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Essay

A personal history concerning a chance discovery of a road leading to organopolysilane chemistry

Makoto Kumada*

Kyoto University, Kyoto, Japan

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Dedicated to the memory of Professor Eugene G. Rochow

1. Prologue

It was immediately after World War II that I, then an employee of Toshiba Electric Co. Ltd., was deeply impressed with a series of F.S. Kipping's papers on organosilicon chemistry and with two papers by American research groups, and I decided to devote myself to studies of this area of chemistry. One of these two papers was by J.F. Hyde and R.C. DeLong and the other by E.G. Rochow and W.F. Gilliam, both of which appeared in the *J. Am. Chem. Soc.* in 1941 and dealt with synthesis and hydrolysis of organosilicon 'monomers.' Under awfully severe post war conditions that you could hardly imagine, I started synthesis of some alkylsilicon chlorides by means of the classical Grignard reaction that had been used by Kipping since 1904 and by both Hyde and Rochow as well.

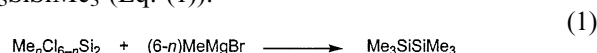
Meanwhile, information became available in Japan on the 'Rochow Direct Process' and commercial production of methyl- and phenylchlorosilanes by this process was commenced both at Toshiba Electric Co. and Shin-Etsu Chemical Industry, a few years after I moved, in 1950, from Toshiba to the Institute of Polytechnics of Osaka City University to join the Faculty staff. Keeping intimate contact with Toshiba, I was very familiar with the Rochow process and became particularly interested, for the following two reasons, in the investigation into the higher-boiling fraction or 'still-pot residue' of methylchlorosilanes from the direct process, the residue being put aside as waste. One reason was that, to my best knowledge at that time, little if any attention was focused upon this

subject, and the other reason was that I thought that if I had made frontal attack on the then rapidly developing organosilicon chemistry in the USA, Europe and USSR I should always be subordinate to foreign researchers.

2. A chance discovery of hexamethyldisilane [1]

Time-consuming fractional distillation of the 'still-pot residue' through a home-made long Fenske-type distillation column could not permit me to separate any substance in a pure state because of a complex mixture of constituents with boiling points in close proximity, so I treated a number of fractions with the methyl Grignard reagent in order to replace all of the chlorine atoms attached to silicon by methyl groups so as to simplify the mixture and hence make separation by distillation possible.

On a very cold winter morning of 1953, when performing fractional distillation of an exhaustively-methylated product from the fraction boiling around 150 °C, I observed a distillate boiling at about 112 °C crystallized just at the exit of the distillation column, thanks to the laboratory not being heated. It took no long time before this crystalline substance, with b.p. 113 °C and m.p. 13 °C, proved to be hexamethyldisilane, $\text{Me}_3\text{SiSiMe}_3$ (Eq. (1)).



I remember clearly that I jumped up with joy when I recognized it, because although this had been a known compound since 1912 (A. Bygden)–1913 (G. Martin) only a very limited range of studies with very small quantities of this compound had been reported, and now it became possible to prepare, with great ease, this lowest member of the peralkylated polysilane family in

* Tel.: +81-726-34-5522. Present address: 2-1-15 Ohike, Ibaraki, Osaka 567-0826, Japan.

E-mail address: tamao@scl.kyoto-u.ac.jp (M. Kumada).

large quantities by using, as starting material, the ‘still-pot residue’ from the Rochow process. I was proud of getting several hundred grams of hexamethyldisilane for the first time throughout all ages and countries.

Similar ‘exhaustive’ methylation of many fractions from the ‘still-pot residue’ allowed me to conclude that the residue consists mainly of three types of compounds named ‘disiloxane fraction’, ‘disilane fraction’ and ‘disilmethylene fraction’, with molecular framework and approximate boiling range as shown below:

Disiloxane fraction	Si–O–Si	b.p. 100–150 °C
Disilane fraction	Si–Si	b.p. 150–160 °C
Disilmethylene fraction	Si–CH ₂ –Si	b.p. 160–200 °C

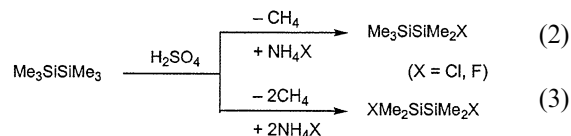
3. Halogen cleavage of the Si–Si bond [2]

Of these three, I, of course, took the greatest interest in the disilane compounds. Immediately after the synthesis of hexamethyldisilane and some mixed methylalkyldisilanes, I observed an enormous reactivity of the Si–Si bond of these molecules to cleavage by halogen: with chlorine was it necessary to pass it slowly into a dilute CCl₄ solution of the disilane with cooling because otherwise the reaction was so violent as to take fire. Addition of bromine to a neat disilane had to be performed with careful cooling, whereas the reaction with iodine required reflux. Each reaction gave the corresponding trialkylhalosilane quantitatively, and later the bromine-cleavage reaction often served as a diagnostic procedure for the existence of the Si–Si bond in peralkylated silicon compounds. These results were published in 1954, unfortunately in Japanese, in a journal of the Chemical Society, Japan, though we obtained a U.S. Patent in 1957 for the process for preparing trialkylhalosilanes by the Si–Si cleavage. This is a story of my studies on organo(mostly methyl) polysilane chemistry.

4. Silicon-functional disilanes [3]

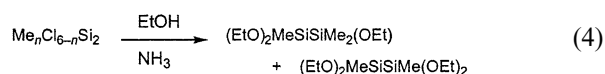
In order to enrich and develop the new area of aliphatic organopolysilane chemistry, I had, above all, to prepare a variety of silicon-functional di- and polysilanes of definite structure as the building block for further synthesis. In 1956, with some of my students, I worked out two approaches particularly convenient for this purpose.

The first method was demethylation of hexamethyldisilane with concentrated sulfuric acid followed by treatment with ammonium chloride or fluoride (or better, ammonium hydrogen fluoride) (Eqs. (2) and (3)):



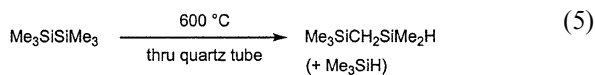
Removal of one methyl group as methane from silicon in 3-(trimethylsilyl)-propionic acid by sulfuric acid (in a homogeneous solution) had been reported very recently by Sommer et al. (1953) and subsequently by Speier et al. (1955). Although hexamethyldisilane, just like liquid saturated hydrocarbons, is insoluble in, and unreactive with concentrated sulfuric acid under ambient conditions, we ventured to stir vigorously a heterogeneous mixture of these two ingredients at room temperature in a flask fitted with a tube connected to a gas collector. To our full satisfaction, relatively rapid evolution of methane did occur until one equivalent of it was collected. Collection of a second equivalent required much longer time or higher temperature, although the reaction system became homogeneous. In this way, the demethylation reaction proceeded in two distinct steps so that either the monohalo- or 1,2,-dihalodisilanes could be prepared in a pure state as one wished in high yields.

The second method for synthesis of silicon-functional disilanes of definite structure involved ethanolysis of the ‘disilane fraction’, which gave a mixture consisting mainly of two compounds, readily separable by fractional distillation: 1,1,2-triethoxytrimethyldisilane and 1,1,2,2-tetraethoxydimethyldisilane (Eq. (4)). This observation indicates that the ‘disilane fraction’ consists mainly of two kinds of methylchlorodisilanes: 1,1,2-trichlorotrimethyldisilane and 1,1,2,2-tetrachlorodimethyldisilane.



5. Disilane to disilmethylene thermal rearrangement

Among many reactions of methyl-disilanes disclosed in the laboratory of Osaka City University, the most impressive was the thermal rearrangement of hexamethyldisilane to pentamethyldisilmethylene occurring when the former was passed through a quartz tube heated to ca. 600 °C, which reaction I, in collaboration with K. Shiina, observed in 1957 (Eq. (5)). We published this unprecedented transformation along with a postulated radical chain mechanism involving initial production of the Me₃Si• free radical in J. Org. Chem., 1958 [4].



In July 1962, I moved from Osaka City University to a recently founded chemistry department at Kyoto University, in company with H. Sakurai and M. Ishikawa who had just obtained his PhD degree. In 1968, the same disilane-to-disilmethylene transformation was observed to occur at as low a temperature as 450 °C in a closed vessel, by Sakurai in our laboratory [5].

In later years, this type of thermal rearrangement aroused considerable interest of researchers engaged in gas-phase kinetics on the one hand, and served as a model reaction underlying the first stage of the Yajima process of silicon carbide fiber production (1975) on the other.

6. Epilogue

I am very happy to say that thanks to the intelligence and efforts of a number of excellent coworkers and students, syntheses of many new compounds and

discoveries of many new reactions associated with the Si–Si bond came out in succession from our Kyoto laboratory, that I believe have contributed not a little to the recent advance in polysilane chemistry and related area.

In conclusion, it is safe to say that a chance discovery of hexamethyldisilane to be prepared conveniently and in quantities from the ‘still–pot residue’ of the Rochow process, together with lucky success in highly selective halogenodemethylation of the disilane, paved the way to a magnificent flower garden of polysilane chemistry.

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