# *Cover Essay*

Dimethyldichlorosilane and the Direct Synthesis of Methylchlorosilanes. The Key to the Silicones Industry[†]

When on May 10, 1940, in the Research Laboratory of the General Electric Company in Schenectady, NY, Eugene G. Rochow carried out an experiment in which he passed gaseous methyl chloride through a crushed 50% Cu−Si mixture (previously activated with gaseous HCl) in a tube furnace at 370 °C and obtained as products a mixture of methylchlorosilanes (among them $(CH_3)_2SiCl_2$, our cover molecule), he planted the proverbial acorn from which grew the proverbial mighty oak, the modern silicones industry.

Before we consider this important reaction and its far-reaching consequences in detail, it is useful to go back in time, more than 175 years, to provide the necessary introduction—the work of earlier chemists that led, finally, to this reaction which we can write in oversimplified form in eq 1.

$$2CH_3Cl(g) + Si/Cu(s) \rightarrow (CH_3)_2SiCl_2(l) \qquad (1)$$
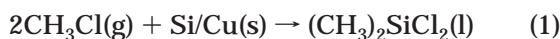
The reaction requires elemental silicon, and this is where our story begins. The most abundant elements in the earth's crust are oxygen (49.5%) and silicon (25.7%). However, there is no *free* silicon in the earth's crust: it is all very firmly bound to oxygen in the form of silica and metal silicates. Because of the high Si−O bond strength of 108 kcal/mol, it is not easy to force silicon out of its oxygen connection and for this reason, despite its high abundance, *elemental* silicon is a relative newcomer to the chemical scene.[1] It was not until 1824 that Jöns Jakob Berzelius prepared silicon as an amorphous brown solid.[2] Friedrich Wöhler was a student of Berzelius when this work was carried out (Nov 1823−Sept 1824) and in later years reported on that time:[3]

"Silicon, without doubt, is one of the most remarkable elements of our planet because it is one of the main substances which has served in its formation. It, therefore, is well worth the effort of determining its properties as completely as possible. As known, it first was prepared and isolated by Berzelius in 1824 by the decomposition of gaseous fluorosilicic acid or of potassium fluorosilicate by potassium. [The latter reaction is: $K_2SiF_6 + 4K \rightarrow Si + 6KF$.]

It was my good fortune to be his student at this time when he was engaged in these instructive investigations and to help him by preparing the required potassium...Berzelius examined and described all of the characteristic properties of this silicon with his usual keenness and precision. However, he obtained it only in amorphous form, as a dull, brown powder. He commented repeatedly how interesting it would be to become acquainted with this material in a dense and crystalline state."[4]

An 1846 chemistry text on my bookshelf[5] describes the Berzelius preparation of amorphous silicon:

"To prepare silicon, (there) is selected...the double fluoride of silicon and potassium ($2SiF_3 + 2KF$), which is a white powder...; a quantity of this substance is to be mixed with nearly its own weight of potassium, cut into little bits, and placed in an iron cylinder, or in a tube of hard glass, which may be held over the flame of a spirit-lamp. As soon as the bottom of the tube has been heated to redness, vivid ignition occurs by the decomposition, which spreads with little need of external heat, throughout the entire mass; when cool, the residual brown matter is to be washed carefully with water: fluoride of potassium dissolves, and the silicon remains behind. The silicon so obtained is a dull brown powder, which, when heated in air or in oxygen, takes fire and burns, forming silicic acid"

Today this reaction would be called a "self-propagating, high-temperature synthesis."

It was only in 1854 that crystalline silicon was first reported by Henri-Étienne Sainte-Claire Deville, who

[†] Dedicated to Eugene G. Rochow on the occasion of his 92nd birthday, October 4, 2001, with respect, admiration, and affection.

(1) A detailed, fully referenced account of the early attempts to isolate elemental silicon and of the various successful preparations, starting with that of Berzelius in 1824, can be found in: *Gmelin Handbook of Inorganic Chemistry*, 8th ed.; Springer-Verlag: New York, 1984; Si, Silicon, Part A1, History, pp 7−50.

(2) Berzelius, J. J. *Ann. Phys. Chem.* [2] **1824**, *1*, 169. (Berzelius (1779−1848), 50 years a professor at Stockholm. He originated the present day symbols of the elements and their use in the formulas of compounds. Pioneer in the determination of atomic weights. Proposer and champion of a dualistic or electrochemical theory and of the "radical" theory. Discovered ceria, selenium, silicon, and thorium. His textbook and annual reports on the progress of chemistry (*Jahresberichte*) were very influential.)

(3) Wöhler, F. *Ann.* **1856**, *97*, 266. (Wöhler (1800−1882), student of Gmelin and Berzelius, professor at Göttingen. Remembered today mainly for his conversion of ammonium cyanate to urea in 1828, which demolished the theory of a "vital force" responsible for the formation of organic compounds and ended the strict separation between inorganic and organic chemistry. Isolated aluminum, beryllium, calcium carbide, siloxene from calcium silicide, trichlorosilane and other inorganic silicon compounds, impure titanium, organic compounds such as hydroquinone. With Liebig, proposed the concept of the benzoyl "radical" from which grew the short-lived radical theory.)

(4) This "amorphous" silicon should not be confused with today's "amorphous hydrogenated silicon." Actually, the brown "amorphous" silicon prepared by the procedure of Berzelius, which visually appears amorphous, even in the microscope under 1000× magnification, is not amorphous (or not completely so), since X-ray diagrams showed a diamond lattice: Manchot, W. *Z. Anorg. Allg. Chem.* **1922**, *124*, 333; **1922**, *120*, 277.

(5) Kane, R. *Elements of Chemistry*; American edition by Draper, J. W.; Harper and Brothers: New York, 1846; p 321.

isolated it from aluminum melts in which it was present as an impurity (sometimes up to 10%) by treating the melt with hot hydrochloric acid.[6] The first report of the reduction of silica by carbon at high temperatures was that of Henri Moissan,[7] and it is this process (eq 2),

$$SiO_2 + 2C \rightarrow Si + 2CO \qquad (2)$$
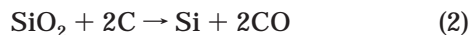
carried out in an electric furnace using graphite electrodes at 3000 °C, which has served, since the beginning of the last century, for the large-scale production of silicon.[8] When pure, white quartzite rock and a pure form of carbon are used, material of ~98% purity is obtained. Crystalline silicon is a covalent, nonmetallic solid with a diamond lattice, density 2.33 g/cm^3, and mp 1414 °C. The commercial silicon has a shiny, blue-gray, metallic appearance. As Wöhler had noted,[3] silicon "without doubt is one of the most remarkable elements." In addition to its long-established applications as a component in useful ferrous alloys and in aluminum and magnesium alloys, there are the more "modern" ones, based on ultrapure silicon—in the preparation of semiconductors (the "chip revolution") and the fabrication of solar cells. Now there are even are light-emitting forms of silicon (porous silicon). However, we are concerned here with elemental silicon *as a reactant*, and there are some reactions of elemental silicon worthy of note, as well as some chemistry of silicon compounds, which require discussion before we return to eq 1.

The first chlorosilane, SiCl$_4$, was obtained by Berzelius in 1824 when he found that his amorphous silicon ignited when heated in a stream of chlorine and was completely consumed. More relevant to the subject of this essay is Buff and Wöhler's reaction of crystalline silicon (for whose preparation Wöhler had developed an improved procedure[3,9]) with anhydrous, gaseous hydrogen chloride.[10] This reaction was carried out by passing the HCl through a long glass tube in which the silicon was spread out throughout its length and which was surrounded by glowing coals (no tube furnaces with temperature controllers in those days). A U-tube connected to the exit of the reaction tube, cooled with an ice–salt mixture, served to condense the volatile products. Any volatiles not trapped in the U-tube were passed into a large volume of water, in which a large amount of white solid was formed during the reaction. The condensed liquid usually was turbid and appeared to be a mixture of several products. Temperature control, difficult under these circumstances, was important. (At red heat, SiCl$_4$ was by far the major product.) Distillation of the contents of the U-trap gave as the major product a colorless liquid boiling at 40–43 °C which had an irritating smell and fumed strongly in air. Its vapors were found to ignite as readily as those of

ether, burning with a weak, luminous, green flame and releasing a smoke of silica and HCl. Pyrolysis of a sample of the distillate in a glowing glass tube gave brown amorphous silicon (a reaction used about one hundred years later, with pure material and under more controlled conditions, to produce highly pure, crystalline silicon). Hydrolysis of the distillate proceeded vigorously and exothermically, giving HCl and a solid silicon oxide different in appearance from SiO$_2$. Analysis of the distillate proved to be difficult because of its volatility, poor thermal stability, and great moisture sensitivity. The product, of course, was trichlorosilane, HSiCl$_3$, a compound of technological importance today in the silicones industry and in silicon-based material science. What Wöhler called "fractional" distillation was a simple one-plate distillation, and it was not sufficient to effect good separation from HSiCl$_3$ of the SiCl$_4$ also produced. Also, the cold trap was not very efficient, as indicated by the formation of a large amount of white solid when the exit gas was passed into water. The elemental analyses of the distillate consequently were high in Cl and low in Si. Wöhler wrote the formula [Si$_2$Cl$_3$ + 2 HCl] for the HCl + Si reaction product (the atomic weight of Si was 14, not 28, in those days). A few years later, for reasons not germane to this discussion, Wöhler doubled the formula to Si$_6$Cl$_{10}$H$_4$ but admitted that, because of the problem of its purity, the constitution of the HCl + Si product remained unsettled. Wöhler was taken to task by Friedel and Ladenburg 10 years later.[11] How could he, they asked, assign a formula of Si$_6$Cl$_{10}$H$_4$ to a compound of reported bp 42 °C when SiCl$_4$ boiled at 59 °C? On the basis of the tetraatomicity of silicon, the expected formula was SiCl$_3$H, and Friedel and Ladenburg proceeded to prove this by very careful isolation and characterization studies.

Relevant to the main subject of this essay is that later workers found that some metal silicides (those of Mg, Fe, V, and Cu) also reacted with gaseous HCl to produce HSiCl$_3$. The use of a commercial copper silicide (20 parts of Cu to 100 of Si) by Combes is noteworthy.[12] A reaction temperature of 300 °C gave HSiCl$_3$ in high yield; higher temperatures favored formation of SiCl$_4$. Later work by Ruff and Albert showed copper silicide to be the most effective of the metal silicides examined.[13]

We shall return to reactions of elemental silicon, but it is instructive to consider first the birth and early development of organosilicon chemistry. The first known organosilicon compound, tetraethylsilane, was prepared by two chemists whose names one finds in all organic textbooks for another important discovery, the aluminum chloride catalyzed acylation of aromatic hydrocarbons, the Friedel–Crafts reaction. Inspired by the syntheses of organotin, -mercury, -arsenic, etc. compounds by Frankland and others in prior years,[14] Charles Friedel and his American co-worker, James Mason Crafts, began research whose goal was the development of organosilicon chemistry along the lines used by these earlier workers who had opened up organometallic chemistry. A reaction of diethylzinc with SiCl$_4$ in a sealed tube, Friedel and Crafts found,

(6) Sainte-Claire Deville, H. E. *Compt. rend. acad. sci.* **1854**, *39*, 321. Curiously, however, it appears that Wöhler was the first to prepare silicon in observable crystalline form. In a letter written in 1843 to his friend Justus Liebig, he reported that when a mixture of H$_2$ and SiCl$_4$ vapors was brought to red heat, silicon was produced in the form of black crystals. But, alas, Wöhler apparently never published this observation: Hofmann, A. W., Ed. *Justus Liebig und Friedrich Wöhler's Briefwechsel in den Jahren 1829/73*; Braunschweig, Germany, 1888; Vol. 1, p 230.

(7) Moissan, H. *Bull. Soc. Chim. Fr.* **1895**, *13*, 972.
(8) Dosaj, V. In *Kirk-Othmer Encyclopedia of Chemical Technology*, 4th ed.; Wiley: New York, 1997; pp 1104–1108.
(9) Wöhler, F. *Compt. rend. acad. sci.* **1856**, *42*, 48.
(10) Buff, H.; Wöhler, F. *Ann.* **1857**, *104*, 94.

(11) Friedel, C.; Ladenburg, A. *Ann.* **1867**, *143*, 118.
(12) Combes, C. *Compt. rend. acad. sci.* **1896**, *122*, 531.
(13) Ruff, O.; Albert, K. *Ber. Dtsch. Chem. Ges.* **1905**, *38*, 2222.
(14) See our last cover molecule essay: Seyferth, D. *Organometallics* **2001**, *20*, 2940.

commenced at around 140 °C and was complete after 3 h at 160 °C. The evolution of a significant amount of gas when the tube was opened and the presence of metallic zinc in the $ZnCl_2$ formed in the reaction (eq 3)

$$2(C_2H_5)_2Zn + SiCl_4 \rightarrow (C_2H_5)_4Si + 2ZnCl_2 \quad (3)$$
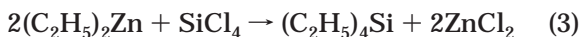
indicated that some diethylzinc had decomposed at the high temperatures used. The liquid products included a hydrocarbon (probably *n*-butane), unreacted $SiCl_4$, and a liquid with bp 152−154 °C, which elemental analysis and vapor density measurements showed to be the desired tetraethylsilane.[15] The preparation of tetramethylsilane was much more difficult. First of all, preparation of $(CH_3)_2Zn$ by Frankland's high-temperature, no-solvent procedure[14] gave poor yields. Then the $(CH_3)_2Zn/SiCl_4$ (no solvent) reaction required longer heating of the sealed tube at 200 °C. The product was a volatile liquid, bp 30−31 °C; its C, H analysis and vapor density were in agreement with its identity as $(CH_3)_4Si$.[16,17] Also reported was a study that demonstrated the much greater kinetic stability of the Si−C bond in tetraethylsilane compared to the Sn−C bond in tetraethyltin with respect to cleavage by Cl_2.[18]

Friedel carried out further research on inorganic and organosilicon chemistry with Albert Ladenburg, while Crafts focused on organic chemistry (the Friedel−Crafts reaction was discovered in 1877). Of interest was the synthesis of the first hexaorganodisilane, $(C_2H_5)_3Si−Si(C_2H_5)_3$, by the reaction of diethylzinc with hexaiododisilane.[19] Ladenburg continued research on organosilicon chemistry when he left Paris to take an academic position in Germany. His studies of the ethylation of tetraethoxysilane were most interesting and are relevant to the subject of this essay.[20] The reaction of diethylzinc with tetraethoxysilane was sluggish, even when the reaction mixture was heated, and did not go to completion. A rapid reaction was observed in the presence of a stoichiometric quantity of sodium, no doubt due to the formation of the much more reactive $NaZn(C_2H_5)_3$.[21] Some heating still was required, and Ladenburg makes the point that the round-bottomed reaction flask should be warmed with a flame-heated

"asbestos bath" (forerunner of our electric heating mantles), since direct heating of the flask, in which large quantities of metallic zinc had precipitated, with an open flame tended to cause cracking of the flask. Since it contained sodium, diethylzinc, and $NaZn(C_2H_5)_3$, the result must have been spectacular. Fractional distillation of the product mixture was impossible: $Si(OC_2H_5)_4$, bp 166.5 °C; $C_2H_5Si(OC_2H_5)_3$, bp 159 °C; $(C_2H_5)_2Si(OC_2H_5)_2$, bp 155.5 °C; $(C_2H_5)_3SiOC_2H_5$, bp 153 °C. However, since the ethylation proceeded in discrete steps, it was possible to adjust reaction conditions so that one of them was the major product. Thus, all could be isolated, but this required large-scale reactions. That the $(C_2H_5)_2Zn/Na/Si(OC_2H_5)_4$ reaction proceeded by way of a substituent exchange process was shown by using $Si(OCH_3)_4$ in place of tetraethoxysilane: the product was $C_2H_5Si(OCH_3)_3$.[22a,b] Among the reactions Ladenburg tried with his products was that of $(C_2H_5)_2Si(OC_2H_5)_2$ with acetyl and with benzoyl chloride. The organosilicon product was $(C_2H_5)_2SiCl_2$ (analytically pure!). On treatment of the latter with water, HCl was formed as well as a viscous, almost odorless, Cl-free syrup. The same product was obtained by the action of aqueous HI on $(C_2H_5)_2Si(OC_2H_5)_2$ (eq 4). Its analysis

$$n(C_2H_5)_2Si(OC_2H_5)_2 + 2nHI \rightarrow$$
$$[(C_2H_5)_2SiO]_n + 2nC_2H_5I + nH_2O \quad (4)$$
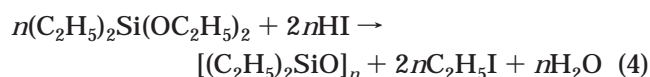
agreed with the empirical formula $(C_2H_5)_2SiO$, and Ladenburg called it "siliciumdiäthyloxid". In fact, this product had been obtained in 1866 by Friedel and Crafts by the oxidation of tetraethylsilane.[23] Therefore, not only had Friedel and Crafts prepared the first organosilicon compound, but they had also prepared the first polysiloxane! Ladenburg had provided a practical synthesis. Had Ladenburg carried out similar experiments with dimethylzinc, $(CH_3)_2SiCl_2$, our cover molecule, would have been known in 1872. Ladenburg found "$(C_2H_5)_2SiO$" to be very thermally stable and very high boiling (leaving an analytically pure residue at 330 °C); it did not solidify at −15 °C. Ladenburg noted the formal similarity to diethyl ketone but commented on the great differences in properties. Attempts to hydrogenate "$(C_2H_5)_2SiO$" to obtain a "silicocarbinol" were unsuccessful.

Ladenburg also prepared the first silicone resin, $[C_2H_5SiO_{1.5}]$, which he called silicopropionic acid and wrote as C_2H_5SiOOH, by hydrolysis of $C_2H_5SiCl_3$ which he had prepared in a similar manner from $C_2H_5Si(OC_2H_5)_3$. The disiloxane was prepared by acid hydrolysis of $(C_2H_5)_3SiCl$; treatment of the latter with aqueous ammonia at room temperature gave the silanol, $(C_2H_5)_3SiOH$.

Ladenburg did indeed carry out a reaction of dimethylzinc with $Si(OC_2H_5)_4$.[22a,c] To do so, he developed a much better procedure for the preparation of dimethylzinc: reaction of methyl iodide (120 parts) with zinc filings (90 parts) in the presence of 1% sodium amalgam (100 parts) and a few drops of ethyl acetate at atmospheric pressure at a temperature up to 90 °C; the

(15) Friedel, C.; Crafts, J. M. *Ann.* **1863**, *127*, 28. (Friedel (1832−1899), pupil of Wurtz, his successor at the Sorbonne in 1884. Research on ketones, pinacone, lactic acid; synthesis of glycerol, Friedel−Crafts reaction 1877, silicon alkoxides, established dimeric formulas of $AlCl_3$, $GaCl_3$, and $FeCl_3$; high temperature and pressure synthesis of minerals. J. M. Crafts (1839−1917) studied at Harvard; in Europe with Plattner, Bunsen and Wurtz. Afterwards, academic positions at Cornell and MIT. In Paris 1874−91, research on organic and organosilicon chemistry with Friedel. Professor of Organic Chemistry at MIT 1892−97; President of MIT 1897−1900.)

(16) (a) Friedel, C.; Crafts, J. M. *Ann.* **1865**, *136*, 203. (b) Friedel, C.; Crafts, J. M. *Bull. Soc. Chim. Fr.* **1865**, *3*, 356.

(17) References 15 and 16 are preliminary communications. A long, detailed full paper that includes these preparations as well as an account of the reactivity of these R_4Si compounds, including the preparation of the first siloxane, $(C_2H_5)_3SiOSi(C_2H_5)_3$, appeared a few years later: Friedel, C.; Crafts, J. M. *Ann. Chim. Phys.* **1870**, *19*, 334.

(18) Friedel, C.; Crafts, J. M. *Ann.* **1866**, *137*, 19.

(19) (a) Friedel, C.; Ladenburg, A. *Compt. rend. acad. sci.* **1869**, *68*, 920; (b) Friedel, C.; Landenburg, A. *Justus Liebigs Ann. Chem.* **1880**, *203*, 241; *Ann. Chim. Phys.* **1880** [5], *19*, 390.

(20) Ladenburg, A. *Ann.* **1872**, *164*, 300. (Ladenburg (1842−1911) studied with Bunsen, Kirchhoff, Carius, and Kekulé and, in Paris, with Wurtz and Friedel. Privatdozent, then associate professor in Heidelberg, professor in Kiel (1872) and Breslau (1880−1909). Research on organosilicon and -tin compounds; benzene and its derivatives. His most important work was on alkaloids.)

(21) See the discussion of this compound in the previous essay.[14]

(22) (a) Ladenburg, A. *Justus Liebigs Ann. Chem.* **1874**, *173*, 143. (b) *Ber. Dtsch. Chem. Ges.* **1872**, *5*, 1081. (c) *Ber. Dtsch. Chem. Ges.* **1873**, *6*, 1029.

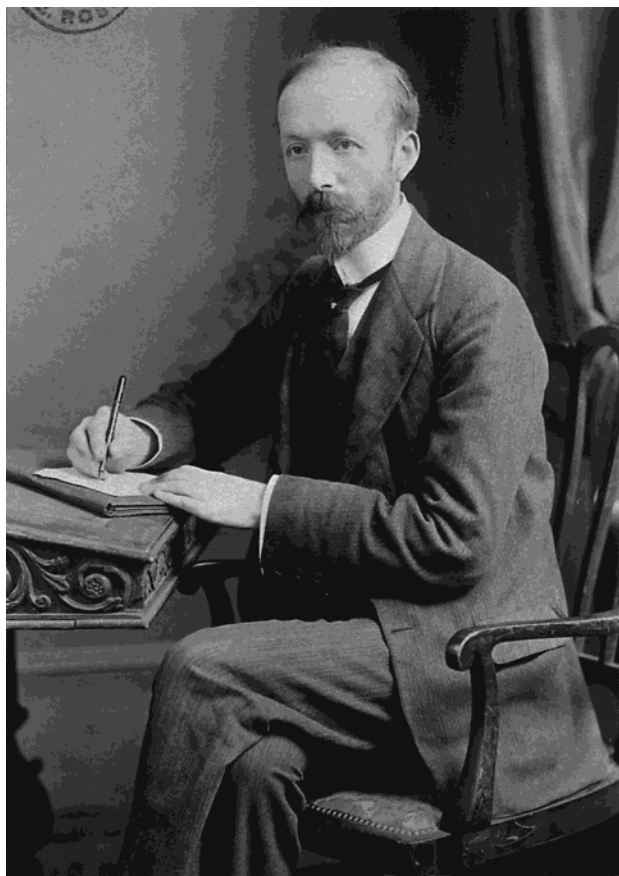(23) Friedel, C.; Crafts, J. M. *Ann. Chim. Phys.* **1866** [4], *9*, 5.

Figure 1. Frederic Stanley Kipping (reproduced courtesy of the Library and Information Centre, Royal Society of Chemistry).

dimethylzinc yield was nearly quantitative. During six $(CH_3)_2Zn/Si(OC_2H_5)_4$ reactions, carried out in sealed tubes at temperatures up to 300 °C, the tubes exploded in four of the experiments. From the contents of the two remaining tubes, $CH_3Si(OC_2H_5)_3$ could be isolated. Treatment of this product with aqueous HI gave $(CH_3SiO_{1.5})_n$, which Ladenburg, believing it was CH_3SiOOH, called "methylsiliconsäure". The disubstituted product, $(CH_3)_2Si(OC_2H_5)_2$, was not obtained.

Ladenburg reported another first: the preparation of the first trialkylsilane, $(C_2H_5)_3SiH$, as a byproduct (together with ethylene) of the ethylation of $(C_2H_5)_3SiOC_2H_5$ with the $(C_2H_5)_2Zn/Na$ system.[20] Its reactivity was in line with its formulation as a silicon hydride: it was attacked rapidly by bromine and concentrated sulfuric acid and explosively by fuming nitric acid.

These then were the beginnings of organosilicon chemistry. Toward the end of the 19th century and at the beginning of the 20th, other researchers became active in this area: there were papers by Pape, Polis, Dilthey, and Schlenk, while Ladenburg continued research in this area. However, it was Frederic Stanley Kipping (Figure 1) (1863−1949) who dominated organosilicon research, from his first communication in 1899 until he retired in 1936, publishing over 50 papers. Kipping was born in England in 1863, the year that the first organosilicon compound was reported. He joined von Baeyer's laboratory in Munich in 1886, where he engaged in research on cyclic carbon compounds as the first student of W. H. Perkin, Jr. (the son of the famous English organic chemist), who was an Assistent. After obtaining his Ph.D., Kipping returned to England, obtaining a D.Sc. from London University in 1887. He joined Perkin, now in Edinburgh, to begin his academic career, working on projects in organic chemistry. In 1897 he was appointed to the chair in organic chemistry in University College, Nottingham, where he stayed until his retirement. It was at Nottingham that he started organosilicon research, which became his main area of interest. However, other projects in organic chemistry were continued. One of Kipping's primary interests was the preparation of a silicon compound of the type $SiRR'R''R'''$ and its resolution into its optically active *d* and *l* isomers. Also, he was interested in seeing how similar the organic derivatives of silicon were to the analogous compounds of carbon. (Of course, Friedel and Ladenburg had already observed some differences.)

At the time Kipping began his research in organosilicon chemistry at Nottingham, the zinc alkyls of Frankland[14] still were the only practical sources of nucleophilic alkyl groups. Soon thereafter things changed: in 1900, Victor Grignard published his first paper on the RMgX reagents, which came to bear his name.[24] The Grignard reagents found rapid acceptance as useful aids in organic synthesis, and in 1904 two papers were published on their application in the synthesis of organosilicon compounds—by Kipping[25] and by Dilthey and Eduardoff[26] in Zürich. This procedure continues to find useful application in organosilicon preparations today. Kipping carried out the reaction of C_2H_5MgI with silicon tetrachloride and found it to be quite unselective, all possible products being formed: $C_2H_5SiCl_3$, $(C_2H_5)_2SiCl_2$, $(C_2H_5)_3SiCl$, and $(C_2H_5)_4Si$. However, a 1:1 reaction of C_2H_5MgBr with $SiCl_4$ gave almost exclusively $C_2H_5SiCl_3$. As Kipping later found,[27] silicon tetrachloride reacts with diethyl ether even at room temperature (certainly at reflux), probably resulting in ether cleavage and formation of products such as $Cl_3SiOC_2H_5$. This, he said, "accounts for previous difficulties in preparing various organic derivatives of silicon. Thus from the product of the interaction of magnesium, ethyl bromide and the tetrachloride, it may not be hard to obtain ethylsilicon trichloride, but the isolation of the di- and tri-ethyl derivatives by fractional distillation is a very troublesome task." Nevertheless, Kipping and others continued to use the Grignard reagents to good advantage, the difficulties apparently being restricted to the silicon tetrahalides and avoided by working at lower temperature.

Much of Kipping's work dealt with arylsilicon compounds—their preparation and reactivity: the reactivity of aryl and benzyl substituents on silicon toward nitration and sulfonation and the reactivity of Si−Cl bonds in Ar_2SiCl_2 and Ar_3SiCl compounds toward sodium, which resulted in Si−Si bond formation. Ph_2SiCl_2 gave, among other products, the cyclic tetramer, $(Ph_2Si)_4$. As mentioned already, a primary interest was in the possibility of preparing optically active organosilanes and, by successive Grignard reactions, he and his students prepared compounds of the type $RR'R''R'''Si$.[28]

(24) Grignard, V. *Compt. rend. acad. sci.* **1900**, *128*, 110.
(25) Kipping, F. S. *Proc. Chem. Soc.* **1904**, *20*, 15.
(26) Dilthey, W.; Eduardoff, F. *Ber. Dtsch. Chem. Ges.* **1904**, *37*, 1129.
(27) Kipping, F. S.; Murray, A. G. *J. Chem. Soc.* **1927**, *II*, 1401.

Of interest to the subject of this essay is that Kipping hydrolyzed $(C_2H_5)_2SiCl_2$, obtaining an oil with the consistency of glycerol, with molecular weight 604.[29] The hydrolysis of many other chlorosilanes was studied. Those of the type R_3SiCl in many cases gave the silanol, R_3SiOH, which could be condensed to the disiloxane, $R_3SiOSiR_3$. Hydrolysis of the diorganodichlorosilanes proceeded via the silanediols, $R_2Si(OH)_2$, which in some cases could be isolated and which underwent condensation to give oligosiloxanes, $(R_2SiO)_n$. The organotrichlorosilanes on hydrolysis gave products of the type $[RSiO_{1.5}]_n$ (which Kipping wrote as RSiOOH, thinking them to be analogues of carboxylic acids). From Kipping's point of view as an organic chemist, organosilicon compounds were organic compounds that happened to contain silicon, and so he used organic-type nomenclature: R_4Si = silicane; R_3SiOH = silicanol; $R_2Si(OH)_2$ = silicanediol; R_2SiO = silicone; RSiOOH = siliconic acid—in analogy to alkane, alcohol, alkanediol, ketone, and carboxylic acid. This point of view led him to expect actual similarities. Kipping's insistence on forcing organosilicon compounds—their properties and reactions—into the framework of organic chemistry was a bias that actually proved to be a handicap to his research in organosilicon chemistry. Superficially, there are many similarities (but also some differences) between compounds of type R_4Si (already well-known in Kipping's time) and R_4C compounds or alkanes in general. However, comparisons between what he called "silicones" (a name that has stuck) and ketones showed them to be very different. About the hydrolysis product of $PhCH_2$-$(C_2H_5)SiCl_2$, Kipping said the following:[31]

"...as benzylethylsilicon dichloride is decomposed by water, giving benzylethylsilicone, we have studied the behavior of this silicone in order to ascertain whether it shows any similarities to the corresponding ketone. We may say at once that it does not; benzyl ethyl ketone boils at 226° under atmospheric pressure; benzylethylsilicone at 305−315° under a pressure of 22 mm. This very high boiling point of the silicone doubtless indicates molecular complexity, and the results of ebullioscopic experiments bear out this indication, the values obtained in acetic acid and in acetone pointing to the termolecular formula, $(BzEtSiO)_3$. ...dibenzylsilicone...is also represented by the molecular fomula $(Bz_2SiO)_3$; and judging from its high boiling point (above 360°), diethylsilicone has an analogous molecular complexity. It would seem, therefore, that silicones, as a class, differ from the ketones in readily forming comparatively stable molecular aggregates, but whether the latter are to be regarded as composed of loosely associated, or of chemically united, molecules, we have as yet no satisfactory evidence before us.

This association, polymerization, or union of simple silicone molecules is probably one of the reasons, but not the only one, why in other respects also the silicones show no relationship with the ketones. ...it is possible to account for the results on the assumption that the group Si:O of the simple silicone does not exist in the associated molecule..."

In his further research, mainly with diarylsilicon systems, Kipping was able to isolate and identify pure, covalently bonded cyclic tri- and tetrasiloxanes and 1,3-disiloxanediols. Throughout his research he was plagued by nonvolatile oils and gums and other materials of higher molecular weight formed in the chlorosilane hydrolysis reactions, which could not be crystallized and which he considered a nuisance.

One reaction of his silicones, however, misled Kipping into thinking that there was indeed an analogy between his "silicones" and ketones. The reaction of a Grignard reagent with a ketone to give, after hydrolytic workup, a tertiary alcohol, i.e., $R_2C{=}O + R'MgX \rightarrow R'R_2COH$, was by 1911 a well-known reaction. As Kipping was able to report:

"As a matter of fact, the silicones were found to react with the Grignard reagents in a normal manner, and it is perhaps hardly too much to say that this is the first instance in which the silicones have been proved to show any analogy to the ketones in chemical behavior."

A reaction reported was

$$[(PhCH_2)_2SiO]_3 + 3CH_3MgI \xrightarrow{\;\;H_2O\;\;} 3(PhCH_2)_2CH_3SiOH \quad (5)$$
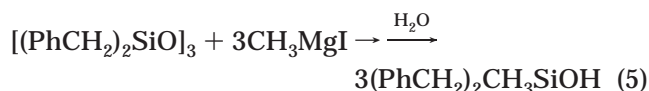
Kipping's explanation, a reasonable one, considering how he thought about his "silicones", was

"As these preparations gave ..good yields of the desired products, it seemed to follow that the termolecular silicones were resolved into the unimolecular compounds [i.e., $R_2Si{:}O$] by the action of the Grignard reagents."

Of course, we know better now.

Kipping laid the groundwork for the explosive growth of organosilicon chemistry that was to come, and he lived to see its early, most important stages. The obviously oligomeric nature and high thermal stability of "silicones" such as $[(C_2H_5)_2SiO]_n$ and $[(PhCH_2)(CH_3)SiO]_n$, the adhesive properties of "benzylsiliconic acid" (sticking to glass, paper, and porcelain), and the film-forming properties of "diphenylsilicone" that he had observed did not move Kipping to think seriously about possible applications. In his Bakerian Lecture,[33] delivered on Dec 19, 1936, in which he reviewed his 37 years of organosilicon research, he was not optimistic: "...the few [organosilicon compounds] which are known are very limited in their reactions, the prospect of any immediate and important advances in this section of organic chemistry does not seem to be very hopeful." Kipping was a "pure" academic, a vanishing species in today's academic chemistry research environment. However, these properties aroused the interest of others who had specific applications in mind. For instance, in his 1935 book, *The Chemistry of Synthetic Resins II*, C. Ellis

(28) A good summary of the individual Kipping papers can be found in: Post, H. W. *Silicones and Other Organosilicon Compounds*; Reinhold: New York, 1949; pp 13−31.
(29) Martin, G.; Kipping, F. S. *J. Chem. Soc.* **1909**, *95*, 302.
(30) Kipping, F. S. *J. Chem. Soc.* **1912**, *101* II, 2106.
(31) Robison, R.; Kipping, F. S. *J. Chem. Soc.* **1908**, *93*, 439.
(32) Kipping, F. S.; Hackford, J. E. *J. Chem. Soc.* **1911**, *99*, 138.
(33) Kipping, F. S. *Proc. R. Soc. (London), A* **1937**, *159*, 139.
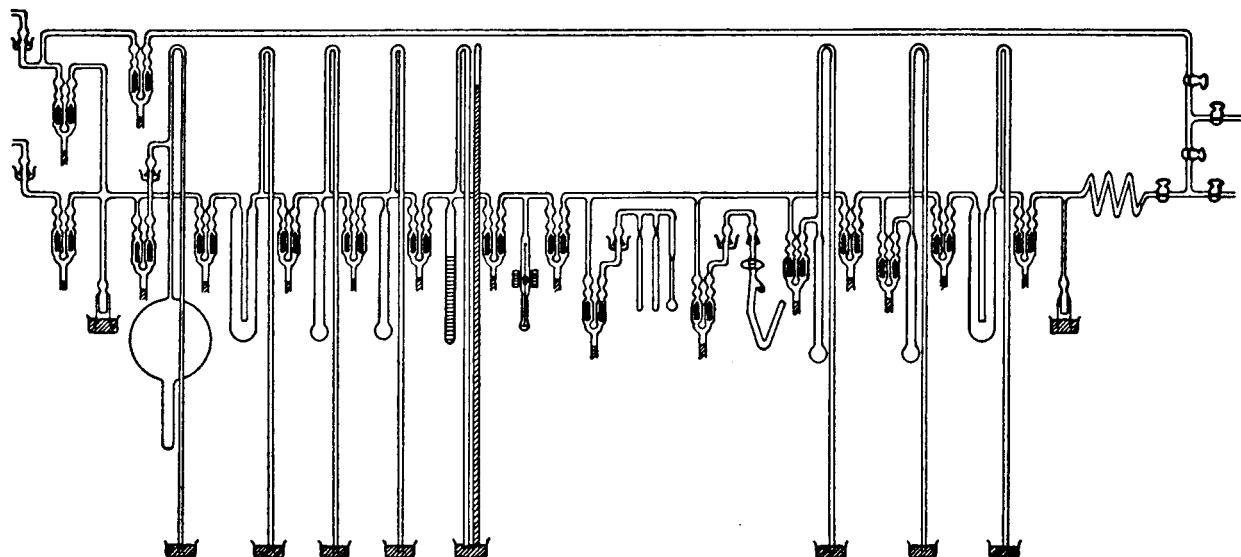
Figure 2. Early form of Stock's high-vacuum system (from ref 36b).

wrote about Kipping's work: "The further development of organosilicon chemistry could lead to the production of cheap and easily preparable compounds which could be used as resins or adhesives." In view of Kipping's important contributions to organosilicon chemistry, it certainly is fitting that there is an American Chemical Society award called the "Frederic Stanley Kipping Award in Organosilicon Chemistry."

Frankland had pointed out a formal relationship of the hydrogen derivatives of the main-group elements and their alkyl compounds, e.g., AsH_3 and $As(C_2H_5)_3$. Thus, in that sense, H_2SiCl_2 can be viewed as the first member of the $(C_nH_{2n+1})_2SiCl_2$ series ($n = 0$), in which our cover molecule, $(CH_3)_2SiCl_2$, is the first (alkyl)$_2SiCl_2$ ($n = 1$) member. The chemistry of H_2SiCl_2 is indeed similar in many respects to that of $(CH_3)_2SiCl_2$ (except for the special reactivity of its Si−H bonds). This consideration brings us to the work of Alfred Stock. Stock is noted especially for his discovery of the boron hydrides and the development of their chemistry. Although Wöhler and Buff were the first to prepare SiH_4,[34] it was Stock and his students who developed and systematized the silicon hydrides and their chemistry.[35] To develop the chemistry of the volatile (gaseous and liquid), highly reactive, usually pyrophoric boron and silicon hydrides, Stock had to invent a completely new methodology for their handling. Stock, like Bunsen and Frankland, was an inventive and expert experimentalist and, what was important, an expert glassblower. To deal with the hydrides of boron and silicon, he devised and built an elaborate high-vacuum system with mercury valves, in which all parts were fused together and in which the chemicals with which one is dealing come in contact only with glass and mercury (Figure 2). Performance of chemical reactions, distillation, sublimation, analysis, determination of physical properties, and

storage, were all possible on the milligram scale in this flexible system and its clever ancillary equipment.[36]

Stock and Somieski prepared H_2SiCl_2 by the $AlCl_3$-catalyzed gas-phase reaction of SiH_4 with 2 molar equiv of HCl.[37] In one example,[37b] a reaction of 284 cm^3 of SiH_4 (all volumes are of the respective gaseous reactant or product) with 594 cm^3 of HCl in the presence of a small amount of $AlCl_3$ at 100 °C for 10 days in a bulb on the high-vacuum system gave a mixture of H_2, 2 cm^3 of SiH_4, 63 cm^3 of HCl, 39 cm^3 of H_3SiCl, and 223 cm^3 of H_2SiCl_2. Isolation of pure H_2SiCl_2 from this mixture was effected by fractional distillation under high vacuum, a process Stock characterized as exceedingly laborious and time-consuming.[38] Of special interest is the gas-phase hydrolysis of H_2SiCl_2,[37b] carried out, in one example, with 49.6 cm^3 of water vapor and 46.9 cm^3 of gaseous H_2SiCl_2 in the chromic acid-washed 8 L bulb shown in Figure 3. The expected reaction was that shown in eq 6. The initial pressure increase suggested to Stock that

$$H_2SiCl_2(g) + H_2O(g) \rightarrow H_2SiO(g) + 2HCl(g) \quad (6)$$
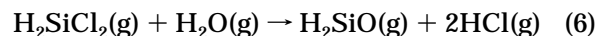
monomeric H_2SiO (which he called "prosiloxane") had been formed in the very dilute gas phase. (Had it polymerized immediately, a large pressure decrease would have been observed.) With time, the pressure in the bulb decreased and $[H_2SiO]_n$ polymer coated the glass surface. This coating, as expected, evolved hydrogen on treatment with aqueous NaOH. Thus, the parent silicone apparently had been prepared. The prosiloxane, in other experiments, could be isolated (∼0.05 mL) as a mobile, clear liquid that quickly became viscous and finally gelled. Years later, our study at MIT showed that the hydrolysis of H_2SiCl_2, either with a stoichiometric amount of water in dichloromethane at −30 to −20 °C or by slow, controlled addition of a slight excess of water

(34) Wöhler, F.; Buff, H. *Ann.* **1857**, *103*, 218.
(35) Stock, A. *Hydrides of Boron and Silicon*; Cornell University Press: Ithaca, NY, 1932; Chapter II. (Stock (1876−1946), chemistry study in Berlin; a year with Moissan in Paris. Privatdozent in Berlin, 1900−1909; professor in University of Breslau, 1909−1916; Berlin (Kaiser Wilhelm Institut), 1916−1926; University of Karlsruhe, 1926−1936; Berlin as emeritus professor to 1943. Best known for his thorough, exacting studies of the boron hydrides.)

(36) (a) For a fascinating, detailed description of this ingenious equipment and how it was used, see Chapter XXX in ref 35. (b) In German: Stock, A. *Ber. Dtsch. Chem. Ges.* **1917**, *50*, 989; **1918**, *51*, 983; **1920**, *53*, 751.
(37) (a) Stock, A.; Somieski, C. *Ber. Dtsch. Chem. Ges.* **1919**, *52*, 695. (b) **1919**, *52*, 1851.
(38) Now pure H_2SiCl_2 is available commercially in gas cylinders containing up to 250 lb.
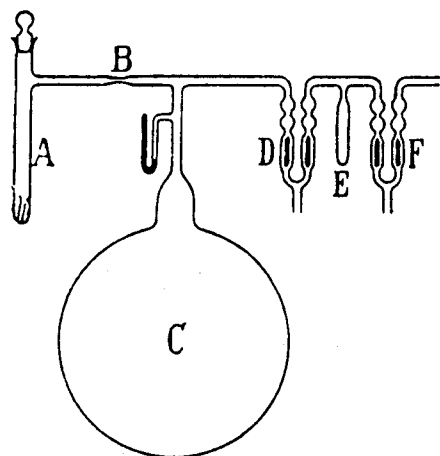
Figure 3. Stock's apparatus used in the H_2SiCl_2 hydrolysis experiment. (from ref 37b).

at 0 °C to a H_2SiCl_2 solution in dichloromethane, results in formation of $(H_2SiO)_n$ siloxanes.[39] In the volatile fraction, cyclic oligomers with n from 4 to 23 were detected and those with $n = 4-6$ were isolated by gas chromatography and characterized by ^1H and ^{29}Si NMR spectroscopy and infrared and mass spectroscopy: this is much easier when you have all these modern tools and can purchase a cylinder of H_2SiCl_2. Stock and his students deserve our unstinted admiration! Stock and Somieski also put Frankland's dimethylzinc into play, using it, again in a gas-phase reaction, to convert H_2SiCl_2 to $(CH_3)_2SiH_2$.[37a] The alkaline hydrolysis of $(CH_3)_2SiH_2$, followed by acidification, gave an oil and some crystals. Evaporation of a benzene solution of these products left a syrup. Stock suggested the sequence $(CH_3)_2SiH_2 \rightarrow (CH_3)_2Si(ONa)_2 \rightarrow (CH_3)_2Si(OH)_2 \rightarrow [(CH_3)_2(HO)Si]_2O \rightarrow [(CH_3)_2SiO]_n$ had taken place. This was only a very small scale experiment (using 5.57 cm^3 of gaseous $(CH_3)_2SiH_2$), but poly(dimethylsiloxane) had been prepared for the first time! Another compound that we will meet again later, CH_3SiHCl_2, also was prepared by Stock and Somieski during this study.

Up until this time, and for a few years more, all organosilicon research was carried out in academic laboratories, where nobody seemed at all interested in possible applications of the chemistry that had been uncovered.[40] And at this point our introduction (a rather long one) ends.

The scene now shifts to industry.[41] Industrial interest and activity arose from definite needs. The first industrial research in organosilicon chemistry was carried out in the 1930s by J. Franklin Hyde (1903−1999) at the Corning Glass Works. When Hyde was hired by Corning in 1930, after Ph.D. studies at the University of Illinois with Roger Adams and postdoctoral work at Harvard with J. B. Conant, it was suggested to him that there

might be some field worth looking at between glass and organic polymers. As it happened, Hyde did not get to organosilicon chemistry right away, but he did read Kipping's papers and soon he prepared some phenylchlorosilanes by the Grignard procedure. In further investigations, he found that their resinous, low-melting hydrolysis products were very thermally stable. In the mid-30s, Corning was trying to apply its glass fiber technology to the fabrication of thermally stable insulating tape for electrical applications. A thermally stable polymer was needed to coat the fibers and to provide the matrix for the glass fibers in fabricating the tape. Kipping's polysiloxanes seemed to be good candidates, and so Hyde began preparing the required starting materials, various organochlorosilanes, by the Grignard procedure and studying their hydrolysis. This now is industrial research, and if journal publications come at all, they come at a later date, after patent applications have been filed or, more often, only after the patents have been issued. Hyde's synthetic work was the subject of a 1941 publication.[42] The compounds prepared were $Ph(C_2H_5)SiCl_2$, $(C_2H_5)_2SiCl_2$, $Ph(CH_3)SiCl_2$, Ph_2SiCl_2, and $(CH_3)_2SiCl_2$. All were hydrolyzed under mild conditions to give liquid products of relatively low molecular weight, except for Ph_2SiCl_2, which gave the solid $(Ph_2SiO)_3$. Such cyclic trisiloxanes appeared to be present also in the hydrolysis products of the other dichlorosilanes. The oligosiloxanes were converted to "resinous polymers" either by heating with aqueous HCl in the case of the phenyl-containing siloxanes (which resulted in Ph−Si cleavage) or, in the case of the phenylalkyldichlorosilanes and dialkyldichlorosilanes, by air oxidation at high temperature, which replaced alkyl groups by Si−O−Si links. The properties of the hydrolysis/condensation/oxidation products of these R_2SiCl_2 compounds must have looked promising, because these studies were continued with applications in mind. With the beginning of World War II, the US Navy, which required thermally stable insulation for the electric motors used in submarines, took an active interest in this research. This ultimately led to the formation of the Dow Corning Corporation in 1942, a joint venture of the Dow Chemical Co., which could provide the magnesium required for the preparation of the Grignard reagents to be used in the organochlorosilane synthesis as well as plant-scale chemical engineering expertise, and the Corning Glass Works, which had developed the chemistry. Dow Corning's research, development, and manufacturing operations were located in Midland, MI, the location of Dow Chemical Co. Hyde and colleagues from Corning and the Corning Mellon Institute Fellowship moved to Midland. Hyde had a distinguished research and development career at Dow Corning, remaining active in research on silicones well past his formal retirement in 1969.

(39) Seyferth, D.; Prud'homme, C.; Wiseman, G. H. *Inorg. Chem.* **1983**, *22*, 2163.

(40) An exception was K. A. Andrianov (1904−1978) in the USSR, who concluded that organosilicon compounds containing Si−O−Si linkages should be useful materials of high thermal stability for applications in electrical insulation. Beginning in 1937, he initiated efforts to develop such materials, first investigating tetraalkoxysilanes and then also Grignard synthesis derived organochlorosilanes. Andrianov was one of the leaders in the development of organosilicon chemistry in the USSR after World War II. See: Zhdanov, A. A. *Zh. Obshch. Khim.* **1979**, *49*, 462.

(41) Accounts of the beginnings of industrial organosilicon chemistry are given in several books. (a) Liebhafsky, H. A. *Silicones under the Monogram*; Wiley-Interscience: New York, 1978. (b) Rochow, E. G. *Silicon and Silicones*; Springer: Berlin, Heidelberg, 1987. (c) McGregor, R. R. *Silicones and Their Uses*; McGraw-Hill: New York, 1954. (d) Warrick, E. *Forty Years of Firsts*; McGraw-Hill: New York, 1990. (e) See also the article: Hyde, J. F. Organic Chemist in a Glass Factory. *Chem. Heritage* **1992**, *9*(2), 12; **1992−3**, *10*(1), 13. References 41a,b describe developments at the General Electric Co. and 41c− e at the Corning Glass Works, at the Mellon Institute, where Corning supported a research project, and at Dow Corning Corp.

(42) Hyde, J. F.; DeLong, R. C. *J. Am. Chem. Soc.* **1941**, *63*, 1194.

Before this happened, however, there were other important developments that are described in more detail in ref 41a,b. After a visit in January 1938 to the Corning laboratories, during which they heard about Hyde's work, chemists from the Schenectady Research Laboratory of the General Electric Co. became interested in silicones for their own applications as insulation of high thermal stability in electric motors. In fact, W. I. Patnode, a GE chemist, had been trying to apply condensation products based on tetraethoxysilane to this purpose. A decision to investigate polyorganosiloxanes at GE followed this visit. A young chemist who had joined the GE Research Laboratory after earning his Ph.D. at Cornell, Eugene G. Rochow, took on this project on his own. After initial work with the thermally cured hydrolysis/condensation product of diphenyldichlorosilane, which did not seem very promising, Rochow changed direction. He reasoned that polydialkylsiloxanes might be worth looking at but that those which contained C−C bonds should be avoided, since they should be less stable thermally. Also, their thermal decomposition would leave conducting carbonaceous residues in the electric motor. That left poly(dimethylsiloxane) as the only candidate, and in August 1938, Rochow began research on methylpolysiloxanes. The Grignard synthesis that Kipping had used was applied to the reaction of CH_3MgBr with $SiCl_4$ in diethyl ether. The problem with this synthesis is that it gives a mixture of products: CH_3SiCl_3, $(CH_3)_2SiCl_2$, $(CH_3)_3SiCl$, and even some $(CH_3)_4Si$. In general, the susceptibility of the chlorosilanes toward nucleophilic attack decreases in the order $SiCl_4 \approx RSiCl_3 > R_2SiCl_2 \gg R_3SiCl$; the process is not selective. The proportion of any one product can be optimized by adjusting the molar ratio of the reactants and the reaction conditions, but mixtures will result in any case. Added to this problem was the possibility of some Si−Br for Si−Cl exchange when CH_3MgBr was used (it being much easier to prepare and more ether-soluble than CH_3MgCl) and the fact that the components present in the final product mixture were extremely difficult to separate by fractional distillation (boiling points: CH_3SiCl_3, 65.7 °C; $(CH_3)_2SiCl_2$, 70.0 °C; $(CH_3)_3SiCl$, 57.3 °C; $SiCl_4$, 57.6 °C; $(CH_3)_4Si$ was not a problem with bp 26.5 °C). In view of these difficulties, it was the mixed methylchlorosilane product which was hydrolyzed and processed to give methylsilicone resins with CH_3/Si ratios of 1.3 to 1.5.[43] These showed remarkable thermal and oxidative stability: stable when heated at 550 °C under vacuum for 16 h and only slow oxidation in air at 300 °C. These properties were very encouraging, and research on polymethylsiloxanes continued, with other chemists at the GE laboratories becoming involved. Attempts to prepare pure $(CH_3)_2SiCl_2$ and CH_3SiCl_3 by the reaction of CH_3MgCl with $SiCl_4$ in di-*n*-butyl ether followed by careful fractional distillation (120 plate column under extremely stable conditions) gave products of empirical composition $(CH_{2.98})_{2.03}SiCl_{1.84}$ and $(CH_{2.89})_{1.13}SiCl_{2.98}$ (by elemental analysis).[44] This now allowed a study of each chlorosilane as a pure compound.

The major stumbling block in the commercialization of the polymethylsiloxanes by GE was the fact that there was no practical, commercially reasonable procedure for the synthesis of the required methylchlorosilanes as individually pure compounds. The only available synthetic route at the time was Kipping's organomagnesium procedure, and some of the problems associated with its use already have been noted above. Carrying the Grignard synthesis out on a plant scale would not be impossible, but minor problems associated with the laboratory-scale reaction would be less minor on the plant scale (e.g., handling large volumes of flammable solvent, disposing or recycling of magnesium salts, and purifying the individual methylchlorosilanes by fractional distillation). An added difficulty was that the Dow Chemical Co. controlled magnesium production in the USA, thus greatly favoring its joint venture with the Corning Glass Works. GE either had to give up the idea of a polymethylsiloxane business or find a new route to the methylchlorosilanes. The GE methylsilicone project was put on hold. However, Rochow was permitted to work part time on alternate routes to the methylchlorosilanes.

Among the experiments Rochow carried out were repetitions of the reactions of gaseous HCl at high temperature with elemental silicon and its alloys, with the idea of somehow converting the $HSiCl_3$ product to CH_3SiCl_3. All attempts to do this were unsuccessful. However, there came the following idea: if HCl reacts with Si/Cu, why not try CH_3Cl? In his first experiment, passing a mixture of HCl and CH_3Cl through a heated tube furnace containing ferrosilicon, only $HSiCl_3$ and $SiCl_4$ appeared to have been formed. However, after carrying out their hydrolysis in diethyl ether solution, Rochow noted that the flask that had contained the ether solution had "a slippery feel—as though a film of methyl silicone had formed there."[41b]

Rochow's research notebook, as quoted in ref 41a,b, records what he did next:

> "*May 9, 1940, cont'd*
> Copper−silicon
> I crushed some of the Niagara Falls Smelting Co. 50% Cu−Si in the jaw-crusher, and packed a Nonex tube with the material (size is about 1/4″ down to fine powder). I arranged the tube in the furnace and arranged to admit both CH_3Cl & HCl. Single CO_2 condensing tube on the outlet end (see Figure 5.1). [Figure 4 in this essay.]
> *May 10, 1940*
> I heated the tube in the furnace to 370 °C and kept it there. I passed through some HCl at first, to attack the alloy superficially, then passed in CH_3Cl slowly. Let it run all day.
> *At 4:40 P.M.* I stopped the stream of CH_3Cl. About 5 cm³ of liquid had collected in the condenser, plus some in the cold end of the furnace tube. I put it all in ice water having a layer of ether on top, and stirred. The material hydrolyzed with some cloudiness, but not large volumes of silica; there seemed to be little CH_3Cl either.
>
> I decanted some of the ether solution into a Petri dish and evaporated the ether. A clear thick glycerol-like substance resulted. This liquid is sticky to the touch, acts very much like the methyl silicone.

(43) Rochow, E. G.; Gilliam, W. F. *J. Am. Chem. Soc.* **1941**, *63*, 798.
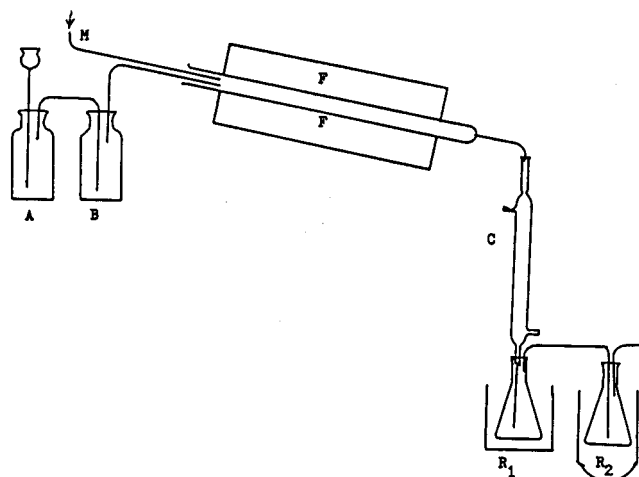(44) Gilliam, W. F.; Liebhafsky, H. A.; Winslow, A. F. *J. Am. Chem. Soc.* **1941**, *63*, 801.

Figure 4. Apparatus used in Rochow's first CH_3Cl + Si/ Cu direct synthesis experiment: (A) HCl generator; (B) bubble counter; (M) CH_3Cl input; (F) tube furnace surrounding reaction tube; (C) condenser; (R_1) = receiver at 0 °C; (R_2) receiver at −80 °C (from ref 41b, by permission of Springer-Verlag).

Some of the thick liquid product from the evaporation of the ether solution was warmed by the rays of the projection lamp for 1 h. At the end of this time, it was a colorless, sticky, almost solid resin. The behavior suggests condensation of the methyl silicols which I believe are produced during the hydrolysis.

The hydrolysis product of the materials resulting from the reaction of CH_3Cl and copper– silicon, then, resembles methyl silicone produced by another method, and I believe it to be methyl silicone.

The reactions which I believe occur are as follows. First HCl is passed through the tube:

$$Si + 3HCl \rightarrow SiHCl_3 + H_2$$
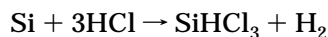
Only a small amount of HCl is passed through, and this is done principally to etch the surface of the alloy. Small amounts are later mixed with the CH_3Cl, in the ratio of perhaps 1 part to 50 parts of CH_3Cl. The CH_3Cl reacts in this way:

$$3CH_3Cl + Si \rightarrow CH_3SiCl_3 + C_2H_6$$

$$2CH_3Cl + Si \rightarrow (CH_3)_2SiCl_2$$
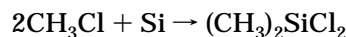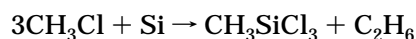
and, to a much smaller extent, this might occur:

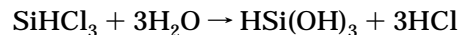$$CH_3Cl + 2HCl + Si \rightarrow CH_3SiCl_3 + H_2$$

The liquid products, which I believe are methyl silicon chlorides, condense in the cooler portions of the tube containing the alloy and are also distilled out into the condensing tube kept at −80 °C. The colorless liquid so collected (in the condensing tube) does not bubble much when warmed to room temperature, hence does not contain much CH_3Cl.
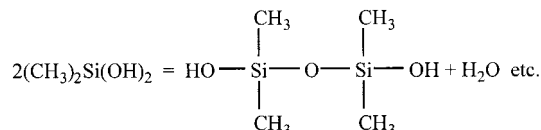
Upon hydrolysis of the combined liquid products,

$$CH_3SiCl_3 + 3H_2O \rightarrow CH_3Si(OH)_3 + 3HCl$$

$$(CH_3)_2SiCl_2 + 2H_2O \rightarrow (CH_3)_2Si(OH)_2 + 2HCl$$
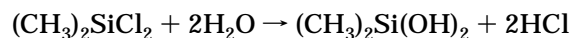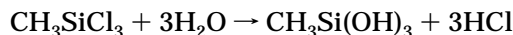
and a small amount of

$$SiHCl_3 + 3H_2O \rightarrow HSi(OH)_3 + 3HCl$$

The methyl silicols undergo partial condensation immediately to form the viscous intermediate products:

$$2(CH_3)_2Si(OH)_2 = HO-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{Si}}-O-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{Si}}-OH + H_2O \text{ etc.}$$

This goes on until sticky liquid products result. On warming, condensation proceeds further, splitting off more water (which evaporates in part or stays behind in globules). The end result is a clear resinous body which I believe to be methyl silicone.

/S/ E.G. Rochow
May 10, 1940"

As Herman Liebhafsky said[41a] about this experiment: "The most important single experiment and the best single day's work in the history of the silicone industry." (Figure 5) This was the breakthrough for which GE had been hoping: a proprietary methylchlorosilane synthesis that, one might hope, even at this early stage, could be scaled up and commercialized, a reaction that does not require a preformed organometallic reagent and a flammable solvent and does not generate large quantities of a magnesium halide.

Further work showed that the use of the silicon/ copper alloy (vs pure silicon) definitely was advantageous: it accelerated the rate of the reaction so that lower reaction temperatures could be used. A fair selectivity favoring $(CH_3)_2SiCl_2$ was observed, but substantial amounts of CH_3SiCl_3 also were formed during the latter stages of the reaction. Of course, a patent application was filed that covered this new chemistry; the patent (U.S. Patent 2,380,995) was issued in Sept 1945 (application on Sept 26, 1941, but issued a few years late since it had been under wartime secrecy restriction), and in June 1945 Rochow published his results[45] (Figure 6). As noted in this paper, the direct RX + Si/Cu synthesis could be extended to RX = CH_3Br, C_2H_5Cl, and C_2H_5Br but gave only poor results with chlorobenzene.[45] However, good results (satisfactory yields and fair selectivity to Ph_2SiCl_2 vs $PhSiCl_3$) were obtained when pellets containing 90% silicon and 10% silver which had been sintered in hydrogen were used.[46]

A short account concerning E. G. Rochow (Figure 7) should be of interest at this point. He was born on Oct 4, 1909, in Newark, NJ. He obtained his undergraduate degree at Cornell University, where he was associated with Professor L. M. Dennis, whose research focused on fluorine and its compounds, and group 13 and germanium organometallic chemistry. Because of the severe depression in the USA at that time, Rochow

(45) Rochow, E. G. *J. Am. Chem. Soc.* **1945**, *67*, 963.
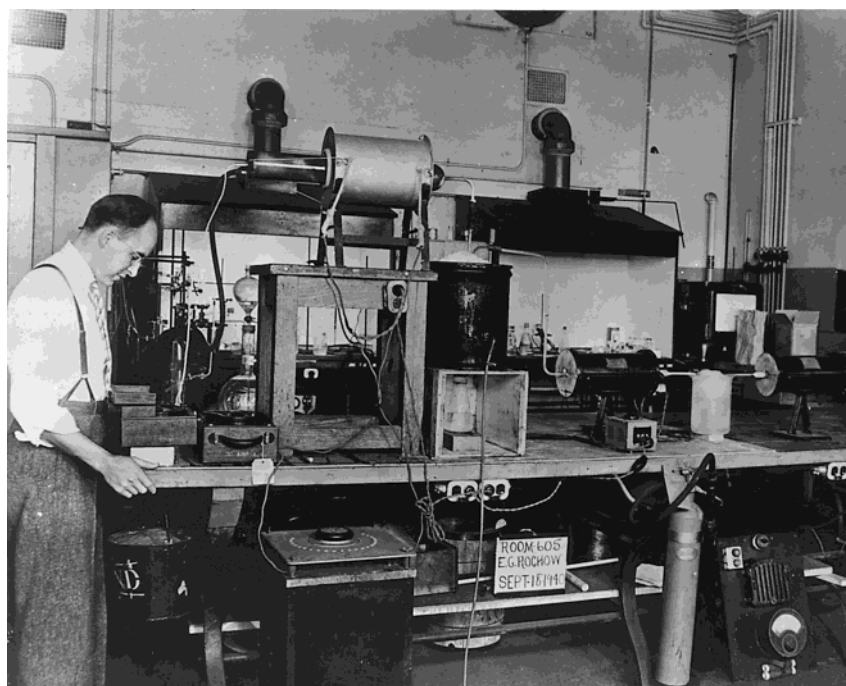(46) Rochow, E. G.; Gilliam, W. F. *J. Am. Chem. Soc.* **1945**, *67*, 1772.

Figure 5. Rochow with his more elaborate direct synthesis apparatus in the GE Research Laboratory (photo by J. P. McNally Photography; American Chemical Society photo archives).

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF THE GENERAL ELECTRIC CO.]

The Direct Synthesis of Organosilicon Compounds

BY EUGENE G. ROCHOW

Organosilicon compounds customarily are prepared by the action of some other organometallic compound upon a silicon halide or an ester of orthosilicic acid. Thus Kipping[1] and his coworkers have employed the Grignard reagent and silicon tetrachloride in their impressive series of investigations,[2] while the alkyls of zinc and mercury were used much earlier by Friedel and Crafts[3] and by Ladenberg.[4] The Wurtz–Fittig synthesis, first used by Polis[5] and later by Kipping and Lloyd,[6] has recently been investigated by Schumb, Ackerman and Saffer,[7] who showed that in certain cases it is advantageous to prepare an organosodium compound separately and then allow it to react with the silicon halide.[8] The action of the Grignard reagent upon ethyl silicate has been described in a series of Russian publications.[9,10]

In all these methods, it has been necessary to prepare the organometallic compound (or a series of organometallic compounds derived one from the other) and then to carry out the reaction with a covalent compound of silicon in a solvent or in an excess of the reagent. The silicon halide must in turn have been prepared from silicon and, if an ester is to be used, it requires reaction of the halide with the corresponding alcohol.

In connection with the investigation of silicone polymers in this Laboratory,[11,12] a simpler and more direct synthesis was highly desirable. Many reactions were tried with negative results, but at length it was found possible to synthesize alkyl- and aryl-substituted silicon halides by the direct reaction of the alkyl or aryl halide with elementary silicon. While this reaction was found first to proceed in the case of methyl chloride passed over an alloy of silicon and copper heated in a tube to a temperature of approximately 360°, subsequent experiments have shown that the reaction is a general one whereby hydrocarbon halides in the liquid or vapor phase are caused to react with silicon in the presence or absence of a metallic catalyst.

Under favorable conditions, the principal product of the reaction between elementary silicon and an alkyl or aryl halide RX is the corresponding dialkyl- or diaryl-dihalosilane, R_2SiX_2. This, may be obtained in yields as high as 70%. Lesser amounts of the related compounds $RSiCl_3$ and R_3SiCl are obtained at the same time, and even some R_4Si and SiX_4. Under conditions which encourage some pyrolysis of free hydrocarbon

(1) Kipping, *Proc. Chem. Soc.*, **20**, 15 (1904). The method also was employed at about the same time by Dilthey, *Ber.*, **37**, 319 footnote 2 (1904).
(2) See bibliography on pp. 290, 291 of Krause and von Grosse, "Die Chemie der metallorganischen Verbindungen," Berlin, 1937.
(3) Friedel and Crafts, *Ann.*, **136**, 203 (1865). See also Friedel and Ladenberg, *ibid.*, **159**, 259 (1871), and **203**, 251 (1880).
(4) Ladenberg, *ibid.*, **164**, 302 (1872); **173**, 151 (1874).
(5) Polis, *Ber.*, **18**, 1540 (1885).
(6) Kipping and Lloyd, *J. Chem. Soc.*, **79**, 449 (1901).
(7) Schumb, Ackerman and Saffer, THIS JOURNAL, **60**, 2486 (1938).
(8) Schumb and Saffer, *ibid.*, **63**, 93 (1941).
(9) Andrianov and Gribanova, *J. Gen. Chem.* (U. S. S. R.), **8**, 552 and 558 (1938).
(10) Andrianov and Kamenskoya, *ibid.*, **8**, 969 (1938).

(11) Rochow and Gilliam, THIS JOURNAL, **63**, 798 (1941).
(12) Gilliam, Liebhafsky and Winslow, *ibid.*, **63**, 801 (1941).

Figure 6. Rochow's 1945 *J. Am. Chem. Soc.* paper.[45] It was concise, only three pages in length, but it was one of the most important papers in the history of organosilicon chemistry.

stayed at Cornell for his graduate studies, continuing research with Dennis. He worked on the electrochemical preparation of fluorine and studied the oxyacids of fluorine but also, in a separate project, worked on the synthesis and properties of trimethylindium and triethylthallium. He became acquainted with silicon chemistry when he was a special assistant of Alfred Stock during the year that Stock was the George Fisher Baker Lecturer at Cornell. (In his book,[35] Stock thanks Rochow for preparing most of the illustrative drawings in the book.) In 1935, Rochow began his career at GE, first spending several years in the area of ceramics. Then came his extensive research in organosilicon chemistry. During these years he continued work on the direct
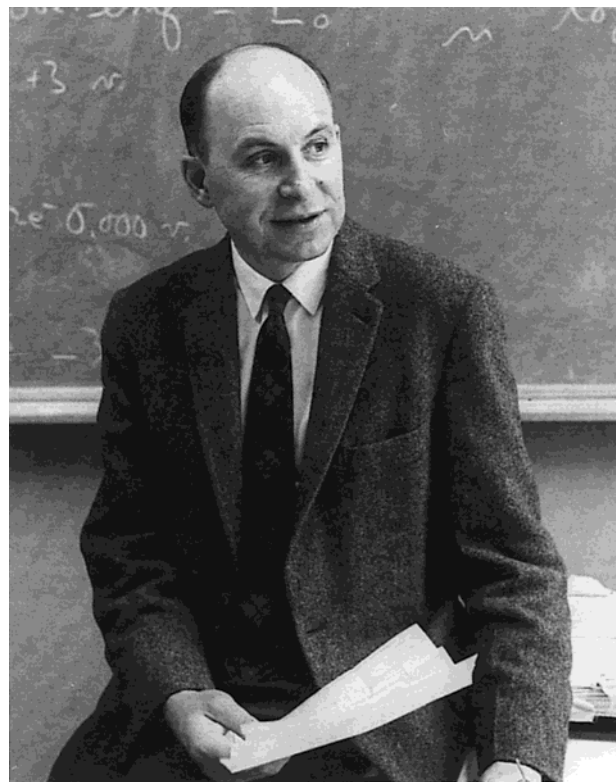

Figure 7. Eugene G. Rochow (courtesy of Prof. E. G. Rochow).

synthesis of methyl- and ethylchlorosilanes and extended it to the synthesis of methyl- and ethylchlorogermanes by reaction of CH_3Cl and C_2H_5Cl, respectively, with a Ge/Cu reaction mass at 320–350 °C.[47] He also found that methanol reacted with a powdered 90% Si/ 10% Cu mixture at 250 °C to give $(CH_3O)_4Si$ as the

(47) (a) Rochow, E. G. *J. Am. Chem. Soc.* **1947**, *69*, 1729. (b) **1950**, *72*, 198.

major product.[48] The reaction, however, gave also minor products containing Si−H and Si−CH$_3$ bonds.

Rochow left GE in 1948 to join the faculty of the Harvard University Chemistry Department. He taught courses in general and inorganic chemistry. His freshman general chemistry lectures were entertaining and instructive and were very popular with the students. His research activities were quite varied. They included topics such as the use of ClF$_3$ as a fluorinating agent, electrode potentials in silicate melts, and extensions of the direct synthesis to the reactions of CH$_3$Cl with molten Sn/Cu at 300−350 °C to produce methyltin chlorides (with very high selectivity to (CH$_3$)$_2$SnCl$_2$)[49] and with arsenic- and antimony/copper mixtures at 350−375 °C to give the monomethyl dichlorides and dimethyl chlorides of these elements.[50] Further studies of the ROH + Si/Cu reaction also were carried out, and the reaction of Si/Cu with ethers at high temperature was investigated. Organosilicon polymers continued to be of interest. Of note were the first low-resolution (broadline) NMR spectroscopic studies of molecular motion in organosilicon polymers and the first syntheses of polysilazanes. Application of the then new high-resolution NMR spectroscopy to the determination of the relative electronegativities of the group 14 elements led to further work, whose culmination was the Allred−Rochow electronegativity scale, which can be found in every inorganic chemistry textbook. This distinguished research career was recognized with many awards, including the 1965 Frederic Stanley Kipping Award in Organosilicon Chemistry and the Alfred Stock Medal of the German Chemical Society. A *Chemical Reviews* article in 1947 on "The Present State of Organosilicon Chemistry"[51] and especially his book, *An Introduction to the Chemistry of the Silicones*,[52] were very influential worldwide by pointing out the known and potential applications of organosilicon chemistry; they attracted many chemists into this field. Rochow retired from his position on the Harvard faculty in 1970, but his interest in organosilicon chemistry and in chemistry in general has not waned. He continued his writing (four books since 1970) and he has attended and spoken at many of the national and international conferences devoted to organosilicon chemistry since 1970. (For a biographical sketch of E. G. Rochow, published on the occasion of his 70th birthday, see Seyferth, D. *J. Organomet. Chem.* **1979**, *178*, ix−xii.)

Unknown to the chemists at GE and Corning, the direct synthesis of methylchlorosilanes was discovered independently, but after Rochow's discovery, by Richard Müller in Germany. Müller had been trying to improve the synthesis of HSiCl$_3$ in the early 1930s for possible use as a military smoke agent. He found that the reaction of gaseous HCl with a high-silicon (>80%) ferrosilicon admixed with a copper compound (CuO, CuCl, CuCl$_2$, CuCO$_3$) proceeded rapidly below 300 °C to give HSiCl$_3$ in good yield. Even better results were

Figure 8. Richard Müller (courtesy of Professor H. Schmidbaur).

obtained when the reaction was carried out under pressure.[53] Further experiments on similar reactions of Si/Cu with chloroform gave, as Müller said,[54] "no organochlorosilanes in the ordinary sense, and, therefore, we abandoned that method." A reaction of methyl chloride with Si/Cu was tried only some years later. It is not exactly clear just when this independent discovery of the CH$_3$Cl + Si/Cu-based methylchlorosilane process was made, since details are lacking. One article says that it was in 1941/1942.[55] Müller, in his short history of organosilicon chemistry,[54] said "I sometimes wonder why the idea took me such a long time so that E. G. Rochow could precede me by nine months." But earlier in this paper, he puts Rochow's discovery as occurring in 1941, not in 1940..... Müller's discovery was disclosed in a German patent application (DRP Anm. C57 411, with a secrecy restriction) in June 1942. After that, the project was discontinued (the German bureaucrats involved did not recognize the importance of this work) and was revived again only after the end of the war, in the early days of the German Democratic Republic (DDR).

A few words about Richard Müller (1903−1999) (Figure 8) are warranted.[56] He was born in Saxony and studied at the University of Leipzig. He obtained his Ph.D. in 1931, having carried out his dissertation research on the system nickel oxide/oxygen/hydrogen. Employment in industry (Chemische Fabrik von Heyden in Radebeul, near Dresden) followed. He worked on various projects; research in silicon chemistry began in

(48) Rochow, E. G. *J. Am. Chem. Soc.* **1948**, *70*, 2170.
(49) Smith, A. C., Jr.; Rochow, E. G. *J. Am. Chem. Soc.* **1953**, *75*, 4103.
(50) Maier, L.; Rochow, E. G.; Fernelius, W. C. *J. Inorg. Nucl. Chem.* **1961**, *16*, 213.
(51) Burkhard, C. A.; Rochow, E. G.; Booth, H. S.; Hartt, J. *Chem. Rev.* **1947**, *41*, 97.
(52) Rochow, E. G. *An Introduction to the Chemistry of the Silicones*; Wiley: New York, 1946 (1st ed.); 1951 (2nd ed.).

(53) Müller, R. *Chem. Tech.* **1950**, *2*, 7, 41. German patents were applied for on this work in 1934 and 1938 and granted in 1936 and 1939, respectively, but were put under a secrecy restriction by the German government and not made public.
(54) Müller, R. *J. Chem. Educ.* **1965**, *42*, 41 (entitled "One Hundred Years of Organosilicon Chemistry"− an eight-page historical review with pictures of all the silicon chemists involved: Friedel, Crafts, Ladenburg, Kipping, Dilthey, Stock, R. Schwarz, Rochow, Hyde, Patnode, Andrianov, Dolgov). German version: *Wiss. Z. Tech. Univ. Dresden* **1963**, *12*, 1633.
(55) Reuther, H. *Chem. Techn.* **1953**, *5*, 297.
(56) For brief biographical sketches, see ref 55 and an obituary: Schmidbaur, H. *Nachr. Chem. Techn. Lab.* **1999**, *47*, 1261.

Figure 9. Eugene G. Rochow and Richard Müller at the "Munich Silicon Days" Conference, August 1992 (by permission, Doris Wacker, Wacker-Chemie GmbH).

1934 and continued until 1942. After the end of World War II, under the DDR, Müller was instrumental in getting silicone production in Nünchritz, near Radebeul, started. He resumed research and development activity on organosilicon chemistry. By 1955, the direct synthesis of methylchlorosilanes was operative in the plant in Nünchritz and Müller became director of the new Institut für Silikon- und Fluorkarbon-Chemie in Radebeul. In 1954, he was appointed Professor in the Technical University of Dresden, where he lectured on silicone, fluorocarbon, and polymer chemistry. He was relieved of all these positions in 1968, at age 65—he had not been a friend of the DDR regime. His research activity in the postwar years dealt primarily with the synthesis and diverse applications of the silicones. He also carried out research in other areas of organosilicon chemistry, returning to the reaction of chloroform with Si/Cu at 300 °C in 1958. Interesting trichlorosilyl derivatives were found: $(Cl_3Si)_2CH_2$, $Cl_3SiCH_2SiHCl_2$, $Cl_3SiCH(SiHCl_2)_2$, $(Cl_3Si)_2CHSiHCl_2$, and $(Cl_3Si)_3CH$.[57] A similar reaction of CCl_4 gave $C(SiCl_3)_4$, $Cl_3SiC\equiv CSiCl_3$, $Cl_3SiCCl=CClSiMe_3$, and smaller amounts of $Cl_3Si-CCl=CCl_2$ and $(Cl_3Si)_2C=C=C(SiCl_3)_2$.[58] Also of interest were studies of the clathrates of linear polysilanes, n-Si_nH_{2n+2},[59a] and of linear mono- and dialkylsilanes with urea and thiourea,[59b] but his most extensive research activities outside of silicone chemistry were devoted to the preparation and chemistry of organofluorosilanes. Of special interest was his pioneering work on the preparation and applications in synthesis of hypercoordinate organofluorosilicates that contained anions of the types $[RSiF_4]^-$ and $[RSiF_5]^{2-}$, which were found to be effective sources of nucleophilic alkyl and aryl groups in aqueous solution ("green" chemistry before its time).[60] In 1992, during a meeting in Munich whose purpose was to celebrate the 50th anniversary of the direct synthesis of methylchlorosilanes, Eugene Rochow and Richard Müller were each honored with a Wacker-Silikon-Preis (Figure 9).

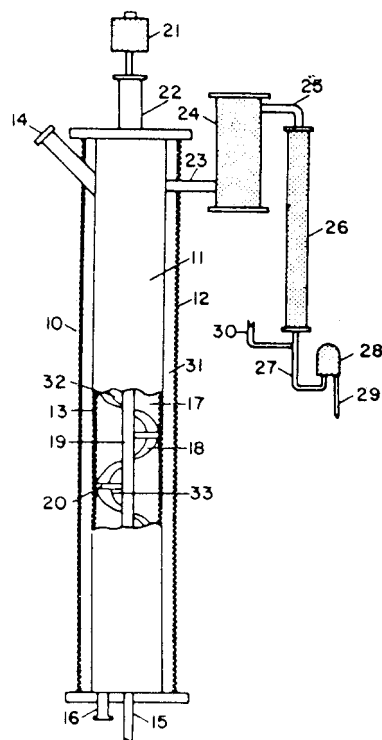We return now to the GE Research Laboratory in order to follow our cover molecule from the laboratory

(57) Müller, R.; Seitz, G. *Chem. Ber.* **1958**, *91*, 22.
(58) Müller, R.; Beyer, H. *Chem. Ber.* **1959**, *92*, 1018.
(59) (a) Müller, R.; Meier, G. *Z. Anorg. Allg. Chem.* **1965**, *337*, 268. (b) **1964**, *332*, 81.
(60) (a) Müller, R. *Z. Chem.* **1965**, *5*, 220. (b) *Organomet. Chem. Rev.* **1966**, *1*, 359.


Figure 10. Stirred bed reactor used initially in the CH_3-Cl + Si/Cu direct synthesis (from ref 41a, by permission of John Wiley & Sons, Inc.).

to the plant.[41a,b] It is a long way from the first successful experiment to the plant—from Rochow's initial 5 cm^3 of product to commercial quantities of methylchlorosilanes. More chemists were assigned to the silicone project. There was much to do in research, scale-up in the pilot plant, and process development. Very quickly, a small-scale pilot operation was started in the Research Laboratory to investigate the problems of larger scale synthesis and to produce the methylchlorosilanes in larger quantities for study of their chemistry. A better Si/Cu reaction mass was developed; but many other metals besides copper were tested to make sure that nothing would be missed. As in the case of the HCl + Si reaction, copper turned out to be the best one for the methyl chloride reaction. Addition of other gases was studied. Dilution of methyl chloride with nitrogen proved to be beneficial, and addition of hydrogen increased the yield of byproduct CH_3SiHCl_2, which later was found to have useful applications. In these early studies, zinc was discovered to be a useful additive to the Si/Cu reaction mass; it was a promotor, and it made the catalyst more effective. The first studies concerning the mechanism of the direct reaction were carried out. (Such studies are still being pursued now, 60 years later.) There was some urgency to all these efforts because there were important real and potential applications of some silicones in the war effort. Silicone fluids and silicone rubber had been discovered. The methylchlorosilane hydrolysis products had been found to be good water repellents and, as such, had found an application in the waterproofing of insulators in radios in military aircraft.

In addition to the methylchlorosilanes, $(CH_3)_2SiCl_2$ (the most desirable product), CH_3SiCl_3, and $(CH_3)_3SiCl$, many other compounds were found to be present in the
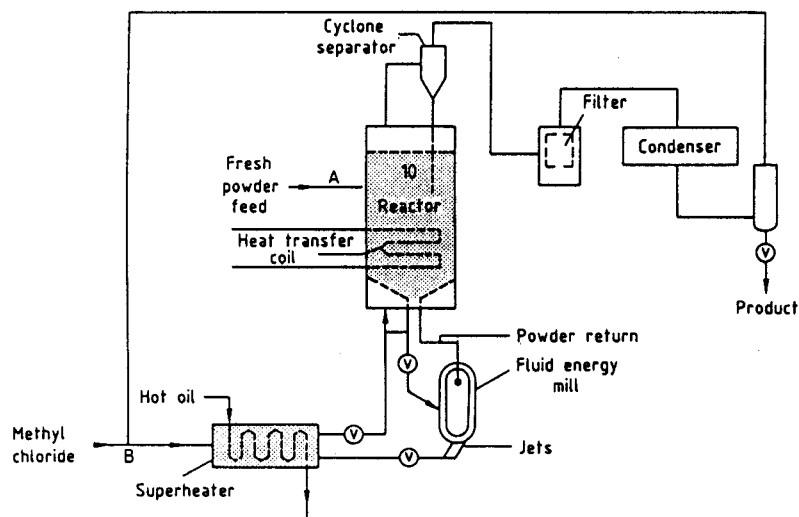
Figure 11. Fluid-bed reactor with associated fluid-energy mill used in the CH_3Cl + Si/Cu direct synthesis: Powdered Si/C feed at A; CH_3Cl feed at B (from ref 41b, by permission of Springer-Verlag).
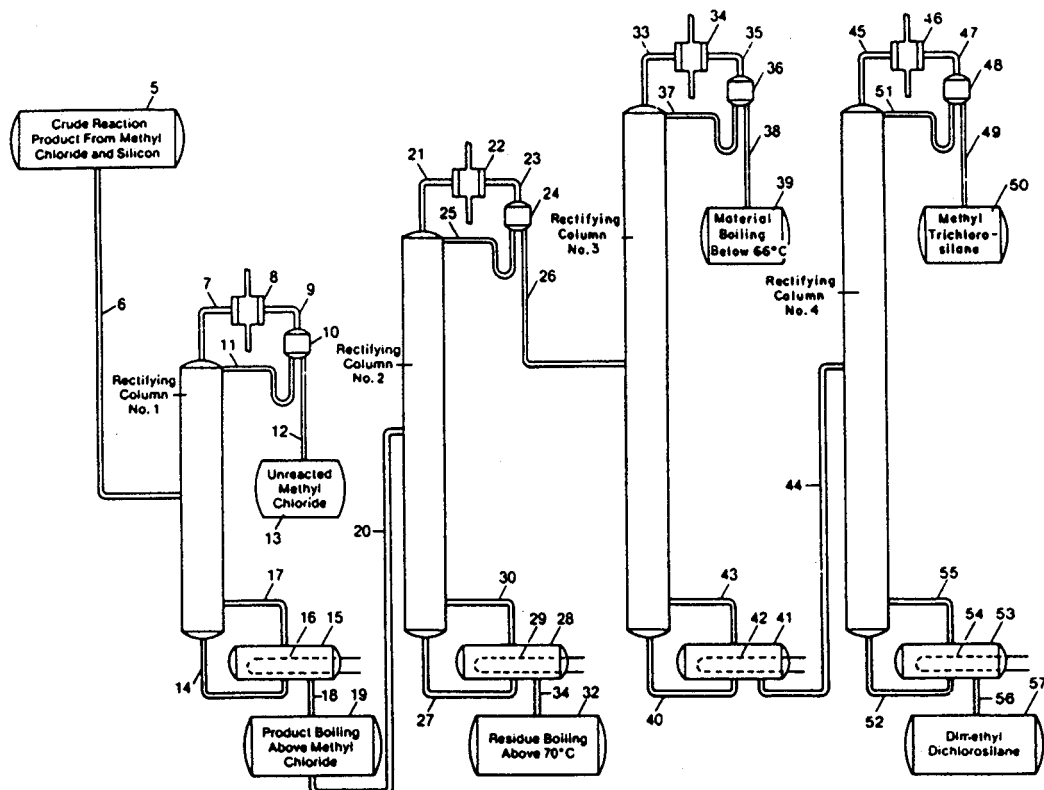

Figure 12. Distillation system used to obtain the pure methylchlorosilanes (from ref 41b, by permission of Springer-Verlag).

reaction product mixture, most of them minor compared to the three above, and these had to be separated and identified. As a result of various studies worldwide, the following compounds were found: CH_3SiHCl_2, $SiCl_4$, $(CH_3)_4Si$, $(CH_3)_2SiHCl$, $HSiCl_3$, H_2SiCl_2, R_nSiCl_{4-n} (R > CH_3); disilanes $((CH_3)_3SiSi(CH_3)_3$, $Cl_3SiSiCH_3Cl_2$, $(CH_3)_3SiSi(CH_3)_2Cl$, $(CH_3)_2ClSiSiCl(CH_3)_2$, $Cl_3SiSiCl_3$, $Cl_2(CH_3)SiSi(CH_3)_2Cl_2$, $Cl_2(CH_3)SiSi(CH_3)Cl_2$); sila-alkanes $(Cl_3SiCH_2SiCl_3$, $[(CH_3)_nSiCl_{3-n}]_2CH_2$, $(CH_3)_n$-$(SiCH_2Si)Cl_{6-n}$, $(CH_3)_n(SiCH_2CH_2Si)Cl_{6-n}$, $(CH_3)_n(SiCH_2$-$SiCH_2Si)Cl_{8-n})$; siloxanes $((CH_3)_2HSiOSiH(CH_3)_2$, $(CH_3)_3$-$SiOSi(CH_3)_3$, $[(CH_3)_nSiCl_{3-n}]_2O$, $(CH_3)_nCl_{6-n}Si_2O)$; some hydrocarbons $(CH_4$, C_2H_6, $C_2H_4)$; H_2.[61] The compounds containing two or more silicon atoms constitute the "high boiling residue", the disilane fraction of which can be converted to useful methylchlorosilanes by several different methods. The direct reaction of methyl chloride with Si/Cu obviously is a process of some complexity.

Over the years, at GE, Dow Corning, Union Carbide, and the other methylchlorosilane producers, many studies devoted to obtaining an understanding of the mechanism of the CH_3Cl + Si/Cu reaction were carried out. Additives to the Si/Cu contact mass were investigated: elemental metals and metal compounds. Tin in combination with zinc was found to be a good promoter; lead

(61) Voorhoeve, R. J. H. *Organohalosilanes. Precursors to Silicones*; Elsevier: Amsterdam, 1967.

Table 1. Properties of the Polysiloxanes

(1) high thermal stability
(2) unusually weak intermolecular forces
   • lower than expected boiling points
   • remarkably low freezing and pour points
   • relatively low surface tension (spreading ability)
   • small variation of physical properties with temperature
     (viscosity: very low E_{act} for viscous flow)
   • high compressibility
   • low glass transition temperatures: $(Me_2SiO)_n$ −120 °C
     vs polypropylene −35 °C, poly(methyl methacrylate)
     +105 °C
(3) higher permeability (gases)
(4) water repellency
(5) nontoxic

Table 2. Some Applications of Silicones (from Ref 41a with Permission of John Wiley & Sons, Inc.)

Automotive	
wire insulation	special lubricants
transmission seals	hydraulic bumpers
spark-plug boots	truck hose
Electrical/Electronic	
motor and transformer insulation	transistor encapsulants
wire and cable insulation	circuit encapsulants
circuit board laminates	television insulation
telephone wire connectors	rubber tapes (adhesive)
Military/Aerospace	
aircraft seals	special lubricants
firewall insulation	heat shields
Paper	
antistick surfaces	process defoamers
Textiles	
water repellents	dyeing-process defoamers
fabric softeners	
Rubber	
tire release coatings	
Food	
coffee defoamers	milk-carton release coatings
bread pan coatings	cooking-process defoamers
Construction	
window and building sealants	weather-durable paints
roof coatings	heat-resistant paints
masonry water repellents	
Plastic Tooling	
furniture molding	jewelry molding
vinyl shoe molding	
Consumer Products	
RTV sealants	eye-glass tissues
tile grout	lubricant sprays
shoe water repellents	
Chemical Specialties and Cosmetics	
auto and furniture polish	hand creams
antiperspirants	bath oils
hair sprays	foaming agents
Medical	
prostheses	contact lenses
artificial organs and skin	catheters
facial reconstruction	drug delivery systems

was a poison. Aluminum, antimony, arsenic, bismuth, and phosphorus were found to have beneficial effects. The study of the mechanism of the reaction of a gas with a solid consisting of two different elements and involving several phases is fraught with difficulties. Obviously, the initial reaction must occur at the surface of the solid phase; therefore, a good understanding of the nature of the surface is required. Where does the initial attack occur—at the copper, at silicon, or at the silicon−copper boundary? What happens then? What surface intermediates are involved? How are the products formed? What determines the selectivity? There are many questions, all difficult to answer. Collaborative surface science analytical studies by Lewis and co-workers at the Union Carbide Silicones Division Research Laboratory and Falconer and co-workers at the University of Colorado in Boulder[62] provided strong evidence that the CH_3Cl + Si/Cu direct synthesis proceeds by way of surface-confined silylenes: CH_3SiCl as the $(CH_3)_2SiCl_2$ precursor and $SiCl_2$ as the precursor for CH_3SiCl_3, with all other organosilicon products except $(CH_3)_4Si$ originating from silylene intermediates. Key experimental support was provided by the observation, by mass spectrometry, of a desorbed species of mass 78 (CH_3SiCl) following CH_3Cl chemisorption on silicon-enriched surfaces of a Si/Cu catalyst.

Further scale-up at GE was a chemical engineering project, and to accomplish this task, Charles A. Reed, an assistant professor of chemical engineering at MIT, was hired in 1942. A larger pilot plant was built in the Schenectady laboratory which contained 12 vertical reactors, each of which produced 5.5−6.5 lb/h of operation and allowed a thorough process study to be carried out. The separation of the pure individual methylchlorosilanes was an important and very difficult problem because of their close boiling points, as noted above. In his book,[41a] Liebhafsky describes the development of the distillation process as "unexpectedly painful, frustrating and costly." However, in the end, the individual methylchlorosilanes were obtained in the required purity.

In December 1943, GE made the decision to go into the silicones business: a silicone production and pilot plant facility was to be built. The plant went on stream in Waterford, NY, in 1947, seven years after Rochow's first experiment, with Reed as first General Manager of the GE Silicone Products Department. At the begin-

ning, the direct reaction of CH_3Cl with Si/Cu was carried out in a stirred-bed reactor (Figure 10) and later using a fluidized bed reactor (Figure 11). The separation of the low-boiling products of the direct synthesis could be accomplished satisfactorily in the plant, despite the close boiling points of the components (a schematic diagram of the distillation unit used is shown in Figure 12). Dimethyldichlorosilane could be obtained in 99.9% purity. This is important for its further utilization in the production of linear silicone fluids and silicone rubber gum, where the presence of the trifunctional CH_3SiCl_3 or the tetrafunctional $SiCl_4$ would result in unwanted cross-linking. The other methylchlorosilanes have found various uses, but it is $(CH_3)_2SiCl_2$, our cover molecule, which is the most important: it is *the* molecule which made the silicone industry a reality.

GE was not alone in the silicones business. Dow Corning, because of the initial military applications, with decisive support from the US Navy, had the plant and the opportunity to start producing and selling silicones before GE began to do so. Initially, their methylchlorosilanes were prepared on a plant scale by the Grignard route, but later they licensed GE's direct

(62) (a) Lewis, K. M.; McLeod, D.; Kanner, B.; Falconer, J. L.; Frank, T. C. In *Catalyzed Direct Reactions of Silicon*; Lewis, K. M., Rethwisch, D. G., Eds.; Elsevier: Amsterdam, 1993; Chapter 16. (b) Lewis, K. M. Abstracts, 34th Organosilicon Symposium, White Plains, NY, May 3−5, 2001; pp HR-2 to HR-6.

process technology. Over the years, their chemists have made outstanding and important contributions to the progress of organosilicon chemistry—in research and in the development of many new and useful silicone products. They became the largest silicone producer in the world.

Union Carbide Corp. also entered the silicones business, as did companies in other countries (among them Wacker-Chemie, Bayer, Shin-Etsu, Toshiba Silicones, and Rhône-Poulenc). The direct synthesis today is being practiced all over the world: in the USA, Japan, Germany, France, Russia, the UK, India, Australia, and China. Over the years, the silicones, as a result of their useful and, in many cases, unique physical and chemical properties (Table 1), have found many important ap-

plications in industry and commerce and also in our everyday lives (Table 2).

Today, 61 years later, Rochow's little acorn has grown into a mighty oak indeed. The annual production of $(CH_3)_2SiCl_2$ is around 1.4 million metric tons. The annual production of the derived $[(CH_3)_2SiO]_n$ hydrolysate is around 800 000 metric tons; this has a value of 3–5 billion dollars. However, $(CH_3)_2SiCl_2$ has found many uses outside of the silicone area: in the preparation of silicon carbide fibers by a complex process,[63] the first step of which is its conversion to polydimethylsilylene, $[(CH_3)_2Si]_n$, by sodium condensation;[64] its use in the synthesis of polysilazanes (which was pioneered by Rochow at Harvard),[65] and its use as a starting material in the synthesis of many thousands of organosilicon compounds over the years throughout the world.[66]

(63) Yajima, S. *Am. Ceram. Soc. Bull.* **1983**, *62*, 893.

(64) Burkhard, C. A. *J. Am. Chem. Soc.* **1949**, *71*, 963.

(65) (a) Krüger, C. R.; Rochow, E. G. *J. Polym. Sci. A* **1964**, *2*, 3179. (b) Krüger, C. R.; Rochow, E. G. *Angew. Chem., Int. Ed. Engl.* **1962**, *1*, 458. (c) Rochow, E. G. *Monatsh. Chem.* **1964**, *95*, 750.

(66) Readers who wish to read more about the silicones and their applications and about organosilicon chemistry in general are referred to the following books: (a) Reference 52. (b) Eaborn, C. *Organosilicon Compounds*; Butterworth: London, 1960. (c) Petrov, A. D.; Mironov, V. F.; Ponomarenko, V. A.; Chernyshev, E. A. *Synthesis of Organosilicon Monomers*; Consultants Bureau: New York, 1964. (d) Noll, W. *Chemistry and Technology of the Silicones*; Academic Press: New York, 1968. (e) Brook, M. A. *Silicon in Organic, Organometallic and Polymer Chemistry*; Wiley: New York, 2000. (f) *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappaport, Z., Eds.; Wiley: Chichester, U.K., 1989; Vol. 1. *The Chemistry of Organic Silicon Compounds*; Rappaport, Z., Apeloig, Y., Eds.; Wiley: Chichester, U.K., 1998; Vol. 2. For a more complete listing, see ref 66e, pp 5–9. Reference 66d gives a good account of the utilization of $(CH_3)_2SiCl_2$ in the preparation of silicones: its hydrolysis and the further processing of the resulting $HO(SiMe_2O)_nH$ linear polymers and $(Me_2SiO)_n$ cyclic oligomers to give, ultimately, the many diverse useful silicone and silicone-derived products.

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