is one with adsorbed water in every instance, or whether hydroxyl groups in a structure like that of the cellulose molecule in themselves are capable of reacting with the chlorosilane. Neither does it matter particularly whether "bound water" is invoked for the reaction. The important point is that the silicon atoms appear to be chemically bound to the substrate, probably through oxygen, and that they can be removed only by resorting to chemical action.

If it is assumed that the reaction follows the course which has been indicated, the organosilicon film deposited by the reaction must be oriented with its oxygen bonds directed toward the substrate and its methyl groups extending outward from the surface. A reasonable configuration for an oriented dimethylsiloxane film is illustrated by the molecular model shown in the frontispiece.[3] Since this model is constructed to scale, it is possible to draw some conclusions about the film from measurements of the model.[2] The methyl groups are about 3 A. apart, and the distance between chains is about 4 A., and so the area of a single $(CH_3)_2SiO$ unit is $3 \times (3 + 4) = 21$ sq. A. From Avogadro's number, one mole of $(CH_3)_2SiCl_2$ should yield a monomolecular film $6.023 \times 10^{23} \times 21 \times 10^{-16}$ sq. cm., or 1.26×10^9 sq. cm. in area. Each gram of dimethyldichlorosilane therefore should cover an area of approximately 1,000 square meters with a single-layer film. The thickness of such a film, as indicated by the model, is about 6×10^{-8} cm.

Measurements which have been made on the water-repellent films

[3] This illustration is reproduced by permission of S. E. Surdam, *FRPS*, and the *General Electric Review*. The model is constructed of Fischer-Herschfelder atomic models, which are designed to the scale 1 cm. = 1 A. = 10^{-8} cm.

themselves, as deposited on steatite cylinders* by vapor treatment, allow some interesting comparisons with the calculated values. The gain of weight during the treatment of one cylinder was 1.9×10^{-5} g. per sq. cm.; so that if the density is taken as 1.0, the film must be 1.9×10^{-5} cm. thick. If it is assumed that the previously calculated thickness of a monolayer is correct, this particular film must have been $1.9 \times 10^{-5}/6 \times 10^{-8}$ or about 300 molecules thick. This is the same order of magnitude as the number of water molecules piled one upon another in the adsorbed film on silica at high humidities, so that, if steatite has approximately the same kind of adsorbed film as silica, the methylchlorosilane reacts molecule for molecule with the water film. The entire water film therefore is replaced by one of methyl silicone.

This picture of the water-repellent action implies that the oriented layer of methyl groups bound to the underlying siloxane network is responsible for the high contact angle to liquid water, and that the water-repellent effect therefore is similar in cause and extent to that shown by the hydrocarbon surface of paraffin wax. If this is true, analogous compounds with other organic groups attached to silicon ought to behave in similar fashion. In general they do, but it is found in practice that each organosilicon compound requires its own conditions for hydrolytic reaction at the surface, and the resulting film has a characteristic effectiveness as a water-repellent treatment.

If the sole object of a treatment were to cover a given surface with hydrocarbon groups in order to make it water-repellent, that object could be attained in many other ways, such as by dipping the object in paraffin or spraying it with a solution of paraffin. Such a layer would not be so durable nor so permanent as the one provided by reaction of the methylchlorosilanes, however. An important advantage of the use of substituted chlorosilanes for water-repellent treatment lies in the fact that it provides a general method for the *chemical attachment* of hydrophobic groups to a surface, and this advantage is not limited by the choice of hydrophobic group. Once attached, the film becomes a part of the object or the substance so treated and remains effective until abraded off or covered up.

USES

Millions of steatite parts have been treated with methylchlorosilane vapor to make them permanently water-repellent and so to maintain

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* Steatite is a magnesium silicate ceramic body used as insulation in high-frequency equipment. The data given are abstracted from the paper by Norton (reference 2).

a high surface resistivity even when water has condensed on the surface. For this work a mixture* of the methylchlorosilanes has been found to be more effective than pure dimethyldichlorosilane or methyltrichlorosilane. The treating procedure is quite simple: before attachment of any metal parts, the steatite pieces are conditioned at 50 to 90 per cent relative humidity and are placed in a cabinet equipped with a fan for circulating the air. A measured quantity of the methylchlorosilane mixture is vaporized in the cabinet, and the vapor is circulated for a few minutes and then withdrawn from the cabinet. The treated pieces are removed and allowed to stand 20 minutes or more while the hydrogen chloride dissipates. The pieces then are ready for use. Some improvement in the electrical properties of the film has been noted during the first 24 hours, but thereafter the effectiveness remains constant unless the film is covered up by dirt or is deliberately removed by chemical means. A dirty piece may be cleaned with alcohol, benzene, or carbon tetrachloride, to restore the effectiveness of the film.

The necessity for treating such steatite pieces arises from the fact that water spreads on a clean untreated ceramic surface and reduces the surface electrical resistivity to very low values. This condition may occur in aircraft radio equipment, for example, when the equipment is cooled during high-altitude flight and then is brought into a warm humid atmosphere. As soon as the dew point is reached, water condenses directly on the surfaces of the ceramic insulators and supports, and, if the surfaces can be wet readily, the condensate spreads out and provides a conducting path, thereby making the entire equipment inoperative. Measurements[2] indicate that in this condition the surface has an electrical resistivity of around 1 megohm per sq. cm. If the surface had been glazed previously, its resistivity under the same conditions is 15 to 70 megohms, and, if it had been waxed, the resistivity is found to be 120 to 400 megohms. All these values are too low for satisfactory operation of the equipment, although the wax treatment gives enough improvement to have been used widely for this purpose. Now a treatment of the unglazed parts with methylchlorosilane vapor raises the surface resistivity under dew-point conditions to more than 200,000 megohms, indicating that the organosiloxane film has superior electrical characteristics.

The water which condenses on a treated or an untreated steatite surface will evaporate as the piece warms to the surrounding tem-

* This and other organosilicon preparations for making surfaces water-repellent are produced and marketed by the General Electric Company under the registered trade-mark of Dri-Film.

perature. The continuous film on an untreated piece does this slowly, requiring (in one test) a period of 20 minutes or more. The droplets on a surface treated with methylchlorosilanes evaporate much more rapidly, requiring 3 minutes in the same test. At the same time the surface resistivity of the treated piece rises to a value higher than any attained by the untreated piece under any conditions.

The over-all effect of the methylchlorosilane treatment of steatite is to stabilize the electrical behavior of the surface under widely different conditions of humidity or condensation. The same surface stability is desired in certain types of fluorescent lamps in order to insure dependable starting of the discharge, regardless of the ambient humidity. Such lamps therefore are treated with the methylchlorosilane vapor in order to make the surface water-repellent, in which condition it has a more constant resistivity and a predictable charge distribution. The starting characteristics then are no longer affected seriously by the moisture content of the air.

Besides such electrical applications as water-repellent surface films, there are many applications where water repellency is an end in itself. Treated glass windowpanes or windshields are not wet by muddy water, and so they stay clean longer and are easier to clean whenever washing is required. Rain does not flood the surface of a treated windshield but stands in small droplets; when the car is in motion the air stream blows the droplets off, leaving the glass clear. Treated tumblers are easier to wash and dry; treated chemical glassware holds water with a flat meniscus; treated vitreous enamel does not stain easily and has improved luster. Cloth and paper may be made water-repellent for protection against rain, and it is possible that all clothes could be so treated.

Many powdered substances may be treated with methylchlorosilane vapor to change their properties. Untreated clay clumps together because the particles pick up water and adhere, but treated clay maintains its individual particles and flows like a liquid when it is shaken with air. Starch granules likewise stay free flowing after treatment. Many pigments and fillers normally are hydrophilic, but after treatment they remain powdery and are more easily wet by oils, so that it should be easier to mill them into paint vehicles or rubber or plastic masses.

If filter paper is made water-repellent with methylchlorosilanes, it will not allow water to pass through but will pass hydrocarbon liquids readily. The same is true of treated porous porcelain or fritted glass filters. On the other hand, an untreated filter allows water to go through but will not pass hydrocarbons while it is wet with water.

Treated and untreated filters therefore are selective in their action, and may be used to separate oil–water mixtures continuously, without resorting to settling and decantation. Some emulsions and some natural products contain wetting agents in the aqueous phase, however, and these agents nullify the selective action of the treated filter, so that it cannot always be used for such separations.

How far the vapor-treating technique will be extended to building materials, minerals for ore-flotation processes, and other large-scale uses remains to be seen. Since the technique requires only a small amount of material, and since mixed methylchlorosilanes may be used directly without distillation or hydrolysis, the process should be much less expensive than using a coating of silicone resin or oil on the same surface. Used without waste, the methylchlorosilanes may prove even less expensive than the traditional water-repellent agents such as waxes and lacquers.

TECHNICAL ASPECTS OF SILICONES

The reader of an introductory work on silicones will have many questions to ask concerning the possible application of these interesting substances to whatever he makes or uses. Many of these questions revolve around the possibility of large-scale production of organosilicon compounds and the ultimate cost of the products. No answer in terms of experience can be given to most of the questions, nor can figures in tons and dollars be extracted from mere speculation and assembled here. It may be justifiable, however, to re-examine the various methods of synthesis and processing from a practical point of view, and so to attempt to point out the course that future developments in the field of silicones logically may be expected to take. It is recognized that new developments may make obsolete whatever conclusions are reached here, even as they are written.

To the purely chemical considerations there must now be added as a major factor the cost of production of organosilicon compounds. This cost derives from the cost of raw materials, the cost of conducting the various reactions and processing operations, and the expense of controlling and managing the entire process. Were all these factors obvious or predictable, it would be possible to devise a " best " method for manufacturing silicone polymers. Unfortunately, there are countless considerations of availability, transportation, patents, accounting practice, and interdependence with other processes, all having an important bearing on the costs and all serving to influence commercial policy. Therefore, it is not possible to evaluate all of these factors and come to any conclusion about the superiority of this process or that; the author intends only to consider the general requirements of each method of synthesis and to point out the probable fields of usefulness. As will be apparent, some products could best be made by a combination of methods.

It is necessary that the discussion be confined to those organosilicon products which, on the basis of available information, show the greatest promise of widespread use. This would seem to mean the methyl, ethyl, and various alkyl–aryl silicone resins, methyl silicone oils and elastomers, and the methylchlorosilanes for water-repellent films.

Future developments may change the relative emphasis on these materials.

THE INTERMEDIATES

As outlined in the previous chapters, the preparation of silicone polymers involves first the preparation of organosilicon halides or esters, secondly the hydrolysis of an appropriate mixture of these intermediates, and finally the condensation or rearrangement of the polymers to achieve the desired molecular arrangement. Only in the first step is there a choice of preparative methods; the second and third steps are carried out in much the same way, regardless of how the intermediates were made. From the standpoint of synthesis, the problem therefore comes down to the preparation of the methyl-, ethyl-, and phenylchlorosilanes or ethoxysilanes. Of these the methyl compounds are the most important, because they are used directly for the water-repellent treatment and are the only intermediates required for the oils, elastomers, and some types of resin.

These considerations seem to rule out the Shtetter synthesis, for this method produces trichlorosilanes with chlorine atoms in the organic groups. Processes for converting these into ethyl- or methyl-chlorosilanes have not been published; supposedly such conversions would have to be extremely simple if the combined procedures are to retain an advantage over the Grignard and direct methods. As such methods of conversion are lacking, the Shtetter synthesis probably will reach commercial importance only after further research has demonstrated how use may be made of its interesting products.

Another method about which too little is known for a fair evaluation in this chapter makes use of the reaction of aliphatic hydrocarbons with silicon chlorides at high temperatures.[1] Silicon tetrachloride, for example, is mixed in the vapor phase with an aliphatic hydrocarbon corresponding to the alkyl group to be attached to the silicon, and the mixture is heated to a temperature of 450° or more. The products then are cooled and condensed, and the organosilicon compounds are separated by distillation. Stated in its general form, the reaction offers decided promise as a means of using hydrocarbons directly in organosilicon syntheses.

Of the other methods for preparing organosilicon compounds, the Grignard and direct methods have been selected for further consideration here. This is not to say that the Wurtz synthesis and the metathetical reactions of silicon tetrachloride with alkyls of zinc and mer-

[1] U. S. patent 2 379 821 to H. C. Miller and R. S. Schreiber.

cury are unsuited to larger-scale development, but only that the two methods have been selected which are being relied upon to furnish the first production quantities of organosilicon intermediates. Similar treatment of the other methods could be made whenever they may be selected for large-scale use.

THE GRIGNARD METHOD

The most straightforward solution to the problem of producing methyl-, ethyl-, and phenylchlorosilanes would be to adapt the classical laboratory methods of synthesis to large-scale operation. A logical choice would be the Grignard reaction, long a laboratory favorite because it is so universally applicable. For the preparation of dimethyl silicone from methyl chloride by the Grignard method, the steps would be:

$$CH_3Cl + Mg \rightarrow CH_3MgCl \tag{1}$$

$$2CH_3MgCl + SiCl_4 \rightarrow (CH_3)_2SiCl_2 + 2MgCl_2 \tag{2}$$

$$(CH_3)_2SiCl_2 + H_2O \rightarrow (CH_3)_2SiO + 2HCl \tag{3}$$
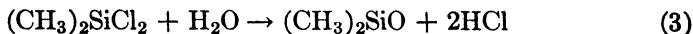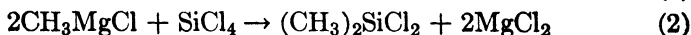
In order to get back to the ultimate raw materials, which might be sand, coke, chlorine, and methane or methanol, some preliminary steps are necessary:

$$SiO_2 + 2C \rightarrow Si + 2CO \tag{4}$$

and

$$Si + 2Cl_2 \rightarrow SiCl_4 \tag{5}$$

or

$$SiO_2 + 2C + 2Cl_2 \rightarrow SiCl_4 + 2CO \tag{6}$$

also

$$CH_3OH + HCl \rightarrow CH_3Cl + H_2O \tag{7}$$

or

$$CH_4 + Cl_2 \rightarrow CH_3Cl + HCl \tag{8}$$

To be complete, the process also should include the preparation of magnesium from magnesium chloride or oxide:

$$MgCl_2 \text{ electrolyzed} \rightarrow Mg + Cl_2 \tag{9}$$

or

$$MgO + R \text{ (reducing agent)} \rightarrow Mg + RO \tag{10}$$

No argument need be presented here for one or another of the optional methods given for the three preparations involved in equations 4 through 10. The choice of method usually is determined by local conditions and does not influence the general consideration of the

Grignard process. Six steps remain necessary: the three operations given in equations 1, 2, and 3, plus the preparations of magnesium, silicon tetrachloride, and methyl chloride.

The entire Grignard process may be written in the form of one equation or summation, in which the combining weights are shown below the formulas:

$$\underset{60}{SiO_2} + \underset{24}{2C} + \underset{32}{2CH_4} + \underset{284}{4Cl_2} + \underset{48.6}{2Mg} + \underset{18}{H_2O} \rightarrow$$

$$\underset{74}{(CH_3)_2SiO} + \underset{190.6}{2MgCl_2} + \underset{146}{4HCl} + \underset{56}{2CO} \quad (11)$$

It is evident from this summation that the chlorine and magnesium are simply processing aids which do not appear in the desired product, and that they weigh 4.5 times as much as the methyl silicone. In any large-scale operation, it would seem necessary that the by-product magnesium chloride and hydrochloric acid be sold or used in some other process or reconverted to the starting materials, for disposal of them as waste would be a difficult problem in itself. If the chlorine and magnesium are to be recovered for reuse, considerable electric energy must be expended to restore them to the elementary condition, though no more than if fresh raw materials were chosen instead. It is simply a requirement of the process that much free energy be expended in the preparation of the starting materials; this energy reappears in the subsequent reactions in the form of heat.

Some economy can be gained in the chlorine cycle by using method 7 for preparing the methyl chloride from by-product hydrochloric acid coming out of the process. This could be accomplished by a catalyzed reaction of the concentrated acid with methanol[2] and would eliminate half of the requirement of free chlorine given in equation 11. The rest of the free chlorine still is necessary for reaction with the silicon, however. The amended summary of the process then becomes

$$\underset{60}{SiO_2} + \underset{24}{2C} + \underset{64}{2CH_3OH} + \underset{142}{2Cl_2} + \underset{48.6}{2Mg} \rightarrow$$

$$\underset{74}{(CH_3)_2SiO} + \underset{190.6}{2MgCl_2} + \underset{18}{H_2O} + \underset{56}{2CO} \quad (12)$$

in which the required free chlorine and free magnesium going into the process represent 2.6 times the weight of methyl silicone obtained.

No *economic* advantage is gained by converting the silicon tetrachloride to ethyl silicate before reaction with the Grignard reagent, for just as much chlorine is required in the process, and it still appears as

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[2] Norris and Taylor, *J. Am. Chem. Soc.* **46**, 753 (1924); Whaley and Copenhaver, *J. Am. Chem. Soc.* **60**, 2497 (1938).

hydrogen chloride. In addition, the reaction with alcohol must be added to the process before reaction 2. At the completion of the process the magnesium appears in the form of the ethylate or as ethoxy magnesium chloride, from which the alcohol may be recovered for recycling.

If equation 11 is set up for the production of phenyl silicone in place of methyl, the combining weights become:

$$SiO_2 + 2C + 2C_6H_6 + 4Cl_2 + 2Mg + H_2O \rightarrow$$
$$\underset{60}{} \quad \underset{24}{} \quad \underset{156}{} \quad \underset{284}{} \quad \underset{48.6}{} \quad \underset{18}{}$$

$$(C_6H_5)_2SiO + 2MgCl_2 + 4HCl + 2CO \quad (13)$$
$$\underset{198}{} \quad \underset{190.6}{} \quad \underset{146}{} \quad \underset{56}{}$$

It is evident at once that a much larger part of the total weight of reactants appears in the product than was shown in equation 11 for methyl silicone. In equation 13 the chlorine and magnesium represent only 1.7 times the weight of product, instead of 4.5 times as in equation 11. Put in another way, the phenyl group which is put to use in phenyl silicone constitutes 68 per cent of the weight of chlorobenzene, whereas the methyl group constitutes only 30 per cent of the weight of methyl chloride. The larger the organic group, then, the higher the weight of silicone polymer obtained from each pound of raw materials. At a uniform price per pound of alkyl or aryl chloride, and all other things being equal, the silicone with large organic groups costs less than the one with small groups.

So far in this discussion, nothing has been said about the multiplicity of products to be expected from the Grignard reaction, or the yield of one desired product in terms of the theoretical yield. As has been pointed out in previous chapters, the Grignard method is a substitution process which results in a mixture of all five possible products ($SiCl_4$, $RSiCl_3$, R_2SiCl_2, R_3SiCl, and R_4Si), the proportion of each in the mixture being a function of the molar ratio of Grignard reagent to silicon tetrachloride. As in the generalized reaction (2), let us assume that two equivalents of $RMgCl$ are used and that R_2SiCl_2 is the principal desired product. The actual yield of R_2SiCl_2 in the reaction mixture under such a condition has been reported to be as high as 70 per cent of theoretical,[3] but such a figure is found to refer to products distilled over a range of boiling points. Closer control of the distillation usually lowers this value. In fact, a general mathematical treatment of the problem as a set of consecutive competitive reactions[4] indicates that the maximum possible yield of R_2SiCl_2 is about 50 per

[3] Kipping, J. Chem. Soc. 91, 214, 720 (1907).
[4] Fuoss, J. Am. Chem. Soc. 65, 2406 (1943).

cent of the theoretical value calculated from equation 2.   The rest of the Grignard reagent goes into products which are either more or less fully alkylated.   Of these, the $SiCl_4$ and $RSiCl_3$ may be separated and recirculated to alkylate them further and thereby to increase the yield of R_2SiCl_2.   The R_3SiCl and R_4Si must be separated from the mixture
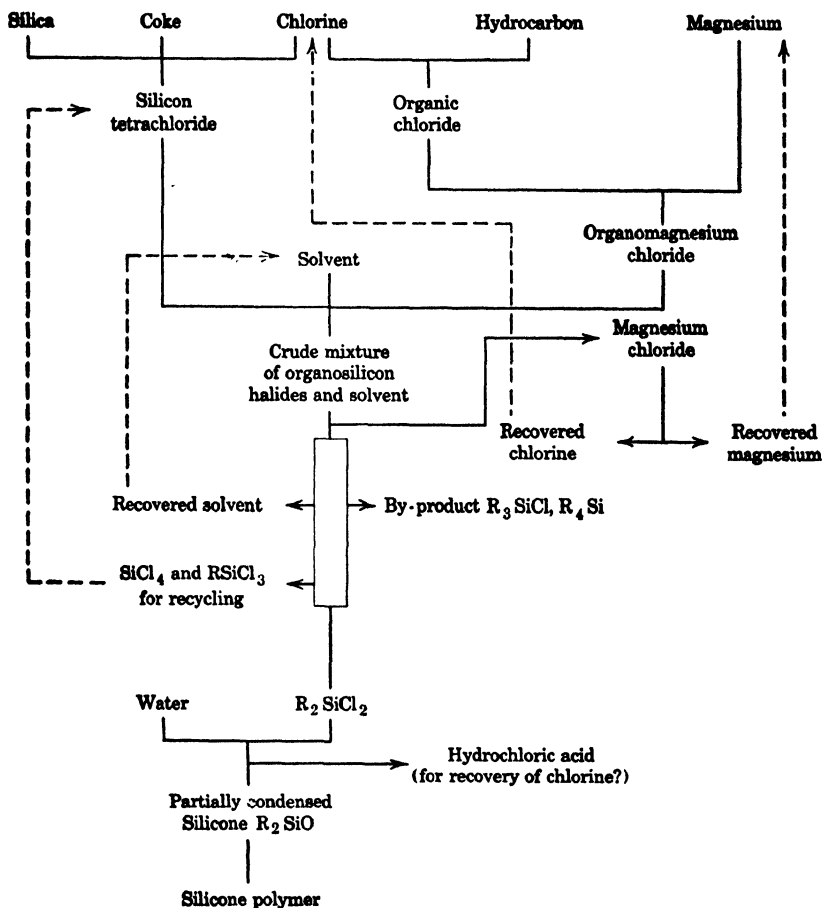
FIG. 1.   Production of Silicone Polymers by Grignard Method

and discarded or put to special uses, such as the use of $(CH_3)_3SiCl$ in " chain-blocked " methyl silicone oils (Chapter 4).

With this discussion as a basis, the entire process for the preparation of a silicone polymer by the Grignard method can be shown in diagrammatic form in Fig. 1.   This flow sheet does not specify the type of

solvent or solvents to be used in the process, because that may vary with the type of halide which is to be used. With methyl chloride it has been customary to use ethyl ether in the laboratory; n-butyl ether has been tried but is less satisfactory because of a lower solubility of methyl magnesium chloride in it.[5] In the reaction of chlorobenzene with magnesium, an excess of chlorobenzene may serve as solvent,[6] or the reaction may be conducted without any solvent.[7] In the latter instance, it might be necessary to take up the phenyl magnesium chloride in a solvent after its preparation in order to carry out the stepwise substitution of chlorine in silicon tetrachloride more effectively.

Bromine could be shown in place of chlorine in reactions 1, 2, 7, 8, 9, 11, 12, and 13. The Grignard reactions with organic bromides in place of chlorides would be easier to start and operate, and the organo-magnesium bromides would be more soluble in the solvent used as reaction medium. The yields also might be increased somewhat by more complete reaction. However, the required bromine for methyl silicone would represent nine times the weight of product, and the cost of this much bromine would make necessary some efficient method of recovery. Even so, the process losses of bromine would add a significant portion to the total cost of the process. The use of chlorides wherever possible therefore seems to be indicated in any large-scale manufacture of organosilicon products.

The Grignard process as outlined herein has one major advantage over the other methods: it is extremely flexible. It can be used for the preparation of alkyl- and aryltrichlorosilanes as readily as for the preparation of the dialkyl- or diaryldichlorosilanes, and with an even greater percentage yield. A wide variety of organic groups may be attached to silicon by the one general procedure. All of the versatility of the laboratory method therefore follows into production. At the same time the well-known objections to the laboratory method, centering around the handling of unstable and reactive Grignard reagents and the separation of precipitates, may hold equally well on a large scale. On economic grounds, the chief drawbacks are (1) the multiplicity of steps, and (2) the dependence upon silicon tetrachloride (which is only 16 per cent silicon) or ethyl silicate (which is only 13.5 per cent silicon) as a source of silicon. Such objections do not constitute insurmountable obstacles to the commercial exploitation of the method, but they do point out the need for a great deal of specialized engineering thought on the design and the operation of the equipment.

[5] Gilliam, Liebhafsky, and Winslow, *J. Am. Chem. Soc.* **63**, 801 (1941).
[6] German patents 660 075 and 697 420 to I. G. Farben. Ges.
[7] Gilman and Brown, *J. Am. Chem. Soc.* **52**, 3330 (1930).

THE DIRECT METHOD

Another process which is appropriate to the production of dialkyl- and diaryldichlorosilanes was discussed fully in Chapter 2 under the name of the direct method. This method is an outgrowth of efforts to prepare organosilicon compounds without resorting to the classical substitution methods involving magnesium, sodium, zinc, or mercury compounds as reagents. Fundamentally, the direct process utilizes the action of hydrocarbon halides (preferably chlorides or bromides) upon elementary silicon to produce a mixture of alkyl- or arylhalo-silanes[8] of the type R_aSiX_b, where $a + b = 4$. Copper is employed as a catalyst for the synthesis of methylchlorosilanes by this reaction, and so any consideration of the direct synthesis must count upon the cost of including minor amounts of copper in the contact mass.[9]

If attention at first is confined to the production of methyl silicone from the previously accepted raw materials, the chemical processes must include reduction of silica to silicon, preparation of the methyl chloride from methane or methanol, reaction of the methyl chloride with silicon, and hydrolysis of the methylchlorosilanes. If the same conventions are used as in the discussion of the Grignard method, and the methanol process for methyl chloride is elected, the steps are:

$$SiO_2 + 2C = Si + 2CO \tag{1}$$

$$CH_3OH + HCl = CH_3Cl + H_2O \tag{2}$$

$$2CH_3Cl + Si = (CH_3)_2SiCl_2 \tag{3}$$

and

$$(CH_3)_2SiCl_2 + H_2O = (CH_3)_2SiO + 2HCl \tag{4}$$
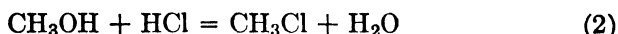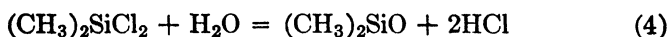
These four steps may be summarized in one equation in which the relative combining weights are given below the formulas:

$$\underset{60}{SiO_2} + \underset{24}{2C} + \underset{64}{2CH_3OH} \rightarrow \underset{74}{(CH_3)_2SiO} + \underset{18}{H_2O} + \underset{56}{2CO} \tag{5}$$
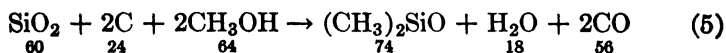
It is evident that this process is simpler in its requirements than the Grignard method and involves fewer chemical operations. Since the silicon need not be chlorinated, no free chlorine is required. The hydrochloric acid produced by the hydrolysis of dimethyldichloro-silane is exactly consumed by the reaction with methanol, so that two

[8] Rochow, *J. Am. Chem. Soc.* **67**, 963 (1945).
[9] U. S. patents 2 380 995 to E. G. Rochow; 2 380 996 to E. G. Rochow and W. I. Patnode; 2 380 997 to W. I. Patnode. See also U. S. patents 2 380 998 and 2 380 999 to M. M. Sprung and W. F. Gilliam for specialized operation of the method with hydrogen and nitrogen added to the hydrocarbon halide.

moles of HCl circulate in the process without application of electric energy. There is no magnesium cycle.

For production of methylchlorosilanes, copper equivalent to about 10 per cent of the weight of the silicon is preferred as a catalyst. This may be added as a powder to the pulverized silicon and the mixture sintered in a hydrogen furnace, or it may be added in other ways. On a molar basis, this copper requirement represents 0.049 mole of copper per mole of silicon entering into the reaction, and all of it remains behind as the silicon is consumed. It is at least theoretically possible to recover the copper after the reaction has run its course, but the limited recovery value of this small amount allows only the simplest methods to be considered.

As in other preparative methods for organosilicon compounds, the direct synthesis produces a mixture of methylchlorosilanes rather than the single compound shown in equation 3. Besides dimethyldichlorosilane, the mixture usually contains silicon tetrachloride, trichlorosilane, methyltrichlorosilane, methyldichlorosilane, trimethylchlorosilane, and even silicon tetramethyl. Under proper conditions, dimethyldichlorosilane is the principal product. Of the other compounds, methyltrichlorosilane usually is next in abundance; this substance finds use in the cross-linked methyl silicone resins, or it can be methylated further by the Grignard method to increase the yield of dimethyldichlorosilane. There is no way of recycling it in the direct process, and so supplemental operations are required for the conversion. The interconversion of this and the other minor products of the direct synthesis, involving the exchange of methyl and chlorine groups as desired, has been a special study in itself.[10]

The production of phenyl silicon halides by the direct method involves techniques which are different from those employed for the methyl compounds, even though the over-all reactions are similar. The technique which has been found to give the highest yields of diphenyldichlorosilane with a minimum of side reactions is the passage of chlorobenzene vapors through a heated tube containing sintered pellets or blocks of powdered silicon and silver, the silver catalyst constituting about 10 per cent by weight of the mass. This reaction operates best at a temperature of 375 to 425° C., which is fully 100° above the range found best for the preparation of methylchlorosilanes. It is also advantageous to use much more chlorobenzene than can undergo the rather sluggish reaction with the silicon–silver mass in one single passage through the reaction tube; the excess chlorobenzene acts as a diluent and sweeps through the very high-boiling phenyl-

[10] Hurd, *J. Am. Chem. Soc.* **67**, 1545 (1945).

chlorosilanes.[11]   In operation, the unchanged chlorobenzene is stripped from the high-boiling products and is returned to the reactor.

The net changes involved in this direct method for preparing phenyl silicone can be represented by the following series of equations:

$$SiO_2 + 2C = Si + 2CO \tag{6}$$

$$C_6H_6 + Cl_2 = C_6H_5Cl + HCl \tag{7}$$

$$2C_6H_5Cl + Si = (C_6H_5)_2SiCl_2 \tag{8}$$

$$(C_6H_5)_2SiCl_2 + H_2O = (C_6H_5)_2SiO + 2HCl \tag{9}$$

These may be summarized in one equation giving the combining weights:

$$\underset{60}{SiO_2} + \underset{24}{2C} + \underset{156}{2C_6H_6} + \underset{142}{2Cl_2} + \underset{18}{H_2O} \rightarrow$$

$$\underset{198}{(C_6H_5)_2SiO} + \underset{146}{4HCl} + \underset{56}{2CO} \quad (10)$$

As was pointed out in the discussion of the Grignard method, a larger part of the chlorobenzene molecule appears in the finished silicone product than is true of the methyl chloride molecule.   At the same price per pound for raw materials, the basic material cost for phenyl silicone therefore would be less than that for methyl silicone.   The difference is accentuated by the fact that chlorobenzene is produced in very large volume at low cost, so that it becomes an inexpensive source of phenyl groups for phenyl silicone.   On the other hand, the factors which act to increase the relative cost of phenyl silicone by the direct method are (1) the cost of recovering the silver catalyst, and (2) the possible uneconomical disposition of the hydrochloric acid, which cannot easily be recirculated in the process.

The different operating conditions for the methyl and phenyl reactions make it desirable to employ two separate flow sheets to illustrate the production of methyl and phenyl silicones by the direct process.   Fig. 2 shows the flow of materials for the production of methyl silicone via the methanol process, and Fig. 3 depicts the production of phenyl silicone from benzene.

If ethylchlorosilanes are desired, they may be made by the direct method by the vapor-phase reaction of ethyl chloride with silicon at 300° C., using 10 per cent of copper as catalyst.[8]   The reactions follow the general plan indicated in the flow sheet for the corresponding methyl compounds (Fig. 2).

Other hydrocarbon halides react in much the same way as the methyl, ethyl, and phenyl chlorides and bromides.   Different condi-

[11] Rochow and Gilliam, *J. Am. Chem. Soc.* **67**, 1772 (1945).

tions of temperature and time of contact and sometimes a different disposition of the catalyst (or even a different kind of catalyst) are known to be required in each individual case in order to attain the maximum yield of organosilicon compounds.

FIG. 2. Production of Methyl Silicone by Direct Method

As for alkyl- and aryltrichlorosilanes, one need only write an equation for their formation by the direct reaction to see why the method is not suitable for the large-scale production of such compounds:

$$3CH_3Cl + Si \xrightarrow{\text{catalyst}} CH_3SiCl_3 + 2(CH_3)$$
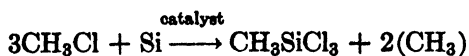
For every molecule of the trichlorosilane formed, three molecules of the alkyl halide are consumed and two organic radicals are thrown
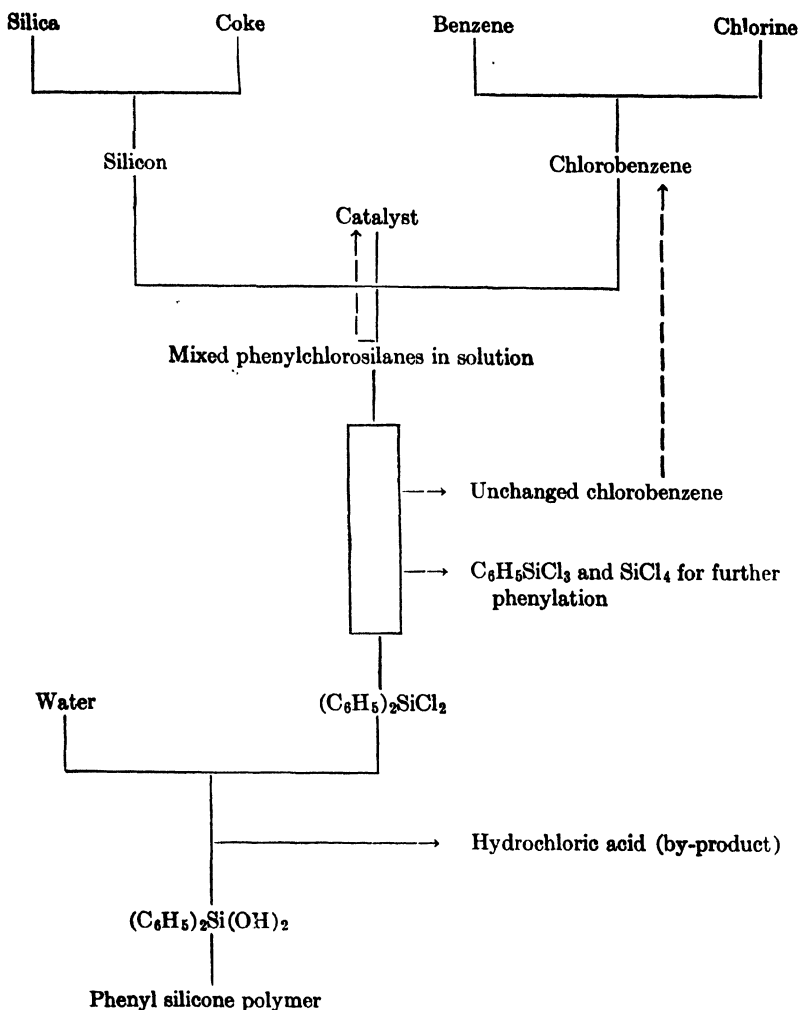
FIG. 3.   Production of Phenyl Silicone by Direct Method

away.   In the example given, the free radicals undergo pyrolysis according to a known pattern:[12]

$$2(CH_3) \rightarrow C_2H_4 + H_2$$
$$C_2H_4 \rightarrow CH_4 + C$$
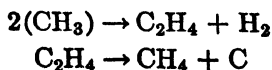
[12] Waring, *Trans. Faraday Soc.* **36**, 1142 (1940).

Free carbon thereby is deposited on the reactive mass of silicon, covering it over and serving as a catalyst for further pyrolysis of methyl groups.   Furthermore, the methane and hydrogen which appear in the exit gases impair the efficiency of the condensers and represent a waste of organic halide.   For these reasons the formation of trichlorosilanes is to be avoided as uneconomical and detrimental to the continued production of dichlorosilanes.

In practice, some trihalosilane always is produced in the direct reaction, and the amount increases as the temperature is raised above the threshold value required for the reaction, or as the catalyst becomes ineffective.   In this respect the degree to which the proportion of trihalosilane exceeds the proportion of trialkylhalosilane in the product is a measure of the inefficiency of the reaction.   Put in another way, the excess of trihalosilane $RSiX_3$ over the halosilane R_3SiX reflects the ignorance concerning the optimum conditions for that particular reaction.

Since moderate amounts of trihalosilane are useful in the cross-linked siloxane polymers, some or all of the quantity produced in the direct process can be used in this way.   If large amounts of alkyl- or aryltrichlorosilanes are required, it would seem more economical to prepare them by the Grignard method or by the action of a mixture of chlorine or hydrogen chloride and organic chloride on silicon.

One limitation of the direct method of synthesis therefore is the inherent restriction of the unmodified reaction to dihalosilanes as principal products.   Another limitation is the lack of general experience with all phases of the reaction; since the first successful experiments go back only to 1940, the method is very new compared with the Grignard and Wurtz methods, and there is no fund of time-tested techniques and recipes to follow.   The latter condition can be remedied only by further research and by continued development of the direct method in use.

PROCESSING

The operations required for converting the organosilicon intermediates into useful polymers are much more conventional than the methods for synthesizing these intermediates.   Such processing operations are quite the same, regardless of the method or methods used for producing the intermediates; from the time the organosilicon halides are formed, the same problems of distillation, hydrolysis, condensation, and curing are encountered.   Only when orthosilicate ester derivatives are used as intermediates will the methods of handling necessarily be

different, but even here the general operations as expressed by equations 11, 12, and 13 are quite similar to those drawn up for halides.

If the methylchlorosilanes are taken as examples, the first major problem to be encountered in their processing is that of distillation. Since methyltrichlorosilane boils at 66° C. and dimethyldichlorosilane boils at 70° C., their separation by rectification is a challenge to engineering skill and to the best design of distillation equipment. Not only must the plate efficiency of the column be high, but special considerations are made necessary by the chemical behavior of the substances being distilled. All storage, fractionating, and transfer manipulations must be carried out under anhydrous conditions, for, although the dry methylchlorosilanes are not corrosive to mild steel or the other common metals of construction, any introduction of moisture generates hydrogen chloride in high local concentration, a condition seriously corrosive to brass, steel, copper, stainless steel, chromium, aluminum, and even lead. The only answer seems to be the exercise of continual care that containers, transfer lines, and distillation equipment are scrupulously dry, and that only thoroughly dried air or nitrogen be permitted access to the system. With these precautions, plain mild steel is entirely serviceable as a material of construction.

The next step, the hydrolysis of methylchlorosilanes, necessarily involves the handling of hydrochloric acid or anhydrous hydrogen chloride. The equipment therefore must be designed to resist their corrosive effects. This usually means glass, porcelain, stoneware, or glass-lined equipment. After thorough removal of halogen from the hydrolysis product, as by repeated washing with water or weakly alkaline solutions, the organosilicols or siloxanes are noncorrosive and again may be handled in equipment made of the common metals.

The further processing of methyl silicone polymers is more straightforward from a chemical engineering standpoint. Much of the equipment customarily used for compounding and curing natural rubber, for example, may be used without change to process methyl silicone elastomer. In the process of curing silicone resins *in situ*, it often is necessary to resort to temperatures much higher than those customarily used with organic plastics, and hence different equipment or modified equipment may be required. In view of the higher service temperatures which are expected, it seems reasonable to accept the higher processing temperatures, for it is a general requirement of many fabricated materials (glass, porcelain, metals, and most plastics, for example) that their processing temperatures exceed their maximum service temperatures. In silicone resin technology it seems likely

that the same kind of requirement will lead to electrically heated press platens and higher-temperature ovens as processing equipment.

The very characteristics which set apart the organosiloxane polymers from the purely organic polymers also militate against blends and mixtures of the two. The high service temperature of a methyl silicone resin cannot be realized if the resin is coated upon cotton cloth; in the same way, the performance of any combination of organic and siloxane materials at elevated temperatures is limited to that of the less heat-resistant material. Moreover, organic and organosilicon materials usually are found to have only limited mutual solubility and compatibility, or to be quite completely immiscible. In order to gain the greatest possible advantage from the use of organosilicon polymers it therefore becomes necessary to develop organosilicon plasticizers and modifying agents of equal stability and acceptable solubility. These factors make it seem likely that the field of applied organosilicon chemistry will develop separately, with its own technology and its own balanced production of intermediates, polymers, and modifying agents.

TOXICITY

The possible toxicity of methylchlorosilanes and of all the silicone resins, oils, and elastomers is naturally a matter of concern in their manufacture and use. The methylchlorosilanes hydrolyze immediately they are inhaled and so have the odor and effect of hydrogen chloride; at all low concentrations they cause no ill effects. Four years' experience on the part of a group of laboratory workers has not revealed a single instance of toxic effect, either acute or chronic, from the inhalation of methylchlorosilanes. Fluoroscopic examination has revealed no deposits in the lungs, nor have the individuals in the group suffered any other disorder that could be attributed to silicon or its compounds. It must be concluded that there is no accumulation of organosilicon substances in the body that can be detected over this interval of time.

Similarly, ordinary handling of the methyl and methyl phenyl silicone polymers of all the types described and of their intermediate condensation products as well has not resulted in a single symptom of toxicity. The oils appear to be bland and to cause no skin disorders; the resins are sticky but are readily washed off the skin with hydrocarbon solvents. The absorption of oil and resin through the skin seems to be inconsequential.

So far as is known, the hemolytic and other injurious effects of ethyl and methyl orthosilicates (Chapter 1) must be specific to their

structure; no similar effect has been observed with the volatile silicon alkyls or organosiloxanes. It can be concluded that silicon does not cause poisoning of the type experienced with the heavy metals and that the organosilicon compounds so far encountered do not seem to be toxic in themselves.

FUTURE EXPANSION

It would be interesting at this point to predict from the present uses of the silicone materials the future trends of application. However, it is doubtful that present experience gives any dependable basis at all for such predictions. When research on silicone resins began, interest centered in their high-temperature performance, and it could not have been predicted at that time that some oily polymers would become important purely for their *low*-temperature performance, or that some types of silicone resin would be valued purely for their electrical characteristics, or that some intermediates required for methyl silicone production would render many different kinds of surfaces water-repellent. Neither can it be expected that these unrelated and unforeseen outcomes of research have all appeared and that the flow of discoveries will now cease; it is more likely that new developments will appear more rapidly as more people become interested and research in the field accelerates. Extrapolation of the present trend would therefore seem to be idle and misleading.

From discussion of the various organosilicon polymers it is evident that the siloxane systems provide unlimited opportunity for designing new polymers. Many different types of organic groups can be hung on the silicon–oxygen framework, and in various proportions. The degree and type of cross linking can be varied within wide limits as a separate parameter. The organic groups can be halogenated, nitrated, sulfonated, dehydrohalogenated, polymerized, and subjected to all of the reactions and techniques known to organic chemistry. The field therefore has all the breadth of carbon chemistry plus a generous margin allowable for the behavior of silicon.

If such a view is taken, it becomes equally evident that only a few possibilities have been investigated, and these sketchily. Chemistry is by no means a completed or even a predictable science; this particular portion of it is distinctly crude and elementary. Very few organosiloxanes have been investigated by physical methods to find out how they are put together, and hence no one knows how to plan experiments directed at improvement of the structures that now "just happen" in hydrolytic and condensation reactions. We have only working hypotheses based upon empirical knowledge and upon infer-

ences.   The state of the art is roughly equivalent to that of organic chemistry in the year 1860.

With this in mind it can only be said that a start has been made in organosilicon chemistry and that something may come of it.   In the first 40 years, the early investigators found that organic compounds of silicon could be made and that they behaved more or less like other organic compounds; in the second 40 years Kipping and his contemporaries learned how to make a great many organosilicon compounds more easily, and conducted the first systematic surveys of these substances, leading to an appreciation of the differences between organic and organosilicon compounds.   The third 40 years have begun with the commercial exploitation of a few materials developed through the application of previous knowledge plus some recent research.   It will be the privilege of the present workers to see what happens in the remainder of the period, now that commercial and scientific interests have widened and research is accelerating.   With an expanding literature, a more standardized nomenclature, and a greater variety of synthetic methods available to today's worker, progress should be ever faster.

Chapter 7

ANALYTICAL METHODS

The ultimate analysis of organosilicon compounds is an important subject to every worker in the field of siloxane polymers and their intermediates, for without dependable analytical methods the research chemist gropes blindly, at a loss concerning the composition of his products and unable to evaluate the effects of chemical attack. It is the purpose of this chapter to trace very briefly the development of adequate analytical procedures for organosilicon compounds, with particular emphasis upon those methods which may be used for investigating the composition of silicone polymers.

The early investigators employed contemporary macrocombustion methods to determine *carbon* and *hydrogen* in their organosilicon preparations, sometimes with modifications of the combustion tube to accommodate the higher combustion temperatures of the silicon compounds.[1] Silicon was determined separately by wet-oxidation procedures, such as a Kjeldahl-type digestion with concentrated sulfuric acid and a drop of mercury,[2] or oxidation with nitric acid in sealed tubes,[3] followed by dehydration of the silica. More recently the Parr bomb has been used for both liquid and solid materials as a means of attaining complete oxidation, the silica again being dehydrated and weighed in the manner common in inorganic analyses.[4] A micromethod for fusing organosilicon materials with carbonates and nitrates, followed by colorimetric determination of the silicon as the blue silicomolybdate, has been reported.[5] Compounds containing silicon–silicon bonds have been treated with aqueous alkalies or with piperidine[6] to liberate hydrogen in a closed system, one molecule for each silicon–silicon bond.

[1] See discussion of analytical methods in Bygdén, Silicium als Vertreter des Kohlenstoffs organischer Verbindungen, p. 71 (Almqvist and Wiksells Boktryckeri –A.-B. Upsala, 1916). The combustion tube preferably is packed with platinized asbestos and rolled platinum gauze.

[2] Bygdén, *loc. cit.*, p. 74.

[3] Polis, *Ber.* **19**, 1024 (1886); Kipping and Lloyd, *Proc. Chem. Soc.* **15**, 175 (1899).

[4] Chao-Lun Tseng and Tsung-Yi Chao, *Science Repts. Natl. Univ. Peking*, **1**, No. 4, 21 (1936).

[5] Pincussen and Roman, *Biochem. Z.* **233**, 344 (1931); Kaiser and Wetzel, *Angew. Chem.* **108**, 865 (1937).

[6] Kipping and Sands, *J. Chem. Soc.* **119**, 848 (1921).

More recently, the problem principally has become one of determining carbon, hydrogen, and silicon in solid polymeric compositions,* many of which are too stable and refractory for the older methods. These substances cannot be ashed properly in a platinum crucible because the more volatile low-molecular-weight siloxanes are driven off as stable vapors. Besides, the residue almost always contains silicon carbide as a result of having been ignited in an inadequate supply of oxygen. If a wet oxidation of these materials is attempted in a sealed tube, the difficultly oxidized mass may require an excessively high reaction temperature, more than the tube permits. However, wet oxidation in an open tube of high-melting glass, followed by ignition of the silica in the same tube, has been used successfully to determine silicon as silica in many condensation polymers.[7] The sample is weighed in the tube and then heated cautiously with concentrated sulfuric and nitric acids. Successive portions of nitric acid are added until the sample is fully oxidized, and then the residue is ignited and weighed as silica.

The dry oxidation of organosiloxanes can be accomplished by heating the sample in oxygen to some subincandescent temperature and oxidizing any escaping vapors on red-hot platinum farther along in the combustion tube. By this means, the sample is caused to oxidize in layers and to fall apart, exposing fresh surface and avoiding the formation of silicon carbide. The process is slow, but nothing in it interferes with the simultaneous collection of water and carbon dioxide from the combustion of the organic groups in the substance. It therefore becomes possible to determine carbon, hydrogen, and silicon simultaneously on a single sample.

Figure 1 illustrates one form of apparatus for carrying out this slow combustion.[8] Oxygen purified by passage over hot platinum in A and through Ascarite and Dehydrite absorbers in C is passed through a fused-silica combustion tube 1.5 cm. in diameter and 18 cm. long. The sample of about 0.05 g. is contained in a small porcelain or plat-

[7] Hyde and DeLong, *J. Am. Chem. Soc.* **63**, 1194 (1941).

[8] The author is grateful to H. A. Liebhafsky for suggestions which led to the development of this method. A comparison of the results on carbon and hydrogen with those obtained by regular microcombustion is given in Rochow and Gilliam, *J. Am. Chem. Soc.* **63**, 798 (1941), the " micro " results having been obtained by Dr. Carl Tiedcke, 366 Fifth Avenue, New York.

* Oxygen is not estimated because there are no simple methods for it. Combustion in a closed system in which a measured volume of oxygen is circulated has been proposed and tried, but the reported results have not been satisfactory. If a polymer is known to contain only carbon, hydrogen, silicon, and oxygen, by virtue of its synthesis or by application of qualitative tests, it is customary to estimate oxygen by difference.

inum boat and is slowly brought up to its oxidation temperature by a movable furnace D.   The vapors and volatile products pass through a roll of fine platinum gauze heated to 850° by a separate furnace E, and any silica smoke formed at this point is retained by the plug of glass wool at the very end of the tube. · The entire combustion tube (filled with oxygen) is weighed before the boat and sample are inserted, and again after the oxidation is complete, the sample having been
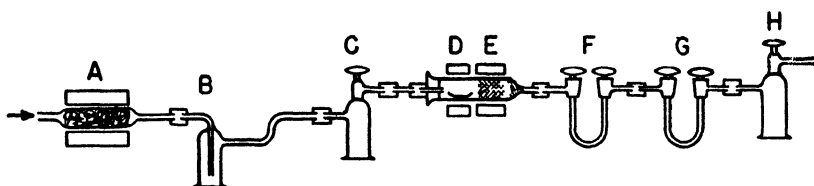
FIG. 4.   Apparatus for Combustion Analysis of Silicone Resins

A — Copper oxide purifier for oxygen
B — Bubble counter
C — H_2O and CO_2 absorber
D — Sample furnace
E — Furnace for Pt gauze
F — HO_2 absorption tube
G — CO_2 absorption tube
H — Protective tube

brought to 800° at the end of the run.   The increase in weight of the combustion tube (less boat) over the initial weight represents silica derived from the sample.   Water vapor and carbon dioxide are absorbed and weighed in the Dehydrite and Ascarite tubes F and G which follow the combustion tube.   The final absorber H protects against back-diffusion of water or carbon dioxide.

The combustion tube may be used repeatedly without being cleaned, since the deposited silica does not hinder combustion.   In order to improve the accuracy of the weighings it is preferable to grind the ends of the tube to accommodate glass plugs, rather than to rely upon rubber plugs.   The tube must be made rather short in order to fit in the balance case, and hence it is necessary to cool the ends with air streams to avoid heating the rubber connections.   To free the silica glass of the resulting annoying electrostatic charges, it is necessary to wipe the outside of the tube with a damp cloth before weighing it.

This method has given results of acceptable reproducibility with a wide variety of organosiloxane polymers, although each type of polymer has its optimum temperature of oxidation in the combustion tube.   In general, the oxidation temperatures for polymers with

aliphatic groups attached to silicon are lower the larger the aliphatic group, methyl silicone requiring a higher temperature than any of the others (about 500° C.). Aryl silicones require about the same temperature as the methyl compounds. Too high an initial oxidation temperature causes the sample to burn with a flame, depositing water droplets in the system and leaving in the residue some silicon carbide which is not completely oxidized during the final heating of the residue to 800° C. A satisfactory combustion leaves an entirely white residue.

The determination of chlorine, bromine, or iodine attached to silicon in organosilicon compounds is achieved readily by hydrolyzing the sample in water or aqueous alkali, neutralizing, and then titrating the halide ion with a standard solution of silver nitrate, using potassium chromate as indicator.[9] If a gravimetric determination of halogen as silver halide is to be used, all insoluble silicon-containing hydrolysis products must be removed before the silver nitrate is added, a step which sometimes is difficult because of the colloidal or gelatinous character of the products.

A simpler and easier method for all halogens[10] attached to silicon consists of hydrolyzing the sample in ice and water and then titrating the resulting hydrohalogen acid with standard base.[11] In practice, the sample is pipetted into a small vial which serves as weighing bottle and then is hydrolyzed by dropping the vial and stopper into a flask containing cracked ice and ether. The stoppered flask is shaken vigorously to complete the hydrolysis, and the acid which is formed is titrated in the same flask in the usual manner. The method is most accurate for substances like the dialkyldichlorosilanes which hydrolyze to form ether-soluble products; substances like silicon tetrachloride yield insoluble precipitates which may retain hydrolyzable chlorine and make the end point slow to attain. Hydrolyzable halogen attached to carbon will add to the total acid produced and so is indistinguishable (except in rate of hydrolysis) from halogen attached to silicon. Organic halogen which does not hydrolyze readily must be split from carbon by fusion, as in a Parr bomb, and then determined as halide ion.

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[9] Bygdén, loc. cit., p. 73; Stock and Somieski, Ber. 52, 713 (1919).

[10] The method has not been tried with compounds of the type R_3SiF, which are said to hydrolyze slowly or with difficulty. Titration of the other fluorosilanes is feasible if the sample is hydrolyzed in a known volume of standard base and the excess is then back-titrated with acid. The titration is carried out at 100° to decompose any fluosilicate ion [see Swinehart and Flisik, Ind. Eng. Chem. Anal. Ed. 16, 419 (1944)].

[11] This acidimetric method was developed by Dr. W. I. Patnode for use with methylchlorosilanes and has since been adapted to many other halosilanes. A similar method was used by Hyde and DeLong, J. Am. Chem. Soc. 63, 1194 (1941).

Hydrogen attached to silicon can be determined by treating the sample with a 30 per cent solution of sodium hydroxide in a closed system and measuring the evolved hydrogen.[12]   Silicon–silicon bonds must be known in order for the proper correction to be made.

Hydroxyl groups in organosilicon compounds may be determined by reaction with methyl magnesium iodide,[13] provided that no other "active" hydrogen is present to react similarly with the Grignard reagent.   The sample is treated with a solution of methyl magnesium iodide in a closed system of proper design[14] and the evolved methane is measured.

Nitrogen in organosilicon compounds can be determined by the standard Kjeldahl method.   Both silicon and nitrogen can be determined on the same sample by digesting it in concentrated sulfuric acid to which a drop of mercury has been added;[15] the silica is filtered from the diluted acid, and ammonia is distilled from the filtrate after alkali sulfide and caustic solution have been added.   The distilled ammonia is absorbed in standard acid, and the excess of acid is titrated in the usual manner.

[12] Stock and Somieski, *Ber.* **52,** 713 (1919).

[13] Sauer, *J. Am. Chem. Soc.* **66,** 1707 (1944).

[14] Shriner, Quantitative Analysis of Organic Compounds, p. 57 (Ann Arbor, Mich., 1938).

[15] Bygdén, *loc. cit.*, pp. 74–5.

GLOSSARY

ACETYLACETONATE. A compound of a metal with the enolic form of acetylacetone, CH_3—C=CH—C—CH_3. Most of these compounds are of
$$\overset{|}{O}H \qquad \overset{\|}{O}$$
chelate form; that is, they are linked through both oxygens to the metal:
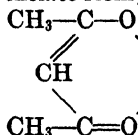
$$CH_3—C—O$$
$$\overset{/\!/}{CH} \qquad \overset{\diagdown}{M}.$$ They are useful in demonstrating the maximum
$$\overset{\diagdown}{CH_3}—\overset{\nearrow}{C}{=}O$$

covalence of the metal or metalloid atom M.

ACTIVATION ENERGY. The energy required to overcome the chemical inertia of molecules; the energy required to institute a chemical reaction between given reactants.

ALCOHOLYSIS. The reaction of the hydroxyl group of an alcohol with a substance; a reaction on the part of an alcohol analogous to that of water.

ALIPHATIC. Pertaining to a straight-chain or branched-chain structure of linked carbon atoms, rather than a cyclic structure.

ALKOXY. A group of the type —OR′, where R′ is an aliphatic hydrocarbon radical or a substituted aliphatic radical; a linear or branched-chain organic group linked through oxygen, as methoxy (—OCH_3), ethoxy (—OC_2H_5); an aliphatic ester group.

ALKOXYSILANE. An alkoxy derivative of a silane; a compound of silicon having at least one Si–OR linkage, where R represents an aliphatic group.

ALKYL, adj. Aliphatic; pertaining to a straight- or branched-chain grouping of carbon atoms; derived from methane or a homolog of methane. Examples: methyl, ethyl, propyl, butyl, amyl.

ALKYL, noun. A metal alkyl; a compound of a metal atom with as many hydrocarbon radicals as are required to satisfy its "normal" valence; an organometallic compound in which only organic groups are attached directly to the metal. In customary usage, the term includes compounds of the metal with both aliphatic and aromatic radicals.

ALKYLATION. A chemical reaction in which alkyl groups are substituted for some other groups or atoms in a molecular structure.

ALLYL. The —CH_2—CH=CH_2 group, second in the homologous series of olefinic radicals containing one double bond.

AMBIENT. Surrounding, prevailing, encompassing.

ANALOGY. Correspondence between properties of different elements; a prediction of chemical behavior based upon consideration of corresponding behavior of neighboring or similar elements.

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AROMATIC.   Derived from benzene or one of its homologs; containing one or more phenyl nuclei in its molecular structure.

AROXY.   A group of the type —OR″, where R″ is an aromatic hydrocarbon radical or a substituted aromatic radical; a benzenoid group linked through oxygen, as phenoxy (—OC_6H_5), naphthoxy (—$OC_{10}H_7$); an aromatic ester group.

ARYL, *adj.*   Pertaining to an aromatic grouping; derived from benzene or a homolog of benzene. *Examples:* phenyl, tolyl, naphthyl, anthracyl.

ASSOCIATION.   The process by which molecules group together to form molecular aggregates bound by chemical forces; the act of forming a dimer, trimer, tetramer, or higher polymer from monomeric units.

ASYMMETRIC COMPOUND.   A compound having a full complement of substituent groups arranged around a central atom, each group being different from the others so that there is a lack of symmetry in the molecular structure.   The asymmetry gives rise to optical isomers which are capable of rotating the plane of polarized light in opposite directions.

BENZYL.   The phenyl-substituted methyl group, —CH_2—C_6H_5, a predominantly aliphatic radical.

BIFUNCTIONAL.   In a polymer-producing reaction, the term applied to a reactant possessing two functional groups and therefore capable of propagating a chain indefinitely. *Example:*

$$—SiR_2—OH + \underline{R_2Si(OH)_2} = —SiR_2—O—SiR_2—OH + H_2O$$
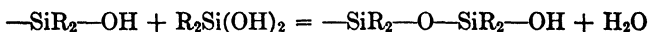
BOND.   The summation of forces by which two atoms are bound together in a chemical compound (sometimes called link, linkage, or chemical bond). See COVALENT, ELECTROVALENT.

BOND ANGLE.   The angle included between lines drawn through the centers of three of the atoms in a spatial representation of a molecule. *Example:* the H–C–H bond angle in methane is 109°.

BOND ENERGY.   The energy required to separate the two participating atoms of a chemical bond to an infinite distance.

BROMOSILANE.   A bromine derivative of a silane; a compound of silicon containing at least one silicon–bromine bond.

CARBIDE.   A binary compound of carbon and some other element.

CARRIER.   As used here, a substance which facilitates a reaction by undergoing a cycle of changes, thereby transferring one reactant to another and reducing the activation energy otherwise required for the reaction.

CATALYST.   A substance which facilitates a chemical reaction without undergoing permanent change; a substance which by some chemical or physical mechanism reduces the activation energy for a reaction.

CERAMIC.   Pertaining to the art of making pottery, glass, porcelain, and similar products ordinarily composed of inorganic silicate materials.

CHELATE.   Literally, resembling the claw of a crab; a term used to describe heterocyclic molecular structures, usually those formed by attachment of

both ends of a chain to the same atom, as in beryllium acetylacetonate,

$$H_3C—C—O \qquad O—C—CH_3$$

$$CH \qquad Be \qquad CH$$

$$H_3C—C{=}O \qquad O{=}C—CH_3$$
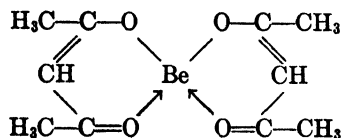
Chelate structures commonly are formed by certain dyes which are held in place by metallic atoms on the surface being dyed.

CHLOROSILANE. A chlorine derivative of a silane; a compound containing at least one silicon–chlorine bond.

COCONDENSATION. An intermolecular condensation between two or more different species of reacting molecules, resulting in a copolymer.

CONDENSATION. The process of reducing to a smaller compass, as in condensing a gas or vapor to a liquid; as used herein, the process of combining two or more relatively simple molecules into a more complex molecule by splitting out the elements of water or similarly volatile material. CONDENSATION POLYMER. A polymer derived by splitting out the elements of water (or of ammonia, and so on) from reacting substances, as in

$$2R_2Si(OH)_2 = HO—SiR_2—O—SiR_2—OH + H_2O \qquad etc.$$
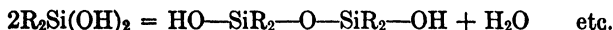
CONDUCTANCE. The current in amperes which will flow through a given system under a pressure of one volt.

CONDUCTIVITY OR SPECIFIC CONDUCTANCE. The quantity of electricity transferred through a unit cube of the substance per unit time per unit of potential difference.

CO-ORDINATION. The formation of a co-ordinate covalent bond, that is, the formation of a chemical bond in which both the shared electrons come from one of the participating atoms, hence a bond of some polarity; chemical linkage of the type illustrated by the formation of hydrates, ammonates, chelate compounds.

COPOLYMER. A compound in which two or more different unit structures are repeated at random throughout the body of the molecule; usually, a high polymer composed of large numbers of two or more different but chemically related groups joined together at random, giving a compound with properties different from those of a mere mixture of the separately polymerized constituents.

CORNEA. The transparent covering over the iris and lens of the eyeball.

COVALENT. That type of chemical binding in which the electron systems of the participating atoms merge without complete transfer of charge from one atom to another; employing one or more shared pair bonds; opposite of electrovalent.

CRACKING GASES. The mixed hydrocarbon gases, many of them unsaturated, which are obtained from the thermal dissociation of larger hydrocarbon molecules during the refining of petroleum.

CROSS-LINKED. Having a molecular structure consisting of chains joined together by bridges or cross links which limit the freedom of motion.

CUPRIC. Pertaining to copper combined in the divalent state or in the form of the doubly charged ion Cu^{++}.

CYCLIC. Arranged in a closed ring rather than an open chain.

DEHYDRATE. To remove water or the elements of water from a substance; to drive off or extract combined or " bound " water from a substance.

DEHYDROCHLORINATION. A reaction in which hydrogen and chlorine are split out from a chlorinated organic compound in the form of hydrogen chloride. Various agents accelerate the removal by absorbing the hydrogen chloride as it is formed.

DERIVATIVE. A compound obtained from a parent substance by chemical change such as the attachment of a new atom or group.

DEW POINT. The temperature of a surface upon which atmospheric moisture first begins to condense; the temperature at which a gas is saturated by a given amount of water vapor.

DICHLOROSILANE. The compound H_2SiCl_2; in general, a silane in which two hydrogen atoms have been replaced by chlorine atoms.

DIELECTRIC. A nonconductor of electricity.

DIELECTRIC CONSTANT. The capacitance of a system of conductors and dielectric material referred to the capacitance of the same system with air or vacuum as dielectric, hence a measure of the recoverable energy stored within the dielectric material.

DIELECTRIC STRENGTH. The electric stress, measured in volts, at which a given thickness of dielectric material breaks down and is punctured by an electric discharge.

DIFUNCTIONAL. In a polymer-producing reaction, the term applied to a reactant possessing two functional groups in its structure, hence capable of propagating a chain and forming a linear polymer. *Example:*

$$-SiR_2-OH + \underline{R_2Si(OH)_2} = -SiR_2-O-SiR_2-OH.$$

DIMER. A compound existing in the form of a double molecule composed of two identical units linked together.

DISILANE. The compound Si_2H_6, second in the homologous series of silanes.

DISPROPORTIONATION. That type of chemical reaction in which some molecules of a single compound are oxidized and other molecules are reduced; a reaction of the type $2A = B + C$, where B and C differ in degree of saturation or oxidation.

DISSOCIATION. The separation of a molecule into fragments, atomic or ionic or otherwise, under the influence of heat, electric energy, or solvent medium.

ELECTROPOSITIVE. Having or capable of assuming a positive coulombic charge; a condition of electric charge associated with a loss of electrons or a surplus of positive over negative unit charges.

ELECTROVALENT. That type of chemical linkage in which elements are bound by the coulombic force between ions of opposite charge; ionized; the opposite of covalent.

ELEMENT. A substance which cannot be subdivided under the conditions of ordinary chemical reactions; a substance in which all the atoms have the same chemical properties.

ELEMENTARY. Existing as an element rather than in the form of a compound.

ELASTOMER. A term used to distinguish a polymer which is elastic or rubber-like from one which is plastic or rigid.

EQUIVALENT. The combining weight of a reactant taken in grams; the reacting weight of a substance as indicated by the equation for the particular reaction desired; a stoichimetric proportion.

ESTER. A compound formed from an alcohol and an oxyacid by elimination of water; here used specifically in the sense of an alkoxy- or aroxysilane, such as may be considered to result from the combination of an alcohol with the hypothetical silicic acids; a compound comprising the structure SiOR' where R' is an organic group.

ETHYL. The —C_2H_5 group, second of the homologous series of saturated aliphatic radicals of the type C_nH_{2n+1}.

ETHYNYL. The —C≡CH group, derived from acetylene.

EXTRAPOLATE. To extend the results of a study beyond the limits within which that study was conducted; to apply to a new set of conditions a conclusion determined under a more restrictive set of conditions; to extend a graph beyond the known points used in plotting that graph.

FERRIC. Pertaining to iron combined in the trivalent state or in the form of the triply charged ion Fe^{+++}.

FERROSILICON. An alloy containing principally iron and silicon, usually derived by a blast-furnace or electrothermal reduction of an ore containing the oxides of iron and silicon.

FLAMEPROOF. Incapable of burning with a continuous flame in air.

FLUOROSILANE. A fluorine derivative of a silane; a compound of silicon (other than fluosilicic acid or a fluosilicate) containing at least one silicon-fluorine linkage.

FLUOSILICATE. A salt of fluosilicic acid; a compound of the anion $SiF_6^=$.

FREE RADICAL. A group or radical existing momentarily by itself, rather than in combination as part of a molecule.

GEL. A glutinous semisolid mass resulting from coagulation of a colloidal liquid; in polymer chemistry, a somewhat elastic but not plastic mass.

GLYCOL. Ethylene glycol, HO—CH_2—CH_2—OH; also a general term for dihydric alcohols, that is, dihydroxy derivatives of the aliphatic hydrocarbons.

GRIGNARD REACTION. The reaction of metallic magnesium with a suitable organic halide to form an organomagnesium halide or Grignard reagent;

also, the metathetical reaction of a Grignard reagent with some reactive substance, as in the reaction with water:

$$RMgX + HOH = RH + Mg(OH)X$$
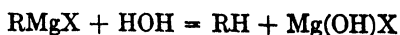
GRIGNARD REAGENT. An organomagnesium halide of the type RMgX, where R is any organic group incapable of reacting with the reagent and X is a halogen. The reagent is a true organometallic compound; that is, the organic group is linked directly to the metal by a carbon–magnesium bond. Such substances were first prepared as separate entities and used as reagents for synthesis by Victor Grignard in 1901.

GROUP. See RADICAL.

HALOGEN. An element of Group 7*B* in the short-period representation of the periodic system; an element of the group consisting of fluorine, chlorine, bromine, iodine, and element 85.

HALOSILANE. A halogen derivative of a silane; a compound of silicon containing at least one Si—X bond, where X represents a halogen.

HEMOLYSIS. The process of setting free the hemoglobin of blood by rupture or dissolution of the membrane covering the red corpuscles.

HEXACOVALENT. Given to combination with six atoms or groups, the bonds being of a covalent or nonionized character.

HEXAMER. A molecule consisting of six identical units linked together; a polymer in which the only molecular species is a compound of six monomeric units.

HOMOLOG. A compound forming part of a homologous series, and hence closely related to the other compounds in that series in structure, composition, and physical properties.

HOMOLOGY. The relation between compounds of similar structure and composition in a series, each differing from the last by a constant increment in formula.

HYDRATION. The chemical attachment of water molecules to a molecule, ion, or atom; the co-ordination of water molecules to a covalently unsaturated acceptor.

HYDRIDE. A binary compound of hydrogen with some other element.

HYDROCARBON. A binary compound of carbon and hydrogen; a general term which includes the paraffin, olefin, aromatic, and all other series of hydrides of carbon.

HYDROGENATION. The process of causing chemical combination with hydrogen; the chemical addition of hydrogen to an element or compound.

HYDROLYSIS. The reaction of a substance with water; a metathetical reaction involving water and producing substances containing fragments of the water molecule in their composition.

HYDROPHYLIC. Literally, fond of water; capable of being wet by water, not water-repellent.

HYDROPHOBIC. Literally, afraid of water; water-repellent; incapable of being wet by water.

HYDROXYL GROUP. The —OH radical, common to alcohols and water and responsible for their similarities of behavior.

INTERFACE. The boundary between two phases, such as the meniscus between liquid water and water vapor or the boundary between oil and water.

INTERMEDIATE. A reactive compound containing an essential grouping which, by further processing or reaction, is conveyed to the finished pr*duct; here, a reactive organosilicon compound of relatively simple structure which is used in the preparation of organosilicon polymers.

INTERMOLECULAR CONDENSATION. A condensation reaction which occurs between separate molecules, resulting in their union (hence a process of accretion to form polymers). See example under CONDENSATION.

INTRAMOLECULAR CONDENSATION. A condensation reaction which occurs within a single molecule (hence a process of dehydration, deammonation, and so forth, resulting in a decrease of molecular weight). *Example:*
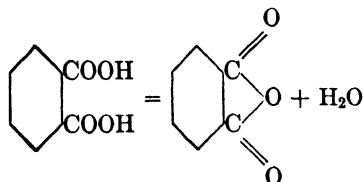
ION. An atom or group of atoms bearing an electric charge through surplus or deficiency of electrons, and hence capable of entering into electrovalent binding with one or more ions of opposite charge.

ISOCYANATE A compound of the isocyanate group, —N=C=O, as distinguished from a cyanate, which contains the grouping —O—C≡N.

KCAL. Abbreviation for kilogram-calorie, the heat required to raise the temperature of one kilogram of water one degree centigrade.

LABILE. Unstable, ephemeral, easily decomposed under ordinary conditions.

LATTICE. The geometric arrangement of the atoms in a crystal.

LINEAR POLYMER. A polymer derived from monofunctional and bifunctional units, and hence consisting of straight-chain or coiled-linear molecules rather than a cross-linked or three-dimensional network.

LINK OR LINKAGE. See BOND.

LOSS FACTOR. As used in dielectric measurements, a factor proportional to conductance per cycle, and hence a measure of the total energy dissipated as heat per unit volume of the dielectric.

MACROCOMBUSTION. A quantitative analysis conducted by burning 0.1 to 5 g. or more of sample, followed by absorption and weighing of the products of combustion. Macrocombustion is distinguished from the newer microcombustion only in the size of the sample and the apparatus used.

MAXIMUM COVALENCY. The maximum number of monovalent atoms or groups with which an element will enter into covalent combination; in the theory of maximum covalency proposed by Sidgwick, a maximum number of possible covalent linkages governed by the position of the element in the periodic system, being two for hydrogen, four for the elements in the first short period, six for the elements in the second short period, and eight or more for the heavier elements.

METAL ALKYL. A compound of a metal with directly linked aliphatic or aromatic hydrocarbon radicals, as in zinc dimethyl, $Zn(CH_3)_2$, or mercury diphenyl, $Hg(C_6H_5)_2$. A " normal " alkyl has sufficient organic groups to satisfy the " normal " valence of the metal and therefore contains no halogen or other substituent in place of organic radicals.

METALLOID. An element of metallic appearance but poor electric conductivity, such as boron or silicon or germanium. Chemically, the metalloids are not so strongly electropositive as the metals and tend principally toward covalent bonding.

METATHESIS. A reaction of the type $AB + CD = AD + CB$ involving an exchange of radicals or ions.

METATHETICAL REACTION. A reaction involving only metathesis, as distinguished from an oxidation-reduction reaction or a condensation reaction.

METHYL. The $—CH_3$ group, first of the homologous series of saturated aliphatic radicals of the type C_nH_{2n+1}.

METHYLATION. The chemical attachment of methyl groups to a structure, usually in place of hydrogen or halogen or alkoxy groups.

METHYLENE. The $—CH_2—$ group or radical.

MIL. One thousandth of an inch.

MIXED ALKYL. A metal alkyl in which the organic groups are not all the same, as in $CH_3(C_2H_5)(C_3H_7)(C_6H_5)Si$.

MOBILE. Capable of easy motion or flow, as in a liquid of low viscosity.

MOLE. A gram-molecular weight of a substance; the atomic or molecular weight of an element or compound taken in grams or pounds, as indicated.

MOLAR. In the proportion of one mole; per gram-molecular weight.

MONOCHLOROSILANE. The compound H_3SiCl; in general, a compound of silicon containing only one silicon–chlorine bond.

MONOFUNCTIONAL. In a polymer-producing reaction, the term applied to a reactant possessing only one functional group, hence capable only of ending a chain. *Example:*

$$—SiR_2—OH + \underline{R_3SiOH} = —SiR_2—O—SiR_3 + H_2O$$
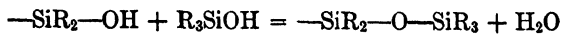
MONOMERIC. Existing in the form of single molecules of weight corresponding to the formula weight; unpolymerized.

MONOMOLECULAR. Pertaining to a property or dimension of a single molecule; comprising a single layer of molecules of a substance. Monomolecular film: a film just one molecule thick spread over a surface or interface, and usually completely covering that interface.

MONOSILANE. SiH_4, the simplest normal hydride of silicon.

MONOVALENT. Capable of combining with one atom of hydrogen, or one atom of chlorine, or their equivalent.

NASCENT. Literally, at the moment of being born; a term applied to gases which ordinarily are diatomic but are briefly monatomic (and hence more reactive) at the moment they are liberated during a chemical reaction.

NUCLEAR. Pertaining to the central core or nucleus of the atom, which always carries a positive charge and in the neutral atom is matched by an equal negative charge in the form of the appropriate number of electrons.

OLEFIN. An unsaturated hydrocarbon of the type C_nH_{2n}, as represented by ethylene, H_2C=CH_2.

ORGANOMETALLIC. Pertaining to a compound of an organic group with a metal in which the organic group is linked directly to the metal atom.

ORGANOSILICON. Pertaining to a compound of silicon with an organic group or groups, in which the two are united by a carbon–silicon bond or bonds (as distinguished from ester).

ORGANOSILOXANE. A siloxane in which organic groups are linked directly to one or more of the silicon atoms by carbon–silicon bonds, as in hexamethyl-disiloxane, $(CH_3)_3Si$—O—$Si(CH_3)_3$.

ORTHOCARBONATE. A derivative of the hypothetical orthocarbonic acid, as ethyl orthocarbonate, $C(OC_2H_5)_4$. The common inorganic carbonates are metacarbonates, derived from metacarbonic acid, H_2CO_3.

ORTHOSILICATE. A compound of orthosilicic acid, q.v.

ORTHOSILICIC ACID. The hypothetical compound $Si(OH)_4$ or H_4SiO_4, known only in the form of its salts and its organic esters.

OXIDATION. Broadly, the removal of electrons from an atom or ion, which thereby increases its charge positivewise; in a more limited sense, the chemical combination of oxygen with a substance.

PENTAMER. A molecule consisting of five identical units linked together; a polymer in which the only molecular species is a compound of five monomeric units.

PERIOD. A single sequence of elements whose atomic numbers lie between those of two successive rare gases; in the periodic system, a sequence of elements starting with an element in group O and ending at the next element in group O; in the long-period representation of the periodic table, a single horizontal row.

PERIODIC SYSTEM. The orderly arrangement of the elements in the sequence of their atomic numbers, and in groups according to their atomic structure; the arrangement of elements in groups according to their chemical behavior, as first proposed by Mendeleef in 1869.

PERIODIC TABLE. See PERIODIC SYSTEM.

PHASE. A material of homogeneous composition separated from other phases by surfaces; in a heterogeneous system, a solid, liquid, or gaseous substance which remains separated from the other phases. Different crystals

of the same substance and different particles of the same liquid (as in an emulsion) are considered to be all of the same phase.

PHENOL. Monohydroxybenzene, C_6H_5OH; also a general term for hydroxy derivatives of the aromatic hydrocarbons.

PHENYL. The cyclic —C_6H_5 group derived from benzene; the simplest aryl radical.

PLASTICITY. The degree to which a substance can permanently be deformed by the application of pressure, usually at a given temperature.

PLATEN. A flat plate of metal which transmits the pressure of a hydraulic press to the object being pressed.

POLYBASIC. Possessing more than one acidic or base-reactive group within its structure, as in phthallic acid, $C_6H_4(COOH)_2$, a dibasic acid.

POLYCONDENSATION. A condensation reaction which yields a polymeric substance as one of the products. See CONDENSATION, POLYESTER.

POLYESTER. A condensation polymer formed by the reaction between a polyhydric alcohol and a polybasic acid, as the polymeric product resulting from the reaction of glycerol and phthallic acid or anhydride.

POLYHYDRIC. Possessing more than one hydroxy group in its structure, as in ethylene glycol, $HO—CH_2—CH_2—OH$, a polyhydric alcohol.

POLYMER. A chemical compound in which some relatively simple unit structure or group is repeated throughout the body of the molecule; a compound in which a number of identical atoms or groups are united by covalent bonds. HIGH POLYMER. a polymer of very high molecular weight, consisting of a large number of identical units and therefore having a molecular weight measured in thousands or millions.

POLYMERIC. Existing in the form of some multiple of the simple formula weight.

POWER FACTOR. As used in dielectric measurements, the cosine of the angle whose tangent is the ratio of loss factor to dielectric constant, and hence a measure of both stored and dissipated energy within the dielectric medium.

PROPYL. The —C_3H_7 group, third in the homologous series of saturated aliphatic radicals of the type C_nH_{2n+1}.

PROSILOXANE. The monomeric compound H_2SiO or polymers of it; a compound composed entirely of multiples of the unit structure $—\overset{\displaystyle H}{\underset{\displaystyle H}{Si}}—O—$.

PYROLYSIS. One type of thermal dissociation; a reaction in which complex molecules (as of a heavy petroleum hydrocarbon) split into relatively simple fragments under the application of heat.

RADICAL. A group of atoms which reacts as a unit; an electrically neutral grouping of elements linked to or capable of uniting with some other atom or group by one or more covalent bonds.

REDISTRIBUTION. A random rearrangement of atoms or groups about a central atom; a statistical distribution of two or more substituents such as

would obtain if all the substituents were removed and then replaced on the central atoms in purely random fashion.

REDUCING AGENT. A reagent which accomplishes chemical reduction of some other substance by undergoing a reaction in which it itself is oxidized to a higher state of valency; an element or compound capable of giving up electrons under the conditions of a particular reaction.

REDUCTION. Broadly, the addition of electrons to an ion or atom, which thereby reduces its charge positivewise; in a more limited sense, the removal of oxygen from an oxide by chemical or electrochemical methods.

REFRACTORY. Capable of being heated without thermal dissociation or fusion; chemically and physically stable at high temperatures.

RESIN. A natural or synthetic substance, usually organic in composition, characterized by being amorphous, isotropic, plastic, often sticky, and usually fusible and soluble at some stage in its manufacture or processing.

RESISTIVITY. The reciprocal of conductivity; the electric pressure required to secure unit flow of electric charge through a unit cube of the substance in unit time.

SATURATED. Chemically combined to the limit of the most commonly exhibited valence; containing no double or triple bonds (organic); incapable of further chemical combination (classical); broadly, combined with other atoms or molecules to the limit expressed by the theory of maximum covalency.

SHARED-PAIR LINK. That type of chemical binding in which the electron systems of the participating atoms merge without complete transfer of charge from one atom to another; a covalent or un-ionized bond; the opposite of ionic bond.

SHTETTER SYNTHESIS. The process of forming chloroalkyl compounds of silicon by absorbing unsaturated hydrocarbons in silicon tetrachloride under pressure and with the aid of metallic chlorides or oxychlorides as catalysts. The method was patented by I. I. Shtetter in 1935.

SILANE. The name given to a hydride of silicon of the type Si_nH_{2n+2}, or a derivative thereof.

SILANEDIOL. A dihydroxy derivative of a silane; a compound of silicon containing two hydroxyl groups attached to the same silicon atom, as in diphenylsilanediol, $(C_6H_5)_2Si(OH)_2$

SILANETRIOL. A compound of silicon in which three hydroxyl groups are bonded to the same silicon atom; a compound containing the structure $-Si(OH)_3$.

SILANOL. A monohydroxy derivative of a silane; a compound of silicon containing a single Si—OH bond.

SILAZINE. A nitrogen derivative of a silane, as disilazine, $H_3Si-NH-SiH_3$.

SILICA. The general name for all the crystalline and amorphous forms of silicon dioxide, SiO_2.

SILICANE. See SILANE.

SILICATE. A derivative of one of the silicic acids, usually orthosilicic acid, $Si(OH)_4$. Two important classes of silicates are the metallic silicates (such as magnesium silicate, Mg_2SiO_4) and the orthosilicate esters [such as ethyl silicate, $Si(OC_2H_5)_4$].

SILICIC ACID. Any oxyacid of silicon, such as orthosilicic acid, H_4SiO_4, metasilicic acid, H_2SiO_3. These substances are hypothetical compounds inferred from their metallic or organic derivatives.

SILICIDE. A binary compound of silicon with some other element.

SILICOCHLOROFORM. $SiHCl_3$, trichlorosilane, so called by analogy to chloroform, $CHCl_3$, trichloromethane.

SILICOETHER. See ESTER; ORTHOSILICATE.

SILICOL. A hydroxyl derivative of a silane; a compound containing at least one Si—OH bond.

SILICON. Element 14 in the periodic system; the second element in the fourth group of Mendeleef's table, placed between carbon and germanium in that group and between aluminum and phosphorus in the second period; a grayish metallic-looking substance melting at 1420° C., boiling at 2,600° C., and with atomic weight of 28.06.

SILICONE. A polymeric organosiloxane composed of multiples of the structure

$$-\overset{\displaystyle R}{\underset{\displaystyle R}{\overset{\displaystyle |}{\underset{\displaystyle |}{Si}}}}-O-$$
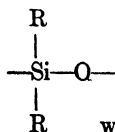
where R is a hydrocarbon radical,

or derived therefrom by substitution of oxygen for a portion of the organic groups; a polymeric organosilicon oxide.

SILICONIC ACID. A hypothetical compound of silicon analogous to a carboxylic acid, that is, of the type $RSi\overset{O}{\overset{\nearrow}{—}}OH$. Substances of this composition have been shown to be polymeric in structure rather than a monomeric "acid," however.

SILICOSIS. The disease resulting from the inhalation of flint or quartz dust, and apparently due to the irritating action of those particles on the lung tissue. It is an incapacitating disease and predisposes the victim to pulmonary tuberculosis.

SILOXANE. A compound of silicon distinguished by an arrangement of alternate silicon and oxygen atoms, as in disiloxane, H_3Si—O—SiH_3; trisiloxane, H_3Si—O—SiH_2—O—SiH_3; tetrasiloxane, H_3Si—O—SiH_2—O—SiH_2—O—SiH_3.

SILOXANE CHAIN OR NETWORK. A chain or network of alternate silicon and oxygen atoms.

SILYL. The term used to designate the —SiH_3 group or a derivative thereof, as the trimethylsilyl group, —$Si(CH_3)_3$.

SLUDGING. The process by which a hydrocarbon oil deposits sludge or precipitate as a result of chemical changes taking place within the oil.

STERIC STRAIN. The strain imposed on a molecular structure by the juxtaposition of two or more large groups about a relatively small central group. Up to a point, the lack of sufficient space to accommodate an added group causes strain; beyond that point, the markedly inadequate space prevents attachment of the group at all and the effect is called steric hindrance.

SUBGROUP. A subdivision of a vertical group in the periodic system of the elements, made necessary in order to group together similar elements in the short-period representation. The long-period table has no subgroups.

SUBSTITUENT. A group or an atom which has replaced some other group or atom in a parent compound, as chlorine replacing hydrogen in monochlorosilane, SiH_3Cl.

SUBSTRATE. The layer below; *biol.:* a substance which is acted upon by an organism or enzyme and which furnishes the nutrient or material for that action; *chem.:* a substance which is acted upon at the surface by a corrosive or reactive external phase.

SYNTHETIC. Derived by chemical methods purposely directed to that end, as distinguished from naturally occurring or natural.

TETRACOVALENT. Given to combination with four atoms or radicals, the bonds being of a covalent or nonionized character.

TETRAFUNCTIONAL In a polymer-producing reaction, the term applied to a reactant possessing four functional groups and therefore capable of establishing four links to other parts of the polymeric structure. *Example:*

$$—SiR_2—OH + \underline{Si(OH)_4} = —SiR_2—O—\underset{\underset{|}{O}}{\overset{\overset{|}{O}}{Si}}—OH$$
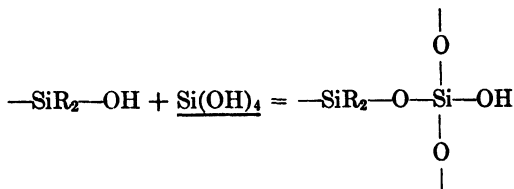
TETRAHEDRON. A geometrical solid form bounded by four plane surfaces; in the stereochemistry of carbon and silicon, the tetrahedral figure represented by the tetravalent central atom and the four valence bonds directed at an angle of 109° 28' to one another.

TETRAMER. A molecule consisting of four identical units linked together, as in octamethylcyclotetrasiloxane, $[(CH_3)_2SiO]_4$, the cyclic tetramer of methyl silicone.

THEORETICAL YIELD. The yield predicted by stoichiometry, that is, the maximum weight of product obtainable from a reaction as indicated by the relation of combining weights in the equation for the reaction.

THERMAL DISSOCIATION. The process of splitting into elements or simpler molecular fragments due to thermal agitation at elevated temperatures.

THERMAL STABILITY. The degree to which a compound resists dissociation or other chemical alteration at elevated temperatures. Magnesium oxide is stable up to its melting point (2800° C.) and beyond, and hence is considered to have high thermal stability; calcium bicarbonate decomposes at 100° to carbon dioxide, water, and calcium carbonate, and hence is thermally unstable. As used in the text, the term indicates chemical integrity up to a designated temperature.

THERMOPLASTIC. Capable of plastic flow or permanent deformation under load when heated; capable of softening repeatedly upon warming.

TOLYL. The methyl-substituted phenyl group, $-C_6H_4-CH_3$.

TRICHLOROSILANE. The compound $HSiCl_3$, sometimes called silicochloroform; in general, a silane in which three hydrogen atoms have been replaced by chlorine atoms.

TRIFUNCTIONAL. In a polymer-producing reaction, the term applied to a reactant possessing three functional groups in its structure, hence capable of propagating a chain and cross-linking it to other chains. *Example:*

$$-SiR_2-OH + \underline{RSi(OH)_3} = -SiR_2-O-SiR-OH$$
$$|$$
$$O$$
$$|$$
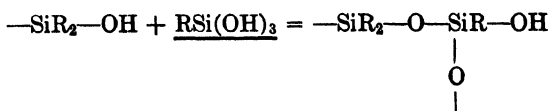
TRIMER. A molecule consisting of three identical units linked together, as in hexamethylcyclotrisiloxane,
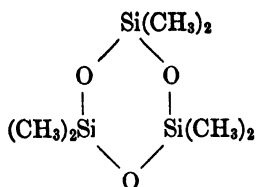
TRIMETHYLSILYL. The $-Si(CH_3)_3$ group, considered to be derived from the silyl group, $-SiH_3$, by complete substitution with methyl groups.

TRISILANE. The compound Si_3H_8, third in the homologous series of silanes.

ULTIMATE ANALYSIS. A quantitative chemical analysis in which the results are expressed entirely in terms of the elements present, as per cent carbon and per cent hydrogen in a hydrocarbon.

UNSATURATED. Capable of further chemical combination; the opposite of saturated, *q.v.*

VINYL. The $-CH{=}CH_2$ group, first in the homologous series of olefinic radicals containing one double bond.

VISCOSITY. That property of a fluid which determines the rate of flow under a given force.

VOLATILE. Capable of relatively rapid evaporation under ordinary conditions, as into an evacuated space at room temperature; capable of exerting an appreciable vapor pressure under the conditions of observation.

WURTZ SYNTHESIS. The condensation reaction between two halides brought about by the action of metallic sodium, as in

$$4C_6H_5Cl + SiCl_4 + 8Na = Si(C_6H_5)_4 + 8NaCl$$