[CONTRIBUTION FROM THE RESEARCH LABORATORY, GENERAL ELECTRIC COMPANY]

Dimethyl Silicon Dichloride and Methyl Silicon Trichloride[1]

BY W. F. GILLIAM, H. A. LIEBHAFSKY AND A. F. WINSLOW

Although organic silicon compounds have been known and studied for almost eighty years the pure methyl silicon chlorides have not been previously prepared,[2] probably because the boiling points of the substances are anomalous; that is, dimethyl silicon dichloride and methyl silicon trichloride, both of which we have made by the Grignard reaction, boil near 70°, appreciably above the temperature range (26–57.6°) fixed by the boiling points of silicon tetramethyl and silicon tetrachloride.

Two attempts at solventless preparation failed.[3] Preparations in dibutyl ether were sufficiently successful to reveal that the boiling points of the chlorides are high enough so that diethyl ether, in which the Grignard reagent is much more soluble, could be used in subsequent preparations without fear of complicating the fractional distillations involved.

Dimethyl Silicon Dichloride.—To 143 cc. (1.25 moles) of silicon tetrachloride and 950 cc. of dibutyl ether in a 5 liter 3-neck flask (equipped with a condenser at −78.5°, mechanical stirrer, separatory funnel, drying tubes of activated alumina, and immersed in an alcohol–carbon dioxide bath at −40°),[4] 3.3 liters of 1 *M* methylmagnesium chloride was added slowly and with constant stirring over two and one-half hours; the Grignard reagent had been previously refluxed to remove methyl chloride. After having been warmed to room temperature, the flask was connected to a series of liquid-air traps, in which 350 cc. of condensate was subsequently collected by reducing the pressure. The liquid was next introduced into a suitable vacuum system equipped with a low temperature fractionating column, where it was subjected to repeated fractionation that did not, however, lead to the isolation of a pure substance.

A portion of the resulting material was therefore distilled at atmospheric pressure in a small column of the total condensation, partial take-off type, equipped with a glass spiral packing and protected from moisture by a phosphorus pentoxide tube. On the 1 cc. of material collected between 67 and 70°, the following information was obtained: Empirical formula by complete analysis, $(CH_{2.82})_{2.10}SiCl_{1.81}$. Molecular weights from vapor densities, 132 at 34.4 mm. and 134 at 69.5 mm., in good agreement with 129 for $(CH_3)_2SiCl_2$, if a slight association of the gas is assumed. Vapor pressures of the liquid, 44.5 mm. at 0° and 133 mm. at 25°.

1.5 cc. obtained by similarly fractionating another portion of the same material had these properties: boiling point, 69.0–70.2° (744.5 mm.). Composition, H, 5.08; C, 20.32; Si, 23.46; Cl, 54.64; for $(CH_3)_2SiCl_2$ these values are 4.69, 18.60, 21.75 and 54.96. Empirical formula by complete analysis, $(CH_{2.98})_{2.08}SiCl_{1.84}$. Freezing point under the pressure of its vapor, −86°. The foregoing experimental evidence establishes that we have prepared dimethyl silicon dichloride.

For the preparation in diethyl ether, 2.05 liters of 2.3 *M* methylmagnesium chloride was added slowly at room temperature to 212 cc. of silicon tetrachloride in 500 cc. of the absolute ether. The solution was centrifuged, then filtered to remove finely divided magnesium chloride. The ether was separated slowly between 32.8 and 35° in a large fractionating column (total condensation, partial take-off type) packed with glass helices. The distillate had no odor of chlorides, but gave a positive test with silver nitrate solution. The residue was then fractionally distilled with the following results

Fraction	1	2	3	4	Residue
Wt., g.	25.3	11.3	16.0	26.5	15.2
B. p., °C.	35–67	67–69	69–70	70–70.3	...

For Fraction 4: Si, 21.18; Cl, 55.29; Si:Cl, 1:2.07. Liquid density, 1.06 g./cc. at 25°. No visible evidence of thermal decomposition after twelve hours at 200° in Pyrex tubing.

Methyl Silicon Trichloride.—321 cc. (2.8 moles) of silicon tetrachloride in 750 cc. of dibutyl ether was treated with 2.9 liters of 1.18 *M* methylmagnesium chloride, at temperatures between −5° and +5°. The ether solution was siphoned off the precipitated magnesium chloride and repeatedly fractionated in the large column, chlorine determinations being made to follow the course of the distillation. About 10 cc. of liquid with the following properties was finally isolated: boiling point, 66.2–67° (765.8 mm.). Composition, H, 2.16; C, 8.95; Si, 18.43; Cl, 70.04; for CH_3SiCl_3, these values are 2.02, 8.03, 18.77 and 71.18. Empirical formula by complete analysis, $(CH_{2.89})_{1.13}SiCl_{2.98}$. Molecular weights from vapor densities, 155 at 33 mm. and 159 at 66.6 mm., in good agreement with 149.5 for CH_3SiCl_3, if a slight association of the gas is assumed. Vapor pressure, 165 mm. at 24°. Freezing point under the pressure of its vapor, −90°. The foregoing experimental evidence establishes that we have prepared methyl silicon trichloride.

To 455 cc. (3.97 moles) of silicon tetrachloride in 1 l. of absolute diethyl ether, 1.6 l. of 3.1 *M* methylmagnesium chloride was added slowly at room temperature. After separation of the solid magnesium chloride and of the ether between 32.5 and 35°, the residue (286.3 g.) of chlorides was fractionally distilled at 755.4 mm. with these results

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(1) This paper was read on September 10, 1940, at the 100th Meeting of the American Chemical Society, held at Detroit, Michigan.

(2) See, however, Martin, *Ber.*, **46**, 2442 (1913).

(3) Silicon tetrachloride was heated with mercury dimethyl and with zinc dimethyl over a temperature range with and without aluminum chloride as catalyst. Methyl silicon chlorides could not be detected in these reaction mixtures.

(4) Had the boiling points of the methyl silicon chlorides been known, these low temperatures would not have been chosen.

Fraction	1	2	3	4
Wt., g.	91.2	1.5	3.1	19.8
B. p., °C.	34.5–60.5	60.5–64	64–65	65–66
% Cl	.....	...	...	...

Fraction	5	6	7	Residue
Wt., g.	53.2	62.2	8.8	46.5
B. p., °C.	66–67	67–67.5	67.5–81	
% Cl	68.59	68.08		

Fractions 5 and 6 were then combined and redistilled at 753.6 mm. to give

Fraction	1a	2a	3a	4a	Residue
Wt., g.	6.9	60.0[a]	8.3	23.9	16.3
B. p., °C.	63.5–66	66–67	67	67–67.5	

[a] For Fraction 2a: Cl, 68.19. Liquid density 1.23 g./cc. at 26.5°.

The redistillation thus resulted in no further purification, indicating that the limit of the fractionating column had been reached if no constant boiling mixture was involved.

Analytical Methods.—Since the methyl silicon chlorides are volatile liquids that hydrolyze instantly, it was necessary to handle them in a vacuum system in the complete absence of moisture. Furthermore, some of the products of hydrolysis are themselves volatile; others gel in aqueous solution, making exact chloride titrations difficult. The accurate analysis of small samples of these substances presented difficult problems of technique that were satisfactorily solved only after repeated efforts. The earlier analytical experiences cannot be described in detail.

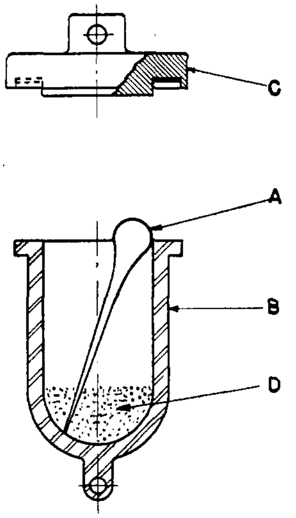

Fig. 1.

An accurately weighed sample for analysis was obtained as follows. A small glass ampoule A (Fig. 1) was dipped in acetone, dried, weighed and inverted into a test-tube sealed to a male ground joint, which was then attached to a vacuum system and exhausted. The substance to be analyzed was distilled into the tube to a depth of 6 mm. or less, liquid nitrogen being used for cooling. The nitrogen bath was then removed, and the solid chloride permitted to melt. The ampoule was now filled by admitting air dried over phosphorus pentoxide into the system; the tube was then re-immersed in liquid nitrogen; when the sample in the ampoule had frozen, the tube was quickly disconnected and the ampoule sealed off before melting began. The sealed ampoule was then dipped in acetone, dried and weighed to give the weight of the sample by difference.

Carbon and hydrogen were determined on 5 to 12 mg. samples in a modified Pregl apparatus.[5] The liquid was centrifuged out of the neck of the ampoule, and the ampoule then broken at the tip and shoved quickly into the combustion tube. In order to avoid explosion of the vapor, the liquid had to be driven out of the ampoule very slowly by gradually advancing a large soldering iron which had been heated to dull redness.

Chlorine determinations were carried out by the Volhard method on 40–70 mg. samples that had been fused with sodium peroxide and sugar in a Parr micro bomb. For the dichloride, 1.5 g. of peroxide and 0.05 g. of sugar were used; for the trichloride, these amounts were increased by 50%.

Fusion in the bomb also preceded the silicon determinations; the contents of the bomb were dissolved in water contained in a platinum dish, and silica was weighed after dehydration with perchloric acid. The ampoules for these determinations were made of a glass containing not over 0.05% Si (spectroscope), which was prepared in platinum from the oxides of boron, aluminum, and barium, and supplied to us by Dr. Navias of this Laboratory.

The following bomb and ampoule technique, which proved uniformly successful, was evolved by trial and error.[6] Ampoules A (Fig. 1) were prepared whose over-all length exceeded by about 3 mm. that of the longest interior diagonal of the bomb B; they were filled, sealed and thoroughly chilled in liquid nitrogen. The tip of such an ampoule was then immersed in the sodium peroxide-sugar charge D, and broken by quickly clamping the cover C in place; ignition followed five minutes later. The ampoules were proportioned so that the break always occurred near the tip.

The methods for chlorine and silicon were tested on redistilled silicon tetrachloride of constant boiling point, 57.7°, with the following results: Si, 16.48; Cl, 82.94 (calculated values, 16.51, 83.49). All analytical results reported are averages of satisfactory duplicate determinations. We are indebted to Mr. J. J. Russell of this Laboratory for several carbon–hydrogen determinations.

Summary

1. Dimethyl silicon dichloride and methyl silicon trichloride have been prepared by the use of the Grignard reagent.

2. The boiling points of these two methyl silicon chlorides are anomalous in the sense that they fall outside the temperature range fixed by

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(5) Niederl and Niederl, "Organic Quantitative Microanalysis," John Wiley and Sons, Inc., New York, N. Y., 1938.

(6) Results obtained when samples were absorbed by the peroxide from an open ampoule were usually slightly high, so that this simple technique had to be abandoned. Reaction between the chlorides and the peroxide is rapid and exothermic; experiments on a vacuum system showed that a slight liberation of oxygen during the reaction was causing the error in question. The proper use of sodium monoxide is a possible remedy.

the boiling points of silicon tetramethyl and silicon tetrachloride.

3. Diethyl ether is a better solvent than dibutyl ether for the preparation of the dichloride. Although the greater yields of the trichloride were obtained with the ethyl ether, the pure trichloride could not be isolated from this solvent.

4. A satisfactory method for the complete analysis of small amounts of easily hydrolyzed volatile compounds containing carbon, hydrogen, silicon and chlorine has been devised.

SCHENECTADY, NEW YORK RECEIVED NOVEMBER 16, 1940

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CALIFORNIA, LOS ANGELES]

The Crystal Structure of Diphenylselenium Dibromide

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Introduction

The investigation of the crystal structure of diphenylselenium dibromide was undertaken for the purpose of studying the effect of the unshared electron pair on the bond orientations and interatomic distances. This subject has recently received attention in the investigations of the structures of the similar molecules, tellurium tetrachloride[1] by the electron diffraction method and the $IO_2F_2^-$ ion in potassium fluoroiodate[2] by means of X-rays. In both cases the evidence favored a trigonal bipyramidal structure with the unshared pair in one of the equatorial positions. This structure is also found in the present study, the bromine atoms forming opposed bonds with selenium, while the phenyl groups form bonds which are in a plane at right angles to the axis of the bromine atoms and making an angle of approximately 110° with each other.

Experimental

Diphenylselenium dibromide was prepared by mixing equimolar quantities of Eastman Kodak Co. diphenylselenium and purified bromine, both dissolved in carbon tetrachloride. The resulting precipitate was dissolved in carbon bisulfide and crystallized by slow evaporation of the solvent. The crystals varied from thin needles along the *b* axis of the unit to plates on (001). Goniometric measurements showed these crystals to be identical to those described by Groth[3] and by Gilta.[4] The crystals are described by both authors as being orthorhombic bipyramidal, the former giving axial ratios $a:b:c = 0.9023:1:0.3758$ and the latter $0.5543:1:0.8334$. These are consistent when the proper transformation is made.

Oscillation photographs were prepared about the three crystallographic axes using Cu-K_α radiation. The photographs about the *b* or needle axis were obtained from an approximately cylindrical crystal having 12 prism faces and a cross-sectional diameter of about 0.1 mm. These photographs were excellent for intensity estimations. The photographs about the *a* and *c* axes were poorer in the order named. This was due to the difficulty of cleaving the thin plates into small enough fragments so that absorption was not troublesome.

Measurements made on these photographs show the size of the unit cell to be $a_0 = 13.95 \pm 0.03$ Å., $b_0 = 5.78 \pm 0.03$ Å. and $c_0 = 15.40 \pm 0.03$ Å. The axial ratios of this cell, $a:b:c = 2.413:1:2.664$, are in excellent agreement with those given by Groth, which on interchange of *b* and *c* axes become $2.401:1:2.662$ and with those of Gilta which become $1:\frac{1}{2}(0.8334):2(0.5543)$ or $2.400:1:2.661$. All indices used in this paper are based on the X-ray unit shown above.

The photographs about all three axes show planes of symmetry as required by the orthorhombic system. The only regular absences found on indexing the photographs were $h0l$ with l odd, $0kl$ with k odd and $hk0$ with $(h + k)$ odd. The space group is accordingly uniquely determined as $D_{2h}^{14} - Pbcn$.

A rough density determination gave the value 2.09 g./cc. which corresponds to 3.98 molecules per unit cell. The calculated density for 4 molecules in the unit is 2.100 g./cc. The intensities used in this analysis were estimated visually with the aid of a calibrated comparison strip and were divided by the Lorentz and polarization factor to obtain values of $|F_{(hkl)}|^2$.

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(1) D. P. Stevenson and Verner Schomaker, THIS JOURNAL, **62**, 1267 (1940).

(2) Lindsay Helmholz and M. T. Rogers, *ibid.*, **62**, 1537 (1940).

(3) P. Groth, "Chemische Krystallographie," Engelmann, Leipzig, 1906, Vol. V, page 40.

(4) G. Gilta, *Bull. Soc. chim. Belg.*, **46**, 275 (1937).