STUDIES ON ORGANOGERMANIUM COMPOUNDS

I. DIPOLE MOMENTS AND NMR SPECTRA OF THE METHYLGERMANES AND THE METHYLGERMANIUM CHLORIDES

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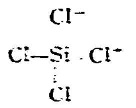
INTRODUCTION

To explain some features related to the chemical bonding in tetrachlorosilane, trichlorosilane, methyltrichlorosilane and monochlorosilane (*e.g.*, the amount of double-bond character; molecular parameters such as internuclear distances and bond angles; physical constants such as electrical dipole moment), Pauling[1] suggested resonance contributions of structures such as:



$$\begin{array}{c} Cl^- \\ Cl{-}Si \cdot Cl^- \\ \vdots \\ Cl \end{array}$$

The methyltin- and methylgermanium halides should have analogous bonding characteristics. These structural particularities stem from the fact that a bond is established between two atoms of unequal electronegativity. We can, therefore, expect that a similar relation exists between the bonding characteristics and the physical constants of the methyltin- and methylgermanium hydrides, although it will be less striking owing to the smaller difference in electronegativity.

Information on this subject can be gained by a study of the vibrational spectra and force constant data, by measuring the electrical dipole moments and by the study of the proton magnetic resonance spectra of such compounds. This series of articles will report on the experimental data obtained from these measurements and their relation to chemical bonding in the methylgermanium chlorides and hydrides.

This paper will deal with the synthesis of the methylgermanium chlorides and hydrides and the measurement of their electrical dipole moments and PMR spectra. An analysis of the vibrational spectra and a general discussion of the experimental data will be published in later communications.

EXPERIMENTAL

I. Preparation of compounds

1. *Tetramethylgermane.* $(CH_3)_4Ge$ can be prepared either by the reaction of dimethylzinc with germanium tetrachloride[2] or by a Grignard synthesis[2-4]. Because

of the danger of manipulating dimethylzinc and because of the high yields reported from the Grignard method of Gladstein[4] and coworkers, the latter method was preferred.

Magnesium turnings (40 g), suspended in 300 ml of dry di-*n*-butyl ether were heated to 40° in a three-necked flask fitted with a stirrer, reflux condenser, separating funnel and thermometer. The reaction was initiated by adding 1 ml of methyl iodide and some iodine crystals. Then the flask was immersed in an ice-salt slush bath and 200 g of methyl bromide, dissolved in 150 ml of di-*n*-butyl ether added at such a rate that the temperature did not rise above 40°. When all the bromide had been added the reaction mixture was heated at 40° until all the magnesium had reacted. The contents of the flask were then cooled to —15° and a solution of 48 g of $GeCl_4$ in 50 ml of di-*n*-butylether added dropwise. After the addition was completed the temperature was raised slowly to 80° and maintained at this level for 2 h. The flask was cooled and water added dropwise to destroy excess Grignard reagent. Then about 100 ml of the reaction mixture was distilled until the boiling point of the solvent, di-*n*-butylether, was reached (143°). The distillate was dried over $CaCl_2$ and yielded on fractionation 20 g of $(CH_3)_4Ge$ (b.p. 43–44°). The reaction mixture remaining in the three-necked flask was then filtered. Fractionation of this filtrate yielded another 4 g of tetramethylgermane thus raising the total yield to 80 %. Mass spectrometric analysis proved that the impurities (mainly CH_3Br and CH_3I) did not exceed 2 %.

2. *Dimethylgermanium dichloride and methylgermanium trichloride.* Rochow[5,6] has reported the synthesis of these compounds by the reaction of methylchloride vapour with a hot mixture of copper and germanium. The relative yields of the products are said to depend on the composition of the copper-germanium mixture[7]. $(CH_3)_2GeCl_2$ can also be synthesised by reacting $GeCl_4$ and $(CH_3)_4Ge$; this reaction is analogous to the Kocheskow reaction for the corresponding tin compound[8]. However, equimolecular amounts of $GeCl_4$ and $(CH_3)_4Ge$, heated together for several hours, and even with anhydrous Al_2Cl_6 as catalyst, did not react as no change was observed in the NMR spectrum of the reaction mixture. Therefore the Rochow method was used for the preparation of these compounds.

A vertical column, packed with small glass helices, was charged with an intimate mixture of copper powder and germanium powder. The column was placed in the center of a vertical tube furnace and fitted with a gas inlet for CH_3Cl at the top, a vertical condenser at the bottom, and a thermocouple. The column was swept with CH_3Cl and the temperature gradually raised. At 350° the first drops of CH_3GeCl_3 and $(CH_3)_2GeCl_2$ were formed in the water-cooled condenser. The reaction products were collected in a flask cooled to —20° and excess CH_3Cl condensed at —80°. Over a period of 48 h the temperature of the oven was raised to 500°. At the end of the reaction hydrogen was mixed in the gas stream to regenerate the reaction mixture. A PMR spectrum and a mass spectrogram of the crude reaction product showed that it consisted mainly of CH_3GeCl_3 and $(CH_3)_2GeCl_2$ with small amounts of $(CH_3)_3GeCl$ and $GeCl_4$ and traces of methylgermanes and methylchlorogermanes.

The products were separated by distillation on a Todd column (15 theoretical plates). The yields were a function of the composition of the metal mixture as shown in Table 1. The fractions with boiling points 112.5° and 124° were then redistilled *in vacuo*, fractions being collected in cooled bulbs at —23° and —64°. The liquids collected in these bulbs were CH_3GeCl_3 and $(CH_3)_2GeCl_2$, respectively.

Mass spectrometric analysis showed that the $(CH_3)_2GeCl_2$ contained less than 0.2 % of CH_3GeCl_3 and $(CH_3)_3GeCl$, and that the CH_3GeCl_3 fraction contained about 0.5 % of $(CH_3)_2GeCl_2$ and 0.2 % $(CH_3)_3GeCl$.

From Table 1 it is evident that the conversion rate of Ge metal into methylgermanium chlorides is highest with an approximately 1/1 ratio of Ge/Cu and that when more copper is used, more of the trimethyl compound is formed.

TABLE 1

Grams of metal		*Atomic ratio Ge/Cu*	*Yields in grams and %*		*Molar ratio* $(CH_3)_2GeCl_2$:CH_3GeCl_3
Ge	*Cu*		CH_3GeCl_3	$(CH_3)_2GeCl_2$	
85	20	3.7:1	30: 12.5%	112: 57.5%	4.18:1
80	30	1.7:1	46: 20%	108: 57%	2.64:1
60	40	1.3:1	60: 35%	67: 46%	1.25:1

3. *Trimethylgermanium chloride.* The preparation of this compound has been described in several papers. It is said to be obtained by the methylation of $(CH_3)_2GeCl_2$ with CH_3MgCl[8,9], CH_3MgBr[7], or CH_3Li[9]. The boiling points reported for the trimethylchlorogermane fraction show considerable variation, ranging from 95–98° (ref. 9, 7) to 115° (ref. 8). A careful survey of the literature shows that the fraction with boiling range 95–98° is most likely to be the $(CH_3)_3GeCl$ fraction. As the report of Schmidt *et al.*[9] had not been published when we started our synthesis, we used Panomarenko's method[7]. We obtained nearly pure $(CH_3)_3GeCl$ (the fraction with boiling point 98° was the pure compound) but the yield was very low. We therefore tried to react gaseous $(CH_3)_4Ge$ and HCl using solid Al_2Cl_6 as a catalyst. The reaction proceeded smoothly at room temperature; starting with a molar ratio $(CH_3)_4Ge/HCl = 2$, the products were $(CH_3)_3GeCl$ and CH_4. The yield was about 90 % *vs.* HCl. Unreacted $(CH_3)_4Ge$ could be separated by distillation for use in the next batch. If equimolar amounts of the reactants were used, the products were $(CH_3)_3GeCl$ and $(CH_3)_2GeCl_2$ which were difficult to separate by distillation. The method is simple and rapid, but the yields are rather small.

The method for this reaction is as follows. A cylindrical glass vessel (1 l) fitted with a cold finger, break-seal and side tube with a B14 cone connection, was filled with 0.01 mole of freshly sublimed Al_2Cl_6. The reaction vessel was evacuated and 0.01 mole of $(CH_3)_4Ge$ and 0.005 mole of HCl were condensed in it at liquid nitrogen temperature. The vessel was sealed off and the contents were allowed to attain room temperature. The tetramethylgermane and hydrochloric acid evaporated and after a few minutes liquid droplets were formed at the catalyst surface. After one hour the reaction was complete. The vessel was cooled to —192° and the methane was pumped off. The reaction mixture was now slowly distilled through bulbs immersed in baths at —23° and —64° to a liquid-nitrogen trap. $(CH_3)_3GeCl$ (0.75 g) was collected in the bulb at —64° (95 % yield *vs.* HCl). Unreacted $(CH_3)_4Ge$ and a few per-cent of higher hydrocarbons were condensed in the liquid nitrogen trap. Mass spectrometric analysis and the PMR spectra of the —64° fraction showed that this was pure $(CH_3)_3GeCl$. The condensate of the bulb at —192° consisted of hydrocarbons with 2–5 carbon atoms.

4. *The methylgermanes,* CH_3GeH, $(CH_3)_2GeH_2$ *and* $(CH_3)_3GeH$. Alkyl derivatives

of monogermane have previously been prepared only by the reduction of the corresponding alkylgermanium halides with LiH, LiD or $LiAlH_4$[10,11] in either diethyl or di-*n*-butyl ether. We have tried to reduce CH_3GeCl_3 with LiH but were not successful in separating CH_3GeH_3. The reasons for this failure are probably two-fold; (*a*) chlorides are more difficult to reduce than bromides or iodides and (*b*) LiH is a hard material that is not easily crushed to the fine powder which is necessary to obtain good contact with reactants. Moreover, our experience in the preparation of methylstannanes and -silanes, by reduction of the chlorides with $LiAlH_4$, had shown us that low yields were usually obtained.

Sujishi and Keith[12], however, reported that they had obtained excellent yields of monogermane by the reduction of $GeCl_4$ with $LiAlH(O\text{-}tert\text{-}C_4H_9)_3$. We therefore tried this method of preparation and obtained yields of 60–70 %. As the three methylgermanes can be prepared by the same method only the procedure for trimethylgermane will be described.

A suspension of 20 g (0.078 mole) of lithium aluminium hydride tri-*tert*-butoxide in anhydrous dioxane was prepared in a two-necked 250-ml flask. The flask was fitted with a dropping funnel, a reflux condenser, a stirrer and a side tube connecting it to a trap filled with dry ice-alcohol (−78°). A solution of 5 g (0.032 mole) of $(CH_3)_3GeCl$ in 20 ml of dioxane was added dropwise with stirring. The contents were then heated slowly to the boiling point of dioxane and the gases evolved were trapped at −78°. This trap was connected to a vacuum line and the contents distilled via a bulb cooled in a bath (−98°) into a trap at liquid-nitrogen temperature. The fraction collected in this trap was pure $(CH_3)_3GeH$ (2.5 g, yield 65 %).

In the preparation of $(CH_3)_2GeH_2$ and CH_3GeH_3 100 % excess of the reductant was always used.

The purity of the products was tested mainly by PMR spectroscopy; the spectra for $(CH_3)_2GeH_2$ and CH_3GeH_3 showed no traces of impurities; in the spectrum of $(CH_3)_3GeH$, however, a very weak quadruplet and a triplet were observed with equal coupling constants which can probably be ascribed to a small amount of CH_3GeH_2Cl.

II. Electrical dipole moments

1. Liquids. The measurements for the three methylgermanium chlorides were carried out on benzene solutions. The moments (μ) were calculated according to the Lorentz–Lorentz formula

$$\mu^2 = \frac{9kT}{4\pi N}\frac{M}{d}\left(\frac{\varepsilon - 1}{\varepsilon + 2} - \frac{n^2 - 1}{n^2 + 2}\right)$$

where the symbols have their usual meaning. This can be transformed to

$$\mu = 0.01281\,[(P_{2\infty} - R_2)T]^{\frac{1}{2}}$$

for very dilute solutions of a solute in an inert solvent, at 25°. $P_{2\infty}$ and R_2 represent the molecular polarisation of the solute at infinite dilution and the molar refraction of the solute, respectively. The dielectric constants were measured with a dipole meter, type DM01 of WTW, operating at 1.8×10^6 Hz. Refractive indices were measured with a Pulfrich refractometer.

2. *Gases*. For the methylgermanes $(CH_3)_2GeH_2$ and $(CH_3)_3GeH$, the polarisation, $P = [(\varepsilon - 1)/(\varepsilon + 2)]M/d$, was obtained by first measuring the dielectric constants of the compounds at different pressures, p. From a graph of ε *vs*. p the slope $d\varepsilon/dp$ was used to calculate ε at a standard pressure of 100 mm of Hg. At this pressure, d is calculated using the general gas law. The molar refraction, R, was taken as equal to the sum of the atomic refractions (C, 2.591; H, 1.028); the atomic refraction of germanium in the hydrides was obtained[11] from the molar refractions of $(CH_3)_3GeH$, $(C_2H_5)_2GeH_2$ and $(CH_3)_2C_2H_5GeH$ using the above values for C and H; the results were, respectively, 9.67, 9.71 and 9.61. As the value for $(CH_3)_3GeH$ was believed to be the most accurate, this value was used in the calculation. The electrical dipole moment is then given by the equation

$$\mu = 0.01281[(P - R)T]^{\frac{1}{2}}$$

All measurements were made at 25° ± 0.1. The gas-cell used for these measurement was of special design and full details will be published elsewhere. The results are summarized in Table 2.

TABLE 2

Compound	$\Delta\varepsilon/\Delta p$	$\varepsilon_{(100\ mm)}$	$d \times 10^3$	$P, (P_{\pm x})$	$R, (R_\pm)$	μ (*in D*)
$(CH_3)_2GeH_2$	0.669	1.0005623	0.503	34.81	23.07	0.758
$(CH_3)_3GeH$	0.709	1.0005956	0.639	36.86	27.72	0.6685
CH_3GeH_3	—	—	—	—	—	0.64
CH_3GeCl_3	—	—	—	181.33	32.16	2.70 ± 0.4
$(CH_3)_2GeCl_2$	—	—	—	234.06	35.52	3.14 ± 0.04
$(CH_3)_3GeCl$	—	—	—	201.07	31.20	2.89 ± 0.04

III. Proton magnetic resonance spectra

The spectra were recorded on a Varian model V 4300-B high resolution spectrometer operating at 56.444 Mc. No solvents were used and the compounds were distilled at low pressure and low temperature into 5-mm o.d. sample tubes containing a capillary filled with a 10% solution of TMS in chloroform as a double external standard. The sample tubes were sealed at the vacuum line. Peak separations were measured using the audio frequency side band technique (audio frequency generator H.P. 200 CD, controlled by a Beckmann frequency counter model 7175).

TABLE 3

Compound	τ (*C–H*)	τ (*Ge–H*)	$J(^{13}C–H)$	$J(H–H)$
CH_3GeCl_3	8.17	—	138	—
$(CH_3)_2GeCl_2$	8.70	—	132	—
$(CH_3)_3GeCl$	9.36	—	128.5	—
$(CH_3)_4Ge$	10.14	—	124.5	—
CH_3GeH_3	10.18	7.00	127.8	4.2
$(CH_3)_2GeH_2$	10.14	6.66	126.8	3.8
$(CH_3)_3GeH$	10.14	6.38	126.2	3.4

The spectroscopic data, obtained by a straightforward first-order analysis of the spectra, are shown in Table 3. Chemical shifts are expressed in τ-values *vs.* TMS and coupling constants in cps.

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SUMMARY

The molecular parameters of silicon tetrachloride and related compounds have been explained by Pauling in terms of resonance contributions of various polar structures.

The resonance contributions of polar structures to the bonding in methylgermanium chlorides and methylgermanium hydrides can be studied by electrical dipole moments and PMR spectra measurements. Improvements in the syntheses of these compounds are reported and data from the measurements are tabulated.

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