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THE CHEMISTRY OF HEXACHLORODIGERMANE

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THE CHEMISTRY OF HEXACHLORODIGERMANE

Richard Wilhelm Kopp  
Master's Thesis

September 1962

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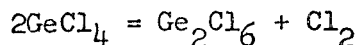
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## I. INTRODUCTION

Only two references to hexachlorodigermane,  $\text{Ge}_2\text{Cl}_6$ , appear in the literature. Both pertain primarily to its preparation.

In 1954 Schwarz and Baronetsky<sup>1</sup> reported the synthesis of a white, crystalline, air-sensitive compound which contained Ge and Cl in a ratio of 1 to 3. Their method, which gave yields of 10 to 20 mg in 4 to 5 weeks, consisted of distilling  $\text{GeCl}_4$  slowly over germanium metal at elevated temperatures in a closed, evacuated system. Using these very small samples, molecular weight determinations led to the values 258 and 261. The theoretical molecular weight of  $\text{Ge}_2\text{Cl}_6$  is 358.2.

Shriver and Jolly<sup>2</sup> succeeded in 1958 in obtaining yields of up to 250 mg per hour according to the reaction:



This was accomplished by passing  $\text{GeCl}_4$  vapor through a microwave discharge. They confirmed the ratio of Ge to Cl as 1 to 3 and further determined that the oxidation number for Ge was +3.

The present work was begun as an extension of the latter investigation, to improve the yields and to study the properties of this new compound.

## II. PREPARATION

### A. Preparation Using a Solenoid Discharge

#### 1. Apparatus and Experimental Procedure

The solenoid discharge<sup>3</sup> consists of a copper coil around a cylindrical discharge tube. It is an electrodeless discharge in the sense that no electrodes extend into the discharge zone. The radio-frequency current through



the solenoid produces an alternating magnetic field parallel to the axis of the solenoid. The magnetic field, in turn, produces an electric field around it. These induced electric forces form closed curves.

The energy acquired by the electrons within the reaction zone is proportional to the square of the distance from the center of the tube. Therefore the diameter of the reaction tube was made as large as was practical.

In all the runs mentioned below, the discharge was run at just below the "quenching" level. That is, the pressure of the gas passing through the discharge was slowly raised to just below the point where the discharge would go out.

The discharge source was a 50-Mc radio-frequency oscillator with a 2.5-kv 500-ma power supply.

Early runs were made using the apparatus as described by Jolly<sup>2</sup> in which  $\text{GeCl}_4$  was passed through the reaction zone, and  $\text{Ge}_2\text{Cl}_6$ , unreacted  $\text{GeCl}_4$ , and  $\text{Cl}_2$  were collected in U-tubes surrounded by cold traps at  $-20^\circ\text{C}$  (ice-HCl),  $-78^\circ\text{C}$  (Dry Ice-acetone), and  $-196^\circ\text{C}$  (liquid nitrogen), respectively. However, no quantitative work was done with this set-up.

Since only a small amount of the  $\text{GeCl}_4$  vapor which passes through the discharge zone reacts, an apparatus was designed and built to permit recycling of  $\text{GeCl}_4$  vapors, Fig. 1. The diameter of the reaction tube was 30 mm.

$\text{GeCl}_4$  was distilled into U-tube A from weighing bulb (a). After a  $-78^\circ$  cold bath was put around B and a  $-196^\circ$  bath around C, the discharge was turned on, and the stopcocks were turned to permit a flow as indicated by the arrows. The flow rate through the discharge tube was regulated by adjusting Stopcock I.  $\text{Ge}_2\text{Cl}_6$  and unreacted  $\text{GeCl}_4$  were collected in trap B, and  $\text{Cl}_2$  was collected in trap C. After all the  $\text{GeCl}_4$  vapor had passed through, a  $-20^\circ$  bath was set

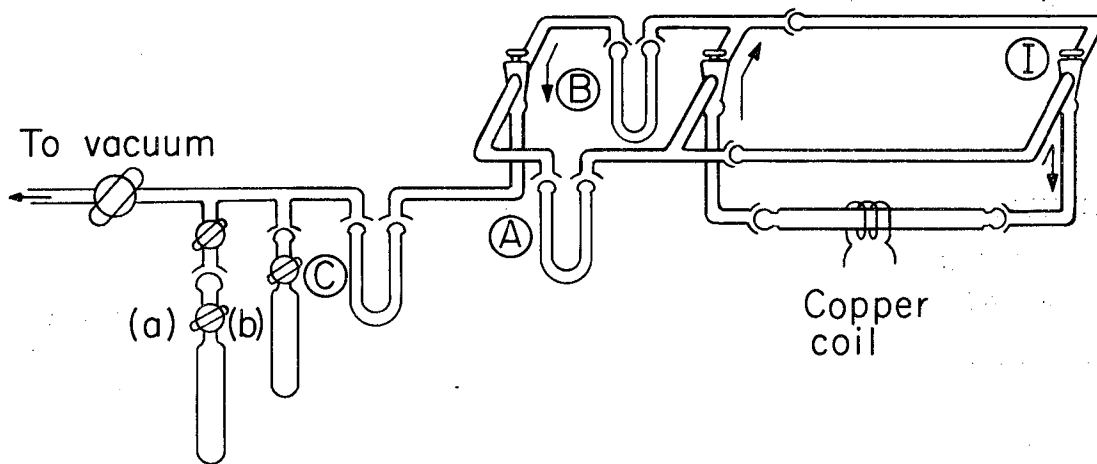


FIG. 1. APPARATUS USED WITH SOLENOID DISCHARGE.

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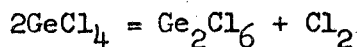
around B, to hold the  $\text{Ge}_2\text{Cl}_6$  but permit the  $\text{GeCl}_4$  to distil, and the  $-78^\circ$  bath around A. The stopcocks were each turned by  $180^\circ$  and the  $\text{GeCl}_4$  again was passed through the discharge zone. If desired, the recycling process could be continued until all of the  $\text{GeCl}_4$  had decomposed. Generally, since the primary concern was not the actual production of large quantities of  $\text{Ge}_2\text{Cl}_6$ , but rather the effectiveness of the conditions used, the reaction was terminated after only a few cycles. The  $\text{Cl}_2$  was pumped off, the  $\text{GeCl}_4$  remaining was collected and weighed in (a) and the  $\text{Ge}_2\text{Cl}_6$  collected and weighed in (b).

## 2. Results and Evaluation

Table I. Synthesis of  $\text{Ge}_2\text{Cl}_6$   
Using a Solenoid Discharge

No.	% $\text{GeCl}_4$ decomposed	% yield* $\text{Ge}_2\text{Cl}_6$	flow rate, mmole $\text{GeCl}_4$ / min	yield, mmole $\text{Ge}_2\text{Cl}_6$ /hr	duration of run, min.
1.	1.23	12.5	2.14	0.11	200
2.	0.79	24.3	2.80	0.16	119
3.	(a)	(a)	0.70	0.26	98
4.	6.18	50.0	0.51	0.45	100
5.	4.38	49.0	0.61	0.40	136

\* Based on the amount of  $\text{GeCl}_4$  decomposed according to the reaction:



(a)  $\text{GeCl}_4$  recovery tube broken

The greater yield of  $\text{Ge}_2\text{Cl}_6$  and greater recovery of  $\text{GeCl}_4$  in run number 2 over run number 1 in Table I above are attributable to a greater proficiency in handling the apparatus.

In run number 3, a plug of bronze wool was placed in the reaction tube about 12 cm past the discharge. It was hoped that the copper in the wool might react with the  $\text{Cl}_2$  formed in the reaction and thus prevent any further reaction of the  $\text{Cl}_2$  with the  $\text{Ge}_2\text{Cl}_6$  formed. The bronze wool did not pick up the  $\text{Cl}_2$  to any observable extent, however, although it did result in a higher pressure and a lower flow rate through the reaction tube.

The bronze wool was put about 1 cm past the coil in run number 4. This resulted in the discharge taking place around the bronze plug itself rather than within the coil. Some reaction did take place with the Cu, but a large amount of  $\text{Cl}_2$  was still recovered in U-tube C.

Two bronze wool plugs were used in the last run, one within the coil and the other about 4 cm past the first. This time the discharge was again established primarily around the wool plug beyond the coil. Again, some reaction did take place with the Cu, but  $\text{Cl}_2$  was still collected in C.

In all cases a small amount of yellow solid and colorless nonvolatile liquid were deposited on the walls of the reaction tube just past the discharge during a run. The solid slowly darkened to brown, which appears characteristic of polymeric  $(\text{GeCl})_x$ . The liquid solidified in several hours to a white solid which also darkened, first to yellow, then to brown. This fits exactly the description of the compound mistakenly reported as  $\text{GeOCl}_2$  by Schwarz and Heinrich<sup>4</sup> in 1930. Schumb and Smyth<sup>5</sup> in 1955 found that this compound was actually a "new form" of  $\text{GeCl}_2$  which spontaneously changes to the more usual white solid form of  $\text{GeCl}_2$ . This  $\text{GeCl}_2$  itself decomposes to  $\text{GeCl}_4$  and lower chlorides with time, darkening as it does so.

The results indicate that the highest yields are obtained with low flow rates and high pressures. Having the discharge occur at a bronze wool surface

seems to increase greatly the yield, as well as causing more of the decomposed  $\text{GeCl}_4$  to end up as  $\text{GeCl}_6$ . This latter result may, however, be caused simply by the lower flow rate.

In the last two reactions in Table I, the copper acted as a reducing agent to form some  $\text{CuCl}$ . Whether it reacted directly with the  $\text{GeCl}_4$  or only with the  $\text{Cl}_2$  formed is not known.

The results above appear sufficient to show that in all probability this form of discharge would not produce yields which would seriously rival the microwave synthesis described by Shriver and Jolly.

#### B. Preparation Using a Bronze Wool Discharge Tube

Since the use of bronze wool gave significant improvement in the yields, it was decided to attempt to apply the discharge tube designed by Wartik,<sup>6</sup> for the preparation of  $\text{B}_2\text{Cl}_4$  from  $\text{BCl}_3$ , to this reaction.

##### 1. Apparatus and Experimental Procedure

For these runs the apparatus shown in Fig. 1 was modified by replacing the tube and coil with the discharge tube shown in Fig. 2. In this tube a glow discharge is set up between the bronze wool plugs. In every case, six approximately spherical plugs, each weighing from 800 to 900 mg, were used. They were separated from one another by about 2 to 3 cm. The diameter of the tube was 30 mm and its overall length was 43 cm. The tungsten electrodes were connected to a high voltage transformer through a Variac to an ordinary 60 cycle a.c. outlet. Beginning with run number 9, a milliammeter was connected in series to the system and a Triplet model 630 voltmeter was used to measure the voltage accurately. Prior to this run a crude kilovolt meter gave the only indication of the strength of the discharge.

The actual experimental procedure used was the same as described above for the solenoid discharge.

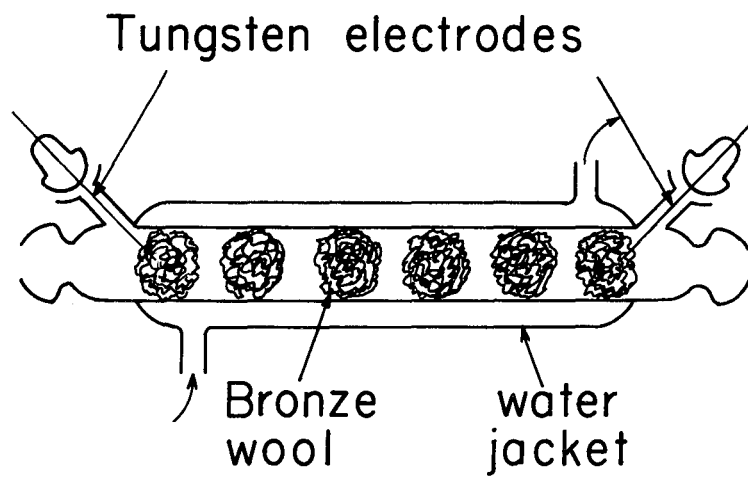


FIG.2. BRONZE WOOL DISCHARGE TUBE.

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## 2. Results and Evaluation

The results of these runs are presented in Table II. Although they clearly do not constitute an exhaustive survey, the results do show several trends. It appears that voltages over 2 kilovolts give consistently lower yields and greater decomposition. High flow rates, above about 0.5 gm  $\text{GeCl}_4$ /min, gave higher yields than low flow rates, with the exception of run 9. No explanation can be given for this inconsistent result. It is logical that, since there are five separate discharge regions, each of which is capable of not only forming  $\text{Ge}_2\text{Cl}_6$ , but also of reducing it further, it would be beneficial to remove the  $\text{Ge}_2\text{Cl}_6$  from the discharge zones as fast as possible. Thus a high flow rate should result in higher yields.

Another factor that may determine the yield under a particular set of conditions is the distance between the bronze plugs since the potential across the electrodes is determined both by the pressure of gas between the electrodes and by the distance between them. Perhaps the variations from tube to tube can account for the lack of a simple relationship between the results.

Most important of all, long reaction times give low yields of  $\text{Ge}_2\text{Cl}_6$ . It appears that after the reaction tube has been used for about an hour, or perhaps less, its ability to produce  $\text{Ge}_2\text{Cl}_6$  in good yield diminishes, quite sharply if the results of runs 13 and 14 can be considered as reliable indications. One may speculate that this might be due to the  $\text{CuCl}$  formed which coats the surface of the wool, preventing further reaction.

Considering the time necessary to put together the reaction tube and its short lifetime, this method also seems unsuitable for the preparation of  $\text{Ge}_2\text{Cl}_6$ .

TABLE II. Synthesis of  $\text{Ge}_2\text{Cl}_6$  Using a Bronze Wool Discharge Tube

No.	% $\text{GeCl}_4$ decomposed	% yield $\text{Ge}_2\text{Cl}_6$	flow rate, mmole $\text{GeCl}_4$ /min	yield, mmole $\text{Ge}_2\text{Cl}_6$ /hr	duration of run, min.	conditions
1*	8.20	3.7	2.33	0.42	16	1 kv
2*	19.0	12.0	1.9	1.34	20	2 kv
3	19.0	17.0	1.4	1.23	25	2 kv
4*	26.8	6.0	2.71	1.28	22	2 kv
5	6.38	29.8	2.67	1.51	13	1.5-2 kv
6*	6.35	11.3	2.67	0.56	17	2-2.5 kv
7	7.36	19.4	2.01	0.87	21	2-2.5 kv
8	8.16	13.6	2.62	0.87	15	2.5 kv
9*	4.79	16.2	2.29	0.53	20	1.8-2.0 kv 30-20 ma
10*	4.14	43.7	0.79	0.42	87	1.7-1.8 kv 20 ma
11	5.39	14.5	2.29	0.53	28	2.1-2.5 kv 20 ma
12	2.98	25.7	0.89	0.28	48	1.95-2.0 kv 18 ma
13*	3.39	36.4	1.03	0.39	59	1.7 kv 11 ma
14	3.40	20.8	1.03	0.22	58	1.7 kv 9 ma

\* New reaction tube; 1. No water jacket; 4. Reason for high decomposition unknown; 10. 2 mm stopcock between discharge and first U-tube-restricted flow considerably.



### C. Preparation Using a Microwave Discharge

Because of the disappointing results above, it was decided to return to the proven successful method of synthesis involving the use of a microwave discharge.

The microwave discharge is another form of electrodeless discharge. Standing electromagnetic waves may be set up in a cylindrical metal tube, called a resonance cavity. The electric field in the wave acts upon electrons and ions, giving them energy. These then cause the chemical reactions.

Another way of using microwaves is through the use of a director. This is a metal plate, which may be of any of several shapes, that reflects and directs the waves to produce a concentrated glow.

#### 1. Apparatus and Experimental Procedure

For this synthesis a modification of Jolly's original system was used, Fig. 3. With it the  $\text{GeCl}_4$  to be weighed need not be distilled into the system before a run, nor out of it after a run. It may be weighed in the U-tube in which it is collected, and this same tube may be used as the source of  $\text{GeCl}_4$  in the next run. A U-tube with 2 mm bore stopcocks was used for the first trap ( $-20^\circ$ ) in one run (not in Table) but this gave only a negligible yield of  $\text{Ge}_2\text{Cl}_6$ , presumably because it decreased the flow rate to a great extent (see later discussion).

The  $\text{Ge}_2\text{Cl}_6$  was collected for weighing and for temporary storage by replacing the tube containing the collected  $\text{GeCl}_4$  by another tube with stopcocks, into which the  $\text{Ge}_2\text{Cl}_6$  was distilled. The stopcock to the vacuum between the first two traps provided a means for evacuating the small space between this new U-tube and the stopcock separating it from the first tube in the event that this collecting tube already contained some  $\text{Ge}_2\text{Cl}_6$ , which must not be exposed to the air.

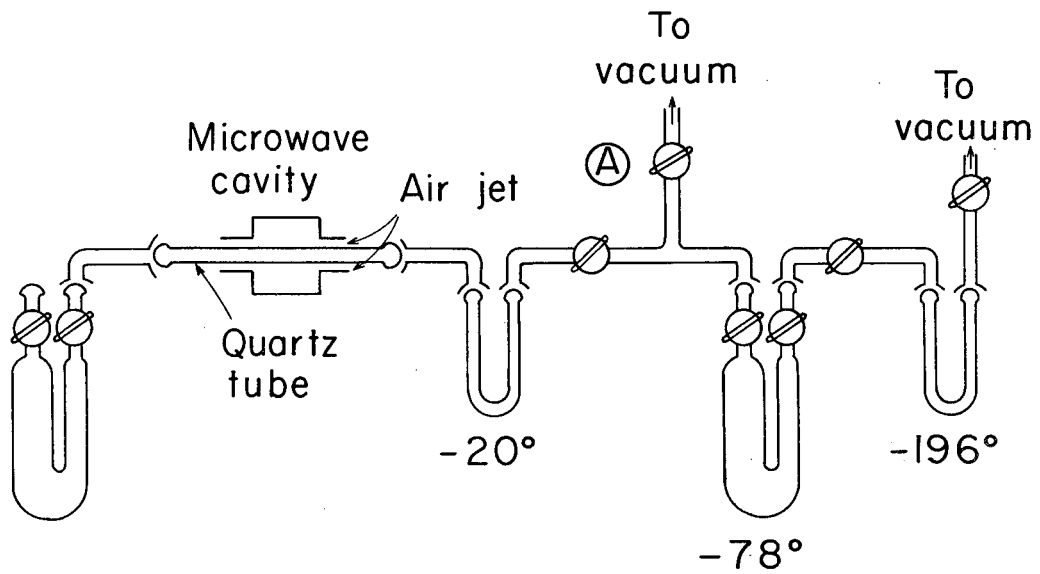


FIG. 3. APPARATUS FOR MICROWAVE DISCHARGE.

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A Raytheon QK60 magnetron tube, which is a source of 10 cm microwaves, was coupled to the resonance cavity. It was powered by a unit with a maximum capacity of 2.5 kv at 0.5 amps. In every case, it was run at 1140 volts and 110 ma.

The other unit was a Baird-Atomic Hg 198 Microwave Exciter. This operates at a wavelength of 12.2 cm in the 2400-2500 Mc band. The energy is carried in a flexible coaxial cable to a C-director which concentrates it at the reaction tube. It has a maximum power output of 125 watts and was run at 95-98% of maximum.

## 2. Results and Evaluation

Table III Synthesis of  $\text{Ge}_2\text{Cl}_6$  Using a Microwave Discharge

No.	% $\text{GeCl}_4$ decomposed	% yield $\text{Ge}_2\text{Cl}_6$	flow rate, mmole $\text{GeCl}_4$ /min	yield, mmole $\text{Ge}_2\text{Cl}_6$ /hr	length of run, min.
1	(a)	-	ca. 2	0.28	25
2	(a)	-	ca. 1	0.59	46
3	3.11	21.4	5.84	1.14	8
4	3.11	33.9	4.49	1.42	11
5	2.31	50.6	3.41	1.18	100
6	3.66	40.3	1.64	0.73	195
7	2.54	18.6	2.10	0.31	145

(a) Not recorded

1. Insufficient cooling of microwave cavity; 2. Baird unit; 5. Cu plug past discharge zone; 6. Cu plug past discharge zone.

From the data in Table III several tentative conclusions can be drawn for the best set of reaction conditions. High flow rates again seem to give higher yields, although 1.25 g  $\text{GeCl}_4$ /min may be too fast. Placing a bronze wool plug a short distance past the discharge zone does not seem to have much affect on the yields, but it does seem to insure that more of the  $\text{GeCl}_4$  which decomposes ends up as  $\text{Ge}_2\text{Cl}_6$ . It may be that the Cu picks up some of the  $\text{Cl}_2$  which might otherwise react with the  $\text{Ge}_2\text{Cl}_6$  already formed. The bronze wool does acquire a thin white coating during a run, although much  $\text{Cl}_2$  is still observed in the liquid nitrogen trap.

### III. PHYSICAL PROPERTIES

The vapor pressure of  $\text{Ge}_2\text{Cl}_6$  was determined over the range  $24.7^\circ$  to  $59.7^\circ$ . Below  $24.7^\circ$  the vapor pressure is so low that accurate measurements are impossible. Above  $59.7^\circ$ , decomposition is rapid.

The apparatus consisted of a manometer with a short side arm, into which the sample was distilled. A mercury float valve allowed one to adjust the level of the mercury in the manometer. The entire apparatus was immersed in a thermostatically controlled constant temperature bath.

Great pains were taken to insure that the  $\text{Ge}_2\text{Cl}_6$  used was pure. Each sample was distilled twice, collecting it at  $-20^\circ$ , to insure that it was free from impurities before it was distilled into the apparatus. It was then pumped on while being held at  $-20^\circ$ . Before each reading the  $\text{Ge}_2\text{Cl}_6$  in the side arm was again pumped on at  $-20^\circ$  before the mercury was raised into the manometer. The constant temperature bath was set at the temperature desired before the apparatus was immersed into it.

The thermometer used was checked against an NBS calibrated thermometer.

Table IV Vapor Pressure of  $\text{Ge}_2\text{Cl}_6$ 

Physical State	t, °C	P mm		$\Delta$
		obs.	calc.	
solid	24.7	0.8	0.7	-0.1
solid	29.7	1.1	1.1	0
solid	34.7	1.5	1.5	0
solid	39.7	2.2	2.2	0
liquid	44.7	3.0	3.0	0
liquid	49.7	4.1	4.2	+0.1
liquid	54.7	5.8	5.6	-0.2
liquid	59.7	6.9	7.6	+0.7

As an example of how the data were obtained, the actual values obtained during the course of a typical measurement at 29.7° are shown in Table V.

Table V Vapor Pressure of  $\text{Ge}_2\text{Cl}_6$  at 29.7°

Time after immersion into bath, min.	pressure, min.
2	1.1
4	1.1
5	1.0
7	1.2
9	1.3
11	1.5
15	1.7

The rise in pressure, starting at about 9 minutes, is believed due to decomposition of the  $\text{Ge}_2\text{Cl}_6$  to the more volatile  $\text{GeCl}_4$ . The constant initial pressure was considered the true pressure. Several

measurements, such as the above, were made at each temperature.

A plot of  $\log P_{\text{mm}}$  vs.  $1/T$  was made, as shown in Fig. 4. The data were not sufficiently accurate to permit separate lines to be drawn for the solid and liquid states. Thus one straight line was drawn through all the points.

The equation for this line is:

$$\log P_{\text{mm}} = - \frac{2801}{T} + 9.29$$

The  $\Delta H^\circ$  of vaporization (either from the solid or liquid) as calculated from the slope of this line was 12.8 kcal/mole.

A typical sample in the vapor pressure apparatus was found to melt sharply at  $41.5^\circ - 42.0^\circ$ .

The infrared spectrum of  $\text{Ge}_2\text{Cl}_6$  was taken in  $\text{CCl}_4$  solution and in  $\text{CS}_2$  solution. Both the NaCl and KBr regions were observed. See Figs. 5 and 6. A known amount of doubly distilled  $\text{Ge}_2\text{Cl}_6$  was distilled into an ampule with a constricted neck. The solvent was then condensed onto it and the ampule warmed to room temperature. The  $\text{Ge}_2\text{Cl}_6$  readily dissolved in both solvents. The ampule was then removed from the vacuum line and a small amount of the solution was transferred into a cavity cell with a hypodermic syringe.

Peaks were observed at 7.1 (w), 11.2 (m), 14.4 (m) and 22.1 (s) microns.

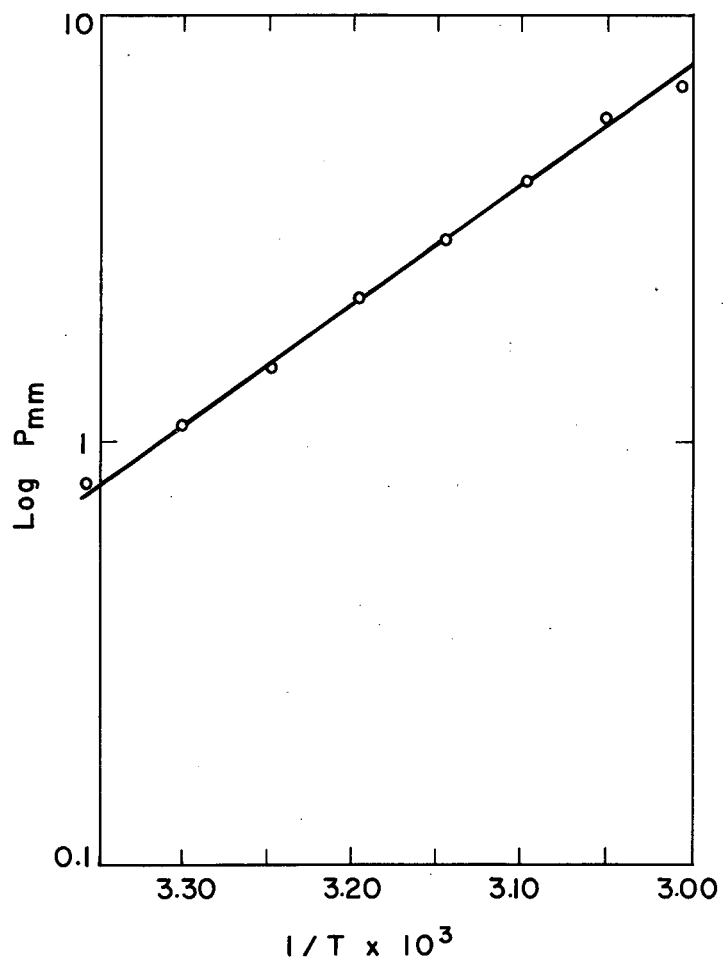


FIG. 4. VAPOR PRESSURE OF  $\text{Ge}_2\text{Cl}_6$ .

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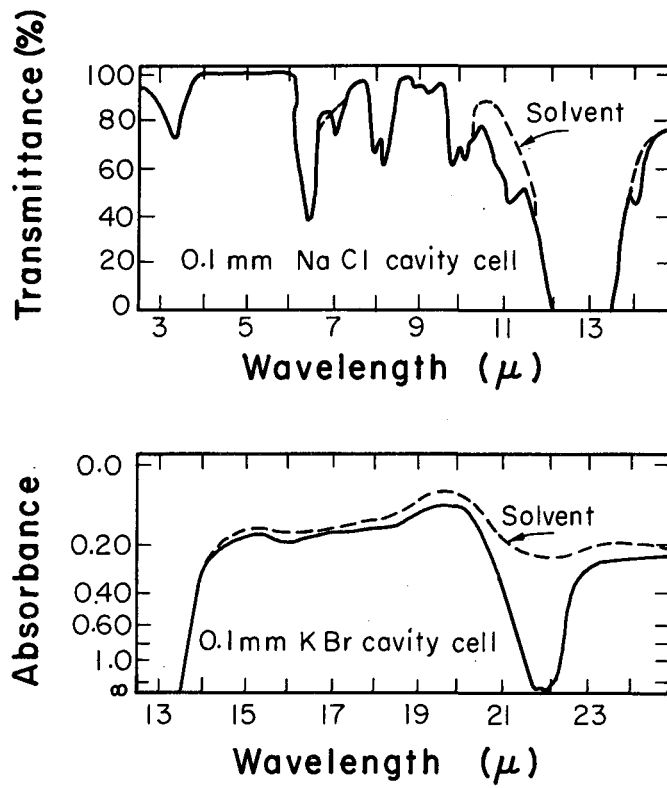


FIG. 5. INFRARED SPECTRA OF 0.3 M  $\text{Ge}_2\text{Cl}_6$  IN  $\text{CCl}_4$  SOLUTION



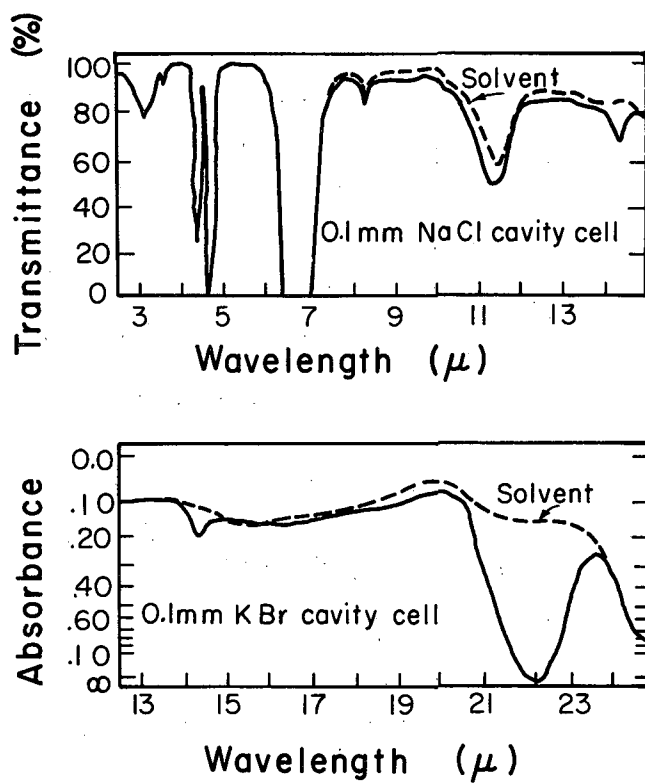


FIG. 6. INFRARED SPECTRA OF 0.25 M  $\text{Ge}_2\text{Cl}_6$  IN  $\text{CS}_2$  SOLUTION.

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#### IV. CHEMICAL PROPERTIES

##### A. Reaction with NaBH<sub>4</sub>

###### 1. Apparatus and Experimental Procedure

A 250 ml three-neck round-bottom flask was equipped with a magnetic stirrer, a nitrogen inlet tube, a dropping funnel with a pressure equalizing side arm, and an outlet tube leading to a vacuum line. The line consisted of four U-tubes, each separated by a mercury float valve, eliminating contact between the contents of the tube and stopcock grease. This kind of line was found necessary, since, in early runs conducted in an ordinary vacuum line, contact of the solvent and the reaction products with the stopcock grease caused the system to leak, making quantitative work impossible. Silicone grease was used at those points where it could not be avoided, such as on the standard taper joints on the flask and on the ends of the vacuum line. No leaks were ever encountered there.

The solvent employed was diethylene glycol dimethyl ether (diglyme). It was dried by first refluxing with CaH<sub>2</sub>, then distilled, the fraction boiling between 161° and 162° being collected. Even with this procedure, some slight reaction of the solvent with the NaBH<sub>4</sub> dissolved in it was observed.

After Ge<sub>2</sub>Cl<sub>6</sub> had been distilled into the dry, evacuated flask, diglyme was added through the dropping funnel to dissolve the sample. Nitrogen was admitted to bring the system to atmospheric pressure so that the NaBH<sub>4</sub> solution could then be introduced into the dropping funnel. After the system had been reevacuated and an ice bath placed around the reaction flask, the borohydride solution was added dropwise, with vigorous stirring.

The reaction flask was open to the vacuum pump through the four U-tubes. The first tube was surrounded by a -78° trap, the other three by liquid N<sub>2</sub>. Pumping and stirring were continued for at least one hour after the last of

borohydride solution had been added. The flask was then isolated from the line. The content of the  $-78^{\circ}$  trap, which was found to be distilled solvent, was discarded, and the reaction products from the liquid nitrogen traps were consolidated. They were then distilled in vacuo through traps at  $-78^{\circ}$  (Dry-Ice-acetone),  $-112^{\circ}$  (carbon disulfide slush), and  $-196^{\circ}$  (liquid nitrogen), respectively.

## 2. Results and Discussion

The  $-78^{\circ}$  trap was found to contain mainly solvent that had passed through the original  $-78^{\circ}$  trap during the run, plus some unidentified material that was probably a decomposition product of the solvent (see Fig. 7) and traces of trigermane as identified by the gas phase infrared spectrum of the material in the trap. The  $-112^{\circ}$  trap contained primarily digermane, along with more of the unidentified material mentioned above. This latter material was separated from the digermane by passing the mixture through Ascarite several times. Only the digermane remained. The  $-196^{\circ}$  trap contained a mixture of germane and diborane. The diborane was decomposed by Ascarite, leaving pure germane, the amount of which could then be ascertained.

At the end of each run, the reaction vessel always contained a light yellow precipitate which darkened to brown over a period of several days.

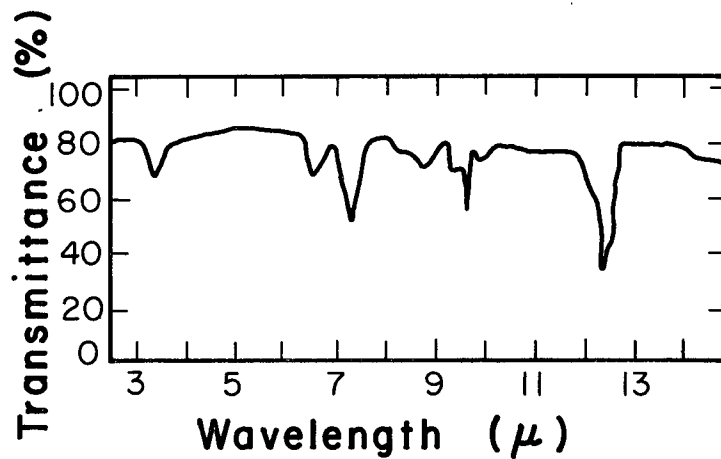


FIG. 7. INFRARED SPECTRUM OF UNIDENTIFIED MATERIAL IN BOROHYDRIDE REACTION (DIGERMANE SUBTRACTED).

MU-27904

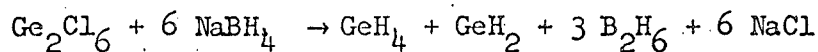
Table VI. Reaction of  $\text{Ge}_2\text{Cl}_6$  With  $\text{NaBH}_4$ 

conc. $\text{Ge}_2\text{Cl}_6$ , moles/liter	conc. $\text{BH}_4^-$ , moles/liter	$\frac{\text{BH}_4^-}{\text{Ge}_2\text{Cl}_6}$	%Ge as $\text{GeH}_4$	%Ge as $\text{Ge}_2\text{H}_6$	%B re- covered as $\text{B}_2\text{H}_6$	rate of addition, ml/min
0.10	0.63	6.5	15.5	trace	27.3	5
0.04	0.27	7.1	29.9	trace	5.6	5
0.13	0.09	6.6	41.1	8	3.3	0.5
0.19	0.10	7.5	41.6*	5	3.1	1

\* Addition of 25 ml of 1N HCl to the reaction flask after the completion of the reaction with borohydride resulted in the evolution of much hydrogen, a trace of digermene, and 43.2% more germane.

As shown in Table VI, germane was always obtained as the major product. The yields of digermene were always poor. Thus one may say that, under the conditions used, borohydride readily cleaves the Ge-Ge bond. It does appear that slow rates of addition and low concentrations of borohydride are more favorable for the formation of digermene, but even then only small amounts of this compound are obtained.

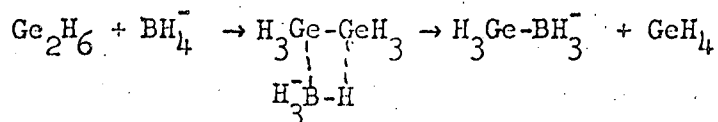
Addition of borohydride always resulted in yields of less than 50% germane. From this one might suggest the reaction:



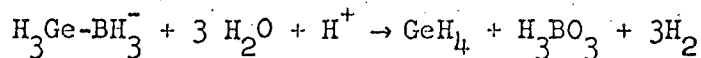
However, two observations tend to suggest that this equation does not describe the reaction completely. First, the addition of acid to the reaction vessel after the completion of the borohydride reaction resulted in the evolution of

43% more germane. Secondly, much less than the expected diborane was recovered.

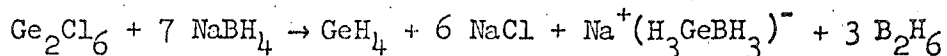
If digermane is formed in any significant amount, it might react further with the borohydride, possibly as follows:



Reaction of an acid solution with the  $\text{H}_3\text{GeBH}_3^-$  anion would result in the formation of germane.



One might then write the reaction in diglyme solution as:



The fate of the boron is unknown.

## B. Reaction with Water

### 1. Apparatus and Experimental Procedure

The reaction vessel in each case was a 20 mm O.D. Pyrex tube, one end of which was rounded, the other provided with a long, fine, capillary tip. A constricted side arm with a ball joint at its end allowed the tube to be attached to a vacuum line. The water, or alkaline solutions, were previously introduced directly into the tube with a micropipette. The water was frozen with liquid nitrogen and the  $\text{Ge}_2\text{Cl}_6$  distilled onto it. The constriction of the side arm was then closed under vacuum, and the tube allowed to warm to room temperature.

To open the sealed tube, the capillary tip was inserted through an open straight-bore stopcock attached to the vacuum line. The tube below.

the stopcock was sealed to the shoulder of the reaction tube with Apiczon W wax, effecting an airtight seal. A liquid nitrogen bath was then put around the contents of the tube and the capillary broken by turning the stopcock. A manometer in the system was used to check for any noncondensable gas.

In each case the sealed tubes were left at room temperature for at least 24 hours to insure complete reaction.

## 2. Results and Discussion

Table VII. . Reaction of  $\text{Ge}_2\text{Cl}_6$  with  $\text{H}_2\text{O}$

mmole $\text{Ge}_2\text{Cl}_6$	Solution added	Normality of <sup>*</sup> final solution	Conditions
0.26	0.5 ml distilled $\text{H}_2\text{O}$	3N HCl	room temp. 24 hrs.
0.34	0.2 ml 0.1N NaOH	10N HCl	room temp. 30 hrs.
0.17	2.0 ml 1N NaOH	0.5N NaOH	room temp. 48 hrs.
0.22	0.2 ml 0.1N NaOH	6.5N HCl	room temp. 24 hrs. 50°, 1 hr.
0.39	0.2 ml 0.1N NaOH	11.6N HCl	room temp. 24 hrs. 70°-100° overnight

\* based on 6 moles HCl forming from each mole  $\text{Ge}_2\text{Cl}_6$ .

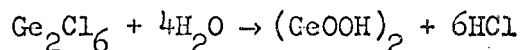
In no case was hydrogen evolved, even in the basic solution. This differs sharply from the analogous reaction of  $\text{Si}_2\text{Cl}_6$  (see Sect. V-C). Visual observations, however, do indicate differences in behavior among the samples.

In the very acidic solutions the reaction product remained pure white, even after heating. Only after the tube was opened and the water distilled off did traces of a yellow color appear. Heating of the dry solid caused it to become bright yellow-orange.

Reaction with pure water, which upon completion of the reaction gave a somewhat acidic solution, left a residue which was mostly white with some yellow. Removal of water from the sample again caused yellowing of the white material.

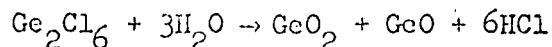
An excess of 1N NaOH resulted in the immediate formation of a bright yellow solid which darkened to orange overnight. No white material was observed.

These results may be explained on the following basis:  $\text{GeO}$  is yellow to brown and is insoluble in water.  $\text{GeO}_2$  is white and is quite soluble in both acid and alkaline solutions. If one assumes that the lack of yellow color indicates that no  $\text{GeO}$  has been formed, then, since no hydrogen was evolved, the Ge-Ge bond must have been retained. One might then suggest that in very acidic solutions the hitherto unknown "germanooxalic acid" is formed according to the reaction:

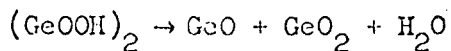


As one approaches a basic solution, or upon removal of water from the above compound, disproportionation results.





or



C. Reaction with NH<sub>3</sub>

1. Solid-Vapor Reaction

a. Apparatus and Experimental Procedure

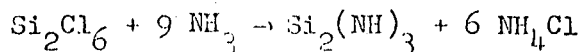
Two different methods were used to study the reaction of Ge<sub>2</sub>Cl<sub>6</sub> with ammonia. In the first, a known amount of sodium-dried vapor was allowed to come in contact with a known amount of Ge<sub>2</sub>Cl<sub>6</sub>. The total volume of the system was known and the pressure of the ammonia in the system could be observed directly by means of a manometer. It was hoped that in this way the course of the reaction could be followed and the completion of the reaction would be marked by no further change in the pressure.

b. Results and Discussion

Table VIII. Reaction of Ge<sub>2</sub>Cl<sub>6</sub> with NH<sub>3</sub>

	1.	2.
mmole Ge <sub>2</sub> Cl <sub>6</sub> :	0.197	0.228
mmole NH <sub>3</sub> added:	3.05	3.31
mmole NH <sub>3</sub> recovered:	1.81	1.73
mmole NH <sub>3</sub> reacted:	1.24	1.58
NH <sub>3</sub> /Ge <sub>2</sub> Cl <sub>6</sub> :	6.3	6.9
reaction time, hrs.:	30	9
temperature:	0° to 25°	-63°

Reaction of  $\text{Si}_2\text{Cl}_6$  with ammonia proceeds by the following equation:  
(see Section V-C).



If this is in fact the reaction which  $\text{Ge}_2\text{Cl}_6$  undergoes (see below), the above results indicate that reaction is incomplete under these conditions.

## 2. Solid-Liquid Reaction

### a. Apparatus and Experimental Procedure

The above method led to results contrary to what one might expect in this reaction. Thus, a sealed tube reaction was performed. The tube was the same as described for the reaction with  $\text{H}_2\text{O}$  except that it had a diameter of 10 mm. About 2 ml of sodium-dried ammonia was condensed onto a known quantity of  $\text{Ge}_2\text{Cl}_6$  in a tube cooled with liquid nitrogen. The tube was sealed and allowed to warm to  $0^\circ$ . After 24 hours its contents were frozen with liquid nitrogen and the tube was opened under vacuum. It was then warmed to  $-63^\circ$  whereupon the excess ammonia distilled off. Finally the tube was allowed to warm to room temperature while the pumping continued to insure removal of all unreacted ammonia.

Two ml of 6N HCl was then distilled into the tube to hydrolyze the product. The tube was opened and its contents quantitatively transferred into a 10 ml volumetric flask and diluted to volume. A nitrogen determination was run on this solution.

### b. Results and Discussion

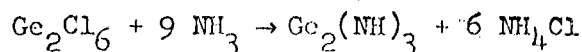
mmole  $\text{Ge}_2\text{Cl}_6$ : 0.102

mmole N in residue: 0.903\*

N/Ge: 8.85

\* determined by micro-Kjeldahl method

This result indicates that a great excess of liquid ammonia is necessary to effect a complete reaction. The reaction may thus be written:



#### D. Reaction with HCl

##### 1. Apparatus and Experimental Procedure

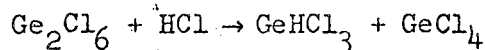
The reaction tube and procedure were the same as described in the reaction with water except that a known excess of hydrogen chloride, previously dried by twice passing it through a  $-112^\circ$  trap, was distilled into the reaction tube. After the tube had been opened, under vacuum with the contents frozen by liquid nitrogen, the tube was surrounded by a bath at  $-63^\circ$ . The unreacted HCl was then volatilized and collected in an adjoining U-tube surrounded by a liquid nitrogen bath.

##### 2. Results and Discussion

Table IX Reaction of  $\text{Ge}_2\text{Cl}_6$  with HCl

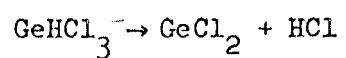
mmole $\text{Ge}_2\text{Cl}_6$ :	0.168
mmole HCl added:	1.35
mmole HCl recovered:	1.19
mmole HCl reacted:	0.16
HCl/ $\text{Ge}_2\text{Cl}_6$ :	0.95

The results above indicate that the following reaction took place.



The infrared spectrum of the vapors above the colorless liquid remaining in the tube, after removal of the hydrogen chloride at  $-65^\circ$ , confirmed the existence of  $\text{GeHCl}_3$  and the possible existence of  $\text{GeCl}_4$ .<sup>7</sup>

(See Fig. 8). Upon slow distillation of this liquid, a small amount of white solid was left behind. This solid darkened to yellow in a matter of hours. Presumably this solid was  $\text{GeCl}_2$  which resulted from the following reaction.<sup>8</sup>



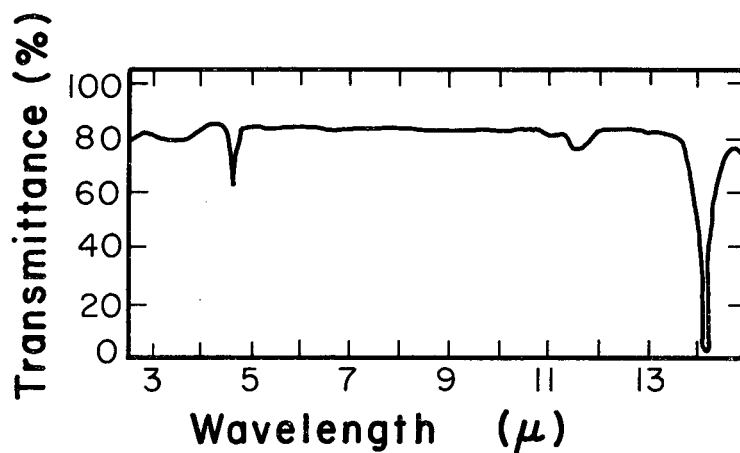


FIG. 8. INFRARED SPECTRUM OF VAPORS OVER PRODUCTS  
OF REACTION OF  $\text{Ge}_2\text{Cl}_6$  WITH HCl.

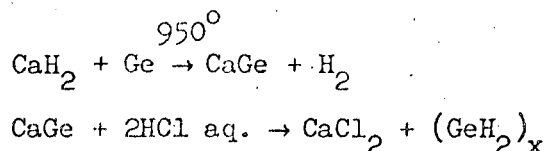
MU-27903

## V. REVIEW OF COMPOUNDS CONTAINING THE Ge-Ge BOND

### A. Inorganic Compounds

Prior to the synthesis of  $\text{Ge}_2\text{Cl}_6$ , the polyhydrides of germanium were the only inorganic compounds known which contained two or more germanium atoms directly bonded. In 1924, Dennis, Corey and Moore<sup>9</sup> first isolated digermane,  $\text{Ge}_2\text{H}_6$ , and trigermane,  $\text{Ge}_3\text{H}_8$ , along with monogermane,  $\text{GeH}_4$ , by the hydrolysis of magnesium germanide with dilute hydrochloric acid. Mixtures of germanes have also been obtained<sup>10</sup> from the reaction of ammonium bromide with magnesium germanide in liquid ammonia. Recently<sup>11</sup> the effect of a silent electric discharge on monogermane has been shown to produce not only  $\text{Ge}_2\text{H}_6$  and  $\text{Ge}_2\text{H}_8$ , but small amounts of higher germanes up to the octagermanes. Vapor phase chromatography was used to separate them.

$(\text{GeH}_2)_x$ , a polymer, may also contain Ge-Ge bonds. It may be formed as follows:<sup>12</sup>



Reaction of  $(\text{GeH}_2)_x$  with boiling aqueous HCl yields  $\text{H}_2$ , Ge,  $\text{GeH}_4$ ,  $\text{Ge}_2\text{H}_6$ , and  $\text{Ge}_3\text{H}_8$ .<sup>13</sup>

### B. Organic Compounds

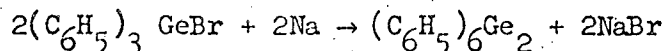
The first organic derivative of a polygermane was hexaphenyldigermane,  $(\text{C}_6\text{H}_5)_6\text{Ge}_2$ , prepared in 1925 by Morgan and Drew.<sup>14</sup> Since that time a considerable amount of progress has been made in the synthesis and study of this and other organodigermanes. In addition, several higher organogermanes have been reported.

The following review contains all known reports of organic compounds known or thought to contain at least one Ge-Ge bond. References to preparations in which a compound such as  $(C_6H_5)_6Ge_2$  was used to make a known reagent, such as  $(C_6H_5)_3GeK$ , for further study have been omitted when repetitive. References to work prior to January, 1950 are from Johnson.<sup>15</sup>

### 1. Synthesis

#### a. Coupling Reaction with an Alkali-Metal.

The most commonly applied method of synthesis of these compounds is the reaction of a halotriorganogermane,  $R_3GeX$ , with an alkali-metal, generally sodium, at elevated temperatures. The following have been reported:



This was the reaction of Morgan and Drew<sup>14</sup> that was first run in 1925. The reaction took place in hot xylene with excess sodium, with a yield of somewhat over 46%.

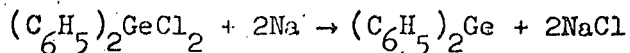
Sodium in boiling xylene did not react with bromotriethylgermane,  $(C_2H_5)_3GeBr$ , to form hexaethyl digermane,  $(C_2H_5)_6Ge_2$ .<sup>16</sup> A 30% yield of this compound was realized, however, by the direct action of sodium at elevated temperatures.

Hexamethyldigermane,  $(CH_3)_6Ge_2$ , was first synthesized by refluxing bromotrimethylgermane,  $(CH_3)_3GeBr$ , with an excess of potassium under nitrogen.<sup>17</sup> The potassium bromide formed hindered the reaction to such an extent that it was necessary to remove the volatile materials from it and condense them on fresh potassium several times. With this procedure, 74% of the germanium was converted to  $(CH_3)_6Ge_2$ .

Hexabenzoyldigermane,  $(C_6H_5CH_2)_6Ge_2$ , has been obtained, in unreported yield, from the reaction of bromotribenzylgermane,  $(C_6H_5CH_2)_3GeBr$ , with sodium in refluxing xylene.<sup>18</sup>

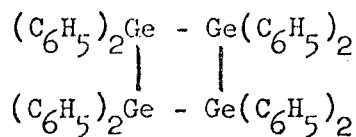
An 85% yield of hexacyclohexyldigermene,  $(C_6H_{11})_8Ge_2$ , was realized when the appropriate bromo compound was refluxed with an excess of sodium in toluene.<sup>19</sup>

A very interesting reaction, worthy of further investigation, has been reported by Kraus and Brown.<sup>20</sup> Dichlorodiphenylgermane,  $(C_6H_5)_2GeCl_2$ , with sodium in boiling xylene formed a compound with the empirical formula  $(C_6H_5)_2Ge$ .

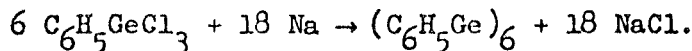


Only about 10-20% of the theoretical amount of  $(C_6H_5)_2Ge$  was obtained in the form of crystals. However, a considerable amount of resinous material approximating in composition  $(C_6H_5)_2Ge$ , was recovered. It could not be crystallized and was considered to be an impure polymer. The dichloro compound with lithium in ethylamine also gave this same resinous, uncrystallizable material.

Molecular weight determinations on the crystals gave a mean value of 903. This would indicate that the compound is a tetramer  $([(C_6H_5)_2Ge]_4$ , molecular weight 907). It has been suggested<sup>15</sup> that this might consist of a four-membered germanium ring.

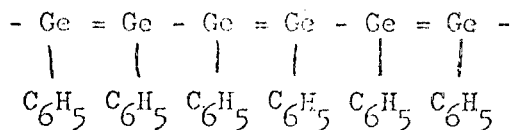


An even more fascinating compound has been prepared in boiling xylene by the reaction of either sodium<sup>21</sup> (refluxed 8 hrs.) or potassium<sup>22</sup> (refluxed 12 hrs.) with phenyltrichlorogermene.





It was suggested by the authors that this was an open chain molecule rather than a benzene-type ring.



Several reasons to support this belief were given. Upon dissolving this white solid, an intense yellow solution resulted, thus indicating to the authors that the substance was a polymeric species which dissociated into six-membered chains upon dissolution, resulting in the color change. More substantial evidence was the fact that each hexameric molecule reacted with 8 atoms of bromine, the halogen, presumably adding across each double bond and, in addition, eliminating the "free valences" at each end of the chain. The same reaction occurred with iodine, leading the authors to believe that no ring opening had occurred. Iodine, they said, being a less vigorous reactant, could not break a ring.

Germanium tetrachloride, p-tolyl bromide, and sodium in refluxing ether react to form an unreported amount of hexa-p-tolyldigermene,  $(\text{p-CH}_3\text{C}_6\text{H}_4)_6\text{Ge}_2$ .<sup>18</sup>

#### b. Grignard Reactions

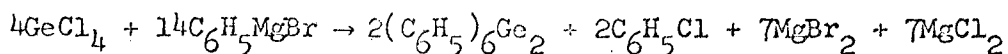
Morgan and Drew<sup>14</sup> detected no hexaphyldigermene among the products of the reaction between germanium tetrabromide and phenylmagnesium bromide,  $\text{C}_6\text{H}_5\text{MgBr}$ . Their solvent for the reaction was ether, or ether plus a small amount of chloroform, which was refluxed for 1 1/2 to 2 hours.

By varying the conditions somewhat, namely using a mixed ether-benzene solvent and increasing the refluxing time to six hours, and by using  $\text{GeCl}_4$ , Bauer and Burschkies<sup>18</sup> were able to isolate some hexaphenyldigermene, although their main product was still tetraphenylgermane,  $(\text{C}_6\text{H}_5)_4\text{Ge}$ . Reaction

with  $\text{GeBr}_4$  gave lower, but still significant amounts of the digermane. In addition, under the same conditions, hexa-p-tolyldigermane was obtained from  $\text{GeCl}_4$  and p-tolylmagnesium bromide. Neither yields nor balanced reactions are reported for these reactions.

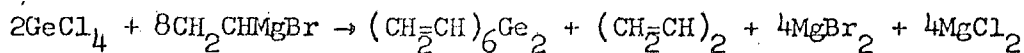
This mixed solvent method was developed by Johnson and Harris,<sup>23</sup> for the phenyl derivative, to give hexaphenyldigermane as the major product. Using a ten-to-one mole ratio of Grignard reagent to  $\text{GeCl}_4$ , and refluxing for 3 hours, in an ether-toluene solvent, almost 60% of the germanium was converted to hexaphenyldigermane. It is of interest that if the ether is removed before the reflux period, tetraphenylgermane is the major product.

The reaction for the formation of the organodigermane was written by the authors as:



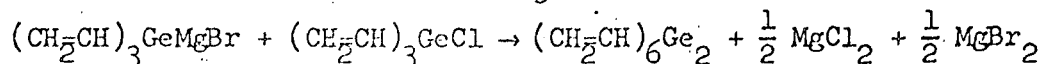
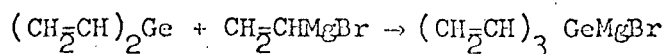
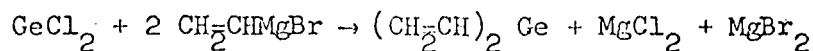
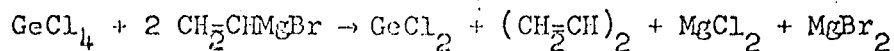
No evidence to support the formation of chlorobenzene is given.

Hexavinylidigermane,  $(\text{CH}_2=\text{CH})_6\text{Ge}_2$ , was prepared in 1957 by Seyferth<sup>24</sup> in yields up to 26% with the vinylmagnesium bromide in tetrahydrofuran. Thirty-five percent of the germanium was recovered as tetravinylgermane,  $(\text{CH}_2=\text{CH})_4\text{Ge}$ . Twenty hours of refluxing was found necessary. The reaction was reported as:



No evidence for the formation of butadiene was given, but a mechanism was proposed to support this reaction. It was suggested that the first step was the reduction of  $\text{GeCl}_4$  to  $\text{GeCl}_2$  by the Grignard reagent, producing the butadiene.  $\text{GeCl}_2$  was then vinylated and the Grignard added to it. Finally, reaction of this latter compound with partially vinylated  $\text{GeCl}_4$  would give

the desired product:



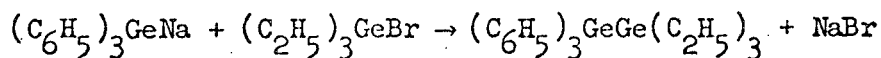
Several analogies are presented to support this mechanism, but its acceptance must await experimental verification.

In support of the reduction to the germanium (II) compound it should be mentioned that the +2 state becomes more stable as one proceeds down Group IVA of the Periodic Table. Tetrahalosilanes show no tendency to couple when reacted with a Grignard, whereas tetrahalotins are known to do this (see below).

In 1959 it was found<sup>25</sup> that up to 8% hexaethyldigermane could be obtained in the preparation of tetraethylgermane by the reaction of ethylmagnesiumbromide with  $\text{GeCl}_4$  or  $\text{GeBr}_4$  in ether. Kraus and Flood,<sup>16</sup> who first prepared tetraethylgermane by this method, did not report the digermane among their products. Thus one is led to believe that the Grignard method might yield a small amount of organodigermanes in more cases than have thus far been reported.

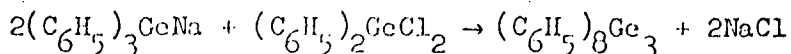
### c. Direct Coupling

The reaction of an alkali metal salt of germanium,  $\text{R}_3\text{GeM}$ , with a halotriorganogermane,  $\text{R}_3\text{GeX}$ , may cause a coupling of the germanium atoms to occur. Kraus and Sherman<sup>26</sup> showed this with the following reaction.



The coupling was accomplished by boiling the reagents in benzene. No yield was given.

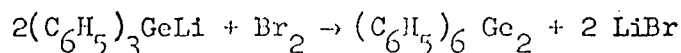
Reaction of an alkali metal germanium salt with a dihalide of germanium resulted in the formation of an organotrigermane.<sup>20</sup>



The solvent and experimental procedure were essentially the same as in the previous reaction. Once again, no yield was mentioned.

This method of preparing organodigermanes, both symmetrical and unsymmetrical, appears to be a good one. However, it does not seem to have been investigated since the above reactions were reported by Kraus and coworkers in the early 1930's.

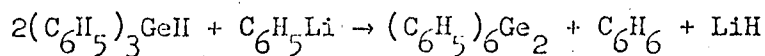
Possibly related to the above is the reaction of triphenylgermyl lithium with bromine in ethylene glycol dimethyl ether for form 78% hexaphenyldigermane.<sup>27</sup>



The fact that up to 12%  $(\text{C}_6\text{H}_5)_3\text{GeBr}$  was obtained as a byproduct leads one to believe that this might indeed also involve a coupling reaction of the type mentioned above.

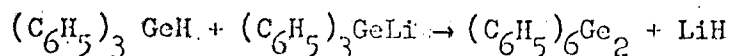
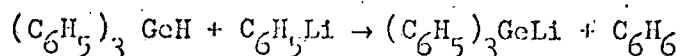
#### d. Organolithium Reactions

In 1950 Johnson and Harris<sup>23a</sup> found that by adding an excess of an ether solution of phenyllithium,  $\text{C}_6\text{H}_5\text{Li}$ , dropwise into a refluxing ether solution of triphenylgermane,  $(\text{C}_6\text{H}_5)_3\text{GeH}$ , up to 60% of the germane was converted to hexaphenyldigermane.



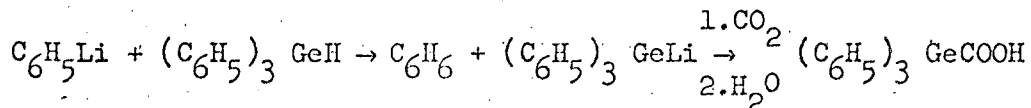
Reverse addition of the reactants gave only tetraphenylgermane. To explain this difference the authors postulated that this might in fact involve a coupling reaction between the germane and its lithium salt, the formation

being possible only because of the excess of the triphenylgermane.



Gilman and Gerow<sup>28</sup> confirmed that this coupling reaction does take place, but found that when equal amounts of the germane and its lithium salt were used, a maximum of only 12%  $(\text{C}_6\text{H}_5)_6 \text{Ge}_2$  could be obtained. Further, in repeating the reaction of Johnson and Harris in every detail except that an equivalent amount, rather than an excess, of phenyllithium was used and that the solution was not refluxed, no hexaphenyldigermane could be recovered. Thus they concluded, but could not explain, that the high yield may in some way be due to the excess phenyllithium - in spite of that fact that the triphenylgermane was actually in excess during most of the addition of the phenyllithium.

They also confirmed the first reaction in the proposed mechanism of Johnson and Harris, obtaining triphenylgermyl lithium in 83% yield. Actually the salt was not isolated as such, but was immediately carbonated to give triphenylgermane carboxylic acid,  $(\text{C}_6\text{H}_5)_3 \text{GeCOOH}$ , which was weighed.



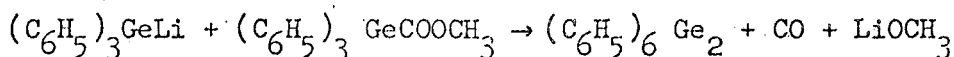
It is noteworthy that the reaction of methyllithium with triphenylgermane gave 10% hexaphenyldigermane when equivalent amounts of the reagents were stirred for three days at room temperature. The digermane probably was also formed from the reaction of triphenylgermane with the lithium salt of the germane initially produced.

It has also been found<sup>25</sup> that the reaction of ethyllithium with  $\text{GeBr}_4$  in ether solution produced 8.6% hexaethyldigermene along with 12% tetraethylgermane and a large amount of polymeric material.

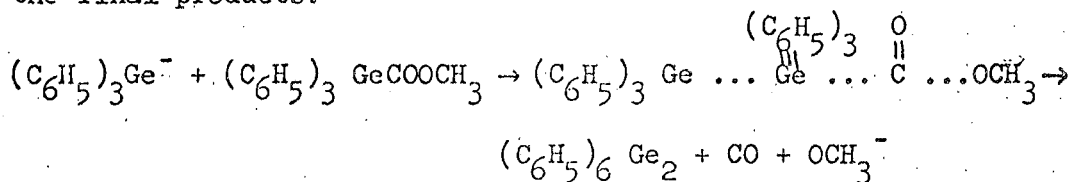
e. Miscellaneous Reactions

In addition to the reactions above, most of which were run for the expressed purpose of forming an organodigermene, several more unusual reactions have resulted, surprisingly, in the formation of hexaphenyldigermene in good yield.

In an attempt to prepare alcohols and ketones containing the triphenylgermyl group, triphenylgermyllithium, dissolved in ethyleneglycol-dimethyl ether, was added to methyl triphenylgermanecarboxylate,  $(\text{C}_6\text{H}_5)_3\text{GeCOOCH}_3$ .<sup>29</sup> Instead of the expected bis(triphenylgermyl) ketone or tris(triphenylgermyl) carbinol, carbon monoxide was vigorously evolved and hexaphenyldigermene was obtained in 75% yield (based on triphenylgermanecarboxylate).



The authors suggested that the mechanism may involve attack of the triphenylgermyl anion on the germanium atom of the triphenylgermylcarboxylate ester. A pentacovalent intermediate is thus formed which leads to the final products.

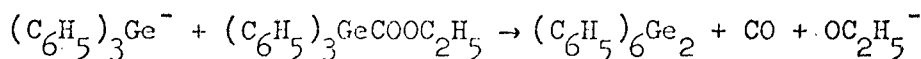
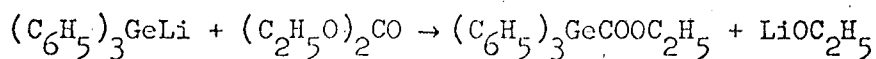


To ascertain the origin of each germanium atom in the product, methyl triphenylgermanecarboxylate was reacted with triphenylsilyl lithium,  $(\text{C}_6\text{H}_5)_3\text{SiLi}$ . The only product isolated was (triphenylgermyl) triphenylsilane,

$(C_6H_5)_3GeSi(C_6H_5)_3$ , indicating that in the formation of hexaphenyldigermene, one germanium atom came from the triphenylgermyl lithium, the other from the ester.

Reaction of triphenylgermyl lithium with diethylcarbonate,  $(C_2H_5O)_2CO$ , also resulted in the evolution of carbon monoxide and the isolation of hexaphenyldigermene as the only product. A yield of 88% was obtained when a deficiency of the carbonate was used and 47% with an excess of carbonate.

The mechanism for this reaction proposed by the authors involves the initial formation of ethyl triphenylgermanecarboxylate, which then reacts as above.

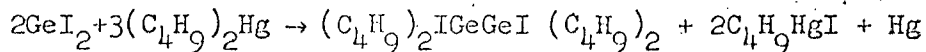


Smith and Kraus,<sup>30</sup> in the course of investigating the reactions of triphenylgermyl sodium with organic polyhalides in ether, discovered that in addition to substitution of one or more of the halides by the triphenylgermyl group, the germyl groups which did not react with the organic compound combined to form hexaphenyldigermene. The amount of hexaphenyldigermene recovered, in fact, was the way in which it was determined how many halogen atoms were replaced. For example, in the reaction of triphenylgermyl sodium with carbon tetrachloride, 84-91% of the germanium was recovered as hexaphenyldigermene. Thus the authors concluded that, at best, not more than one chlorine atom had been replaced by a triphenylgermyl group. No substitution compound was isolated.

Reaction with chloroform yielded 62% hexaphenyldigermene. Bis(triphenylgermyl)methane,  $[(C_6H_5)_3Ge]_2CH_2$ , was obtained in 9% yield, but the source of the second hydrogen was left unexplained.

Acetylene dichloride, ethylene dibromide, and  $\beta$ -butylene bromide gave 63%, 87%, and 91% hexaphenyldigermene, respectively. In no case was any substitution compound identified, only oils and small amounts of triphenylgermyl oxide. The oxide might indicate that compounds which might form decompose on handling. Trimethylene bromide gave 62% hexaphenyldigermene plus a small amount of bis(triphenylgermyl)propane,  $(C_6H_5)_3Ge(CH_2)_3Ge(C_6H_5)_3$ .

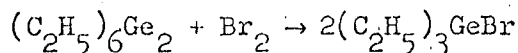
Perhaps potentially the most interesting compound of all those containing a Ge-Ge bond is 1, 2-diiodotetrabutyl digermene,  $(C_4H_9)_2I GeGe I (C_4H_9)_2$ . It is obtained<sup>31</sup> in the reaction of germanium diiodide,  $GeI_2$ , with excess dibutylmercury,  $Bu_2Hg$ , in acetone. It is the only haloorganodigermene known.



## 2. Properties

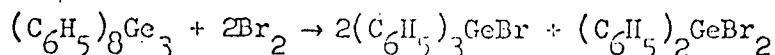
No reactions of the polygermanes or their derivatives are known which retain the Ge-Ge bond. With the exception of hexaphenyldigermene, very little has been done with these compounds.

In every case attempted, reaction with bromine has resulted in cleavage of the metal-metal bond, forming the bromotriorganogermene. When a solution of bromine in ethylbromide is added to hexaethyldigermene, bromotriethylgermane is quantitatively produced.<sup>16</sup>



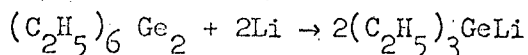
A boiling carbon tetrachloride solution is needed to affect cleavage of hexaphenyldigermene by bromine.<sup>14</sup> Octaphenyltrigermene reacts incompletely with bromine in a carbon tetrachloride solution at room temperature to give bromotriphenylgermane and dibromodiphenylgermane.<sup>20</sup>





The cleavage of the metal-metal bond by halogens was used by Seyferth<sup>24</sup> in his identification of hexavinyl digermane. Both iodine (46% conversion) and bromine (23% conversion) reaction with this compound in chloroform solution to form the corresponding halides.

Reaction of an alkali metal with an organodigermane gives more variable results, depending on the compound, the metal and the conditions. Lithium in ethylamine readily converts hexaethyl digermane to triethylgermyl lithium.<sup>16</sup>



Potassium in the same solvent gives an almost quantitative yield of triethylgermyl potassium. A solution of sodium in liquid ammonia gives no appreciable reaction with hexaethyl digermane, although this might, in part, be due to the insolubility of the digermane in this solvent.

Refluxing potassium does not react with hexamethyl digermane.<sup>17</sup> Even with sodium-potassium alloy in ethylene glycol dimethyl ether, after three days, almost 50% of the hexamethyl digermane was recovered and no yellow color, characteristic of the potassium salt, was observed.

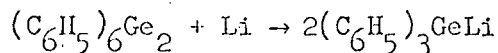
A suspension of hexaphenyl digermane in a sodium-liquid ammonia solution reacts only very slowly, but again this may partially be due to its insolubility in this solvent.<sup>32</sup>

Gilman and Gerow<sup>33</sup> studied the cleavage of hexaphenyl digermane in various solvents in an attempt to prepare triphenylgermyl salts for further study. With sodium potassium alloy in ether no reaction took place. In benzene, 76% of the digermane could be recovered, along with 13% tetraphenylgermane. Apparent complete cleavage took place with this alloy in

refluxing di-n-butyl ether and in refluxing xylene, although no potassium salts could be recovered. Tetrahydrofuran, bromobenzene, and tetraphenylgermane act as initiators in ether solution for the alloy, resulting in a good percentage of the digermane being cleaved.

Using ethylene glycol dimethyl ether as a solvent, some cleavage of hexaphenyldigermane did occur, but again no derivative could be isolated. It is believed that any triphenylgermyl potassium which is formed is further attacked by the alloy.

To date the most effective method for cleaving hexaphenyldigermane to form the triphenylgermyl anion is to react it with lithium in a small amount of the glycol ether.



It is believed<sup>34</sup> that in this case conversion is complete.

Diphenylgermanium tetramer,  $[(\text{C}_6\text{H}_5)_2\text{Ge}]_4$ , in liquid ammonia, adds two sodium atoms for each germanium atom, giving a red solution characteristic of  $(\text{C}_6\text{H}_5)_2\text{GeNa}_2$ .<sup>20</sup>

Of all the organic compounds containing a Ge-Ge bond only hexavinyl-digermane is reported to be air-sensitive.<sup>24</sup> Even for this compound, reaction is very slow.

### C. Comparison to Compounds Containing the Si-Si Bond

A great deal more work has been done with silicon compounds than with their germanium analogs. In fact, many silicon compounds have, as yet, no counterparts in germanium chemistry. This is particularly true for the compounds with metal-metal bonds.

Many symmetric and unsymmetric disilanes have been synthesized and studied. For the most part, only those compounds and reactions which relate to the preceding section will be discussed here.

## 1. Inorganic Compounds

Stock first prepared and characterized the higher silanes up to tetrasilane,  $\text{Si}_4\text{H}_{10}$ .<sup>35</sup> In addition, he was able to isolate an inseparable mixture of several isomers of  $\text{Si}_5\text{H}_{12}$  and  $\text{Si}_6\text{H}_{14}$ . These hydrides were formed by the reaction of hydrochloric acid with magnesium silicide.

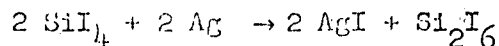
Recently, twenty-one individual silanes have been obtained, and separated by vapor phase chromatography, from the reaction of phosphoric acid with magnesium silicide.<sup>36</sup> The authors were able to identify n- $\text{Si}_4\text{H}_{10}$ , another  $\text{Si}_4\text{H}_{10}$  of undetermined structure, n- $\text{Si}_5\text{H}_{12}$ , iso- $\text{Si}_5\text{H}_{12}$ , and tentatively to identify hexa-, hepta-, and octasilanes.

Disilane has also been obtained by reaction of lithium aluminum hydride with hexachlorodisilane.<sup>37</sup>

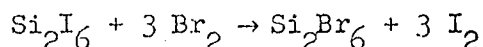
Higher chlorides of silicon have been known for some time. Hexachlorodisilane,  $\text{Si}_2\text{Cl}_6$ , has been prepared in a number of ways.<sup>38</sup> The passage of silicon tetrachloride over silicon at temperatures exceeding  $1000^\circ$  resulted in its formation, as did the reaction of chlorine or mercuric chloride with hexaiododisilane. The passage of silicon tetrachloride-hydrogen mixture through an electric discharge produced not only hexachlorodisilane, but higher chlorides as well. Chlorides up to hexasilane,  $\text{Si}_6\text{Cl}_{14}$ , have been synthesized by the reaction of chlorine on silicon-calcium alloy.

$\text{Si}_{10}\text{Cl}_{22}$ <sup>39</sup> and  $\text{Si}_{10}\text{Cl}_{20}\text{H}_2$ <sup>40</sup> have both been obtained by the reaction of silicon tetrachloride with hydrogen in a "hot-cold" tube. Among other higher chlorides reported are  $\text{Si}_{10}\text{Cl}_{18}$ ,  $\text{Si}_{16}\text{Cl}_{26}$ , and  $\text{Si}_{18}\text{Cl}_{30}$ .<sup>41</sup>

Friedel and Landerburg prepared hexaiododisilane from silicon tetraiodide and silver metal.<sup>42</sup>



They used this disilane to form not only hexachlorodisilane, but also hexabromodisilane by reaction with bromine.

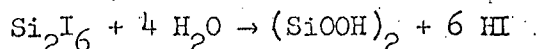


These reactions attest to the stability of the Si-Si bond in these compounds.

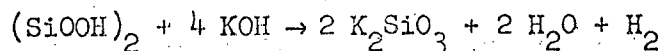
Hexafluorodisilane has been produced by the reaction of hexachlorodisilane with zinc fluoride.<sup>43</sup>

Disilane does not react with pure water in quartz vessels.<sup>35</sup> In an alkaline solution, however, rapid hydrolysis occurs quantitatively to form silicic acid,  $\text{H}_2\text{SiO}_3$ , plus hydrogen. The reaction is so sensitive to alkali that even a small piece of ordinary glass dropped into the quartz tube is sufficient to cause reaction. An acid solution will also cause hydrolysis to occur.

The hydrolysis of a hexahalodisilane was first studied by Friedel and Ladenburg in 1880.<sup>42, 44</sup> Hexaiododisilane reacted with ice water to give a compound probably analogous to oxalic acid.



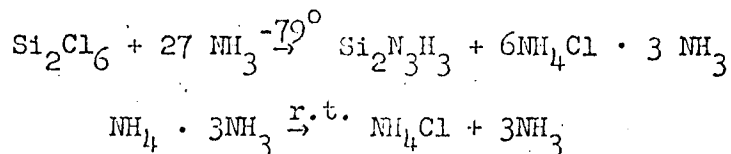
Alkaline solution caused the Si-Si bond to break.



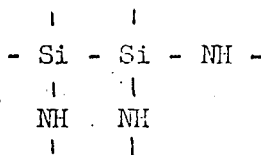
Hexachlorodisilane has also been found to form  $(\text{SiOOH})_2$ .

The evolution of hydrogen in the alkaline hydrolysis of hexachlorodisilane has been used to quantitatively determine the Si-Si bond.<sup>46</sup>

The reaction of hexachlorodisilane with ammonia has recently been studied by Billy.<sup>47</sup> At  $-79^{\circ}$ , 27 molecules of ammonia were taken up for each molecule of hexachlorodisilane. At room temperature, however, 18 of the ammonia molecules are released. The reactions have been written as:



The author proposed that the compound is polymeric, corresponding to



rather than individual molecular units such as  $\text{HN} = \text{Si} \underset{\text{NH}}{-} \text{Si} = \text{NH}$ , as

was previously proposed.<sup>48</sup>  $\text{Si}_2(\text{NH})_3$  is stable at room temperature under a vacuum but is sensitive to the slightest trace of water.

## 2. Organic Compounds

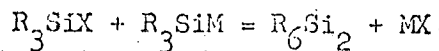
Organosilicon compounds, including those containing a Si-Si bond, have been the subject of a recent book by Eaborn.<sup>49</sup>

As was true in the case of organogermanium compounds, the most popular route to the formation of a metal-metal bond is the reaction of a halotriorganosilane,  $\text{R}_3\text{SiX}$ , with an alkali metal. Reaction with sodium has produced  $[(\text{C}_6\text{H}_5)_2\text{Si}]_4$  and  $[(p\text{-CH}_3\text{C}_6\text{H}_4)_2\text{Si}]_4$  from dichlorodiphenylsilane,  $(\text{C}_6\text{H}_5)_2\text{SiCl}_2$ , and dichlorodi-p-tolylsilane,  $(p\text{-CH}_3\text{C}_6\text{H}_4)_2\text{SiCl}_2$ , respectively. These compounds are also believed to be cyclic. Dichlorodimethylsilane,  $(\text{CH}_3)_2\text{SiCl}_2$ , gives primarily  $[(\text{CH}_3)_2\text{Si}]_6$  along with other higher polymers.

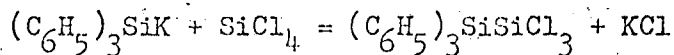
Reaction of organometallic compounds, including Grignards, with tetrahalosilanes have never resulted in a coupling of the silicon atoms.

Direct coupling reactions of an organosilicon halide with an organosilicon alkali metal salt have also been used to synthesize organodisilanes.

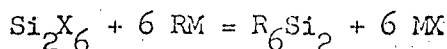
In addition to reactions such as



which are analogous to those mentioned above for germanium, reactions such as the following under proper conditions, have proved successful.

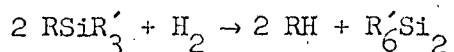


Reaction of organometallic reagents with halodisilanes, yet to be attempted for hexachlorodigermene, has successfully produced organodigermenes.



Hexachlorodisilane has generally been the starting reagent, although both the bromo- and iodo- compounds have been used. Organolithium and organosodium, as well as Grignard reagents have produced symmetric organodisilanes, although some cleavage of the Si-Si bond usually occurs.

A reaction which has no counterpart in germanium chemistry is the hydrogenolysis of a tetraorganosilane.



High temperatures and pressures are essential. Hexamethyldisilane, hexaethyldisilane, and hexaphenyldisilane have been made in this way.

Enough work has been done with organodisilanes to permit one to make several generalizations concerning their behavior.

Hexaryldisilanes are quite resistant to the action of bromine. As with hexaphenyldigermene, hexaphenyldisilane is cleaved only by a boiling carbon tetrachloride solution of bromine. Hexaalkyldisilanes are much more susceptible to cleavage. This difference between aryl- and alkyldisilanes

appears also to be true for the organodigermanes, but as yet, too few of the latter have been studied to permit such a generalization.

The opposite behavior is shown upon exposure of organodisilanes to alkali metals. Hexaalkyls are unaffected, whereas hexaryl- and aryl-alkyl-disilanes are cleaved quite easily. This cleavage has been quite effectively produced by sodium-potassium alloy in ether and by lithium in tetrahydrofuran.

Hexaaryldisilanes show no tendency to dissociate into free radicals. Even hexa-p-biphenyldisilane is unaffected by prolonged treatment with oxygen and iodine,<sup>50</sup> as in hexaphenyldisilane.<sup>51</sup>

#### D. Comparison to Compounds Containing Sn-Sn Bond

The chemistry of distannane compounds is at about the same stage as that of the digermane derivatives, although the number of organic compounds with Sn-Sn bonds is somewhat greater than for the germanes. The distannanes are generally more reactive than their germanium analogs.

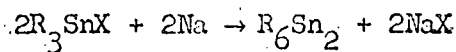
##### 1. Inorganic Compounds

The only inorganic compound known to contain an Sn-Sn bond is the recently prepared distannane.<sup>52</sup> It is very unstable, decomposing completely to tin and hydrogen upon warming to room temperature.

##### 2. Organic Compounds

Organostannane compounds have been the subject of a recent review by Ingham, Rosenberg, and Gilman.<sup>53</sup>

As with germanium and silicon, the most commonly used method of preparing compounds of the type  $R_6Sn_2$  has been the reaction of sodium with a halotriorganostannane.



A great variety of other methods of synthesis have proven successful. For instance, tin alloy reactions with ethyl iodide and with phenyl mercuric chloride form, among their products, hexaethyl distannane,  $(C_2H_5)_6Sn_2$ , and hexaphenyldistannane  $(C_6H_5)_6Sn_2$ , respectively.

Coupling of halotriphenylstannane with triphenylstannyl lithium has been shown to produce hexaphenyldistannane in good yield. Unsymmetrical organodistannane compounds have also been formed in this way.

Along with the expected tetracyclohexylstannane, some hexacyclohexyldistannane was formed in the reaction of tin tetrachloride with cyclohexylmagnesium bromide. Tin dichloride with a phenyl Grignard also forms hexaphenyldistannane.

In addition, the main product of the reaction of tri-*o*-tolylstannyl lithium with *o*-iodotoluene is hexa-*o*-tolyl distannane.

Hexaalkyldistannane compounds are oxidized slowly in air, although hexaaryl and alkylaryls are stable.

Halogens readily cleave all known distannane compounds, as do alkali metals. Particularly good for the latter reactions are sodium in liquid ammonia and sodium-potassium alloy in ether. Lithium metal in THF gave poor yields of triphenylstannyl lithium from hexaphenyldistannane.

Organolithium compounds, as well as several others, are also capable of this cleavage, thereby cutting down the number of reagents which might otherwise be used to form organodistannanes.

Dissociation of distannane compounds into free radicals has been a matter of some uncertainty.



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