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Author
Kopp, Richard Wilhelm.

Publication Date
1962-09-01
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Berkeley, California
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THE CHEMISTRY OF HEXACHLORODIGERMANE

Richard Wilhelm Kopp
Master's Thesis

September 1962
## Contents

I. Introduction

II. Preparation
   A. Preparation Using a Solenoid Discharge
      1. Apparatus and Experimental Procedure
      2. Results and Evaluation
   B. Preparation Using a Bronze Wool Discharge Tube
      1. Apparatus and Experimental Procedure
      2. Results and Evaluation
   C. Preparation Using a Microwave Discharge
      1. Apparatus and Experimental Procedure
      2. Results and Evaluation

III. Physical Properties

IV. Chemical Properties
   A. Reaction with NaBH₄
      1. Apparatus and Experimental Procedure
      2. Results and Discussion
   B. Reaction with H₂O
      1. Apparatus and Experimental Procedure
      2. Results and Discussion
   C. Reaction with NH₃
      1. Solid-Vapor Reaction
      2. Solid-Liquid Reaction
THE CHEMISTRY OF HEXACHLORODIGERMANE - Contents

D. Reaction with HCl
   1. Apparatus and Experimental Procedure 28
   2. Results and Discussion 28

V. Review of Compounds Containing the Ge-Ge Bond 31
   A. Inorganic Compounds 31
   B. Organic Compounds 31
   C. Comparison to Compounds Containing the Si-Si Bond 43
   D. Comparison to Compounds Containing the Sn-Sn Bond 48

Acknowledgements 50

References 51
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\(^1\) 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\(^2\) succeeded in 1958 in obtaining yields of up to 250 mg per hour according to the reaction:

\[
2\text{GeCl}_4 = \text{Ge}_2\text{Cl}_6 + \text{Cl}_2
\]

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\(^3\) 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 propor-
tional 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 dis-
charge 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 2 in which
GeCl₄ was passed through the reaction zone, and Ge₂Cl₆, unreacted GeCl₄, and
Cl₂ were collected in U-tubes surrounded by cold traps at -20°C (ice-HCl),
-78°C (Dry Ice-acetone), and -196°C (liquid nitrogen), respectively. However,
no quantitative work was done with this set-up.

Since only a small amount of the GeCl₄ vapor which passes through the dis-
charge zone reacts, an apparatus was designed and built to permit recycling
of GeCl₄ vapors, Fig. 1. The diameter of the reaction tube was 30 mm.

GeCl₄ was distilled into U-tube A from weighing bulb (a). After a -78°C
cold bath was put around B and a -196°C 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 1.
Ge₂Cl₆ and unreacted GeCl₄ were collected in trap B, and Cl₂ was collected in
trap C. After all the GeCl₄ vapor had passed through, a -20°C bath was set
FIG. 1. APPARATUS USED WITH SOLENOID DISCHARGE.
around B, to hold the Ge₂Cl₆ but permit the GeCl₄ to distil, and the -78°C bath around A. The stopcocks were each turned by 180° and the GeCl₄ again was passed through the discharge zone. If desired, the recycling process could be continued until all of the GeCl₄ had decomposed. Generally, since the primary concern was not the actual production of large quantities of Ge₂Cl₆, but rather the effectiveness of the conditions used, the reaction was terminated after only a few cycles. The Cl₂ was pumped off, the GeCl₄ remaining was collected and weighed in (a) and the Ge₂Cl₆ collected and weighed in (b).

2. Results and Evaluation.

Table I. Synthesis of Ge₂Cl₆
Using a Solenoid Discharge

<table>
<thead>
<tr>
<th>No.</th>
<th>% GeCl₄ decomposed</th>
<th>% yield* Ge₂Cl₆</th>
<th>flow rate, mmole GeCl₄/ min</th>
<th>yield, mmole Ge₂Cl₆/hr</th>
<th>duration of run, min</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.23</td>
<td>12.5</td>
<td>2.14</td>
<td>0.11</td>
<td>200</td>
</tr>
<tr>
<td>2</td>
<td>0.79</td>
<td>24.3</td>
<td>2.80</td>
<td>0.16</td>
<td>119</td>
</tr>
<tr>
<td>3</td>
<td>(a)</td>
<td>(a)</td>
<td>0.70</td>
<td>0.26</td>
<td>98</td>
</tr>
<tr>
<td>4</td>
<td>6.18</td>
<td>50.0</td>
<td>0.51</td>
<td>0.45</td>
<td>100</td>
</tr>
<tr>
<td>5</td>
<td>4.38</td>
<td>49.0</td>
<td>0.61</td>
<td>0.40</td>
<td>136</td>
</tr>
</tbody>
</table>

* Based on the amount of GeCl₄ decomposed according to the reaction:

\[ 2\text{GeCl}_4 = \text{Ge}_2\text{Cl}_6 + \text{Cl}_2 \]

(a) GeCl₄ recovery tube broken

The greater yield of Ge₂Cl₆ and greater recovery of GeCl₄ 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 Cl₂ formed in the reaction and thus prevent any further reaction of the Cl₂ with the Ge₂Cl₆ formed. The bronze wool did not pick up the Cl₂ 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 Cl₂ 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 Cl₂ 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 (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 GeOCl₂ by Schwarz and Heinrich in 1930. Schumb and Smyth in 1955 found that this compound was actually a "new form" of GeCl₂ which spontaneously changes to the more usual white solid form of GeCl₂. This GeCl₂ itself decomposes to GeCl₄ 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 GeCl₄ to end up as Ge Cl₅. 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 CuCl. Whether it reacted directly with the GeCl₄ or only with the Cl₂ 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, for the preparation of B₂Cl₄ from BCl₃, 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 Triplett 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.

Tungsten electrodes

Bronze wool

Water jacket
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 GeCl₄/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 Ge₂Cl₆, but also of reducing it further, it would be beneficial to remove the Ge₂Cl₆ 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 Ge₂Cl₆. It appears that after the reaction tube has been used for about an hour, or perhaps less, its ability to produce Ge₂Cl₆ 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 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 Ge₂Cl₆.
TABLE II. Synthesis of \( \text{Ge}_2\text{Cl}_6 \) Using a Bronze Wool Discharge Tube

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

* 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 GeCl₄ 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 GeCl₄ in the next run. A U-tube with 2 mm bore stopcocks was used for the first trap (-20⁰) in one run (not in Table) but this gave only a negligible yield of Ge₂Cl₆, presumably because it decreased the flow rate to a great extent (see later discussion).

The Ge₂Cl₆ was collected for weighing and for temporary storage by replacing the tube containing the collected GeCl₄ by another tube with stopcocks, into which the Ge₂Cl₆ 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 Ge₂Cl₆, which must not be exposed to the air.
FIG. 3. APPARATUS FOR MICROWAVE DISCHARGE.
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>
<thead>
<tr>
<th>No.</th>
<th>%GeCl₄ decomposed</th>
<th>%Ge₂Cl₆ yield</th>
<th>flow rate, mmole GeCl₄/min</th>
<th>yield, mmole Ge₂Cl₆/hr</th>
<th>length of run, min.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>(a)</td>
<td>-</td>
<td>ca. 2</td>
<td>0.28</td>
<td>25</td>
</tr>
<tr>
<td>2</td>
<td>(a)</td>
<td>-</td>
<td>ca. 1</td>
<td>0.59</td>
<td>46</td>
</tr>
<tr>
<td>3</td>
<td>3.11</td>
<td>21.4</td>
<td>5.84</td>
<td>1.14</td>
<td>8</td>
</tr>
<tr>
<td>4</td>
<td>3.11</td>
<td>33.9</td>
<td>4.49</td>
<td>1.42</td>
<td>11</td>
</tr>
<tr>
<td>5</td>
<td>2.31</td>
<td>50.6</td>
<td>3.41</td>
<td>1.18</td>
<td>100</td>
</tr>
<tr>
<td>6</td>
<td>3.66</td>
<td>40.3</td>
<td>1.64</td>
<td>0.73</td>
<td>195</td>
</tr>
<tr>
<td>7</td>
<td>2.54</td>
<td>18.6</td>
<td>2.10</td>
<td>0.31</td>
<td>145</td>
</tr>
</tbody>
</table>

(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 GeCl₄/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 GeCl₄ which decomposes ends up as Ge₂Cl₆. It may be that the Cu picks up some of the Cl₂ which might otherwise react with the Ge₂Cl₆ already formed. The bronze wool does acquire a thin white coating during a run, although much Cl₂ is still observed in the liquid nitrogen trap.

III. PHYSICAL PROPERTIES

The vapor pressure of Ge₂Cl₆ was determined over the range 24.7° to 59.7°. Below 24.7° the vapor pressure is so low that accurate measurements are impossible. Above 59.7°, 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 Ge₂Cl₆ used was pure. Each sample was distilled twice, collecting it at -20°, 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°. Before each reading the Ge₂Cl₆ in the side arm was again pumped on at -20° 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 Ge₂Cl₆

<table>
<thead>
<tr>
<th>Physical State</th>
<th>t, °C</th>
<th>P mm</th>
<th>Δ</th>
</tr>
</thead>
<tbody>
<tr>
<td>solid</td>
<td>24.7</td>
<td>0.8</td>
<td>-0.1</td>
</tr>
<tr>
<td>solid</td>
<td>29.7</td>
<td>1.1</td>
<td>0</td>
</tr>
<tr>
<td>solid</td>
<td>34.7</td>
<td>1.5</td>
<td>0</td>
</tr>
<tr>
<td>solid</td>
<td>39.7</td>
<td>2.2</td>
<td>0</td>
</tr>
<tr>
<td>liquid</td>
<td>44.7</td>
<td>3.0</td>
<td>0</td>
</tr>
<tr>
<td>liquid</td>
<td>49.7</td>
<td>4.1</td>
<td>+0.1</td>
</tr>
<tr>
<td>liquid</td>
<td>54.7</td>
<td>5.3</td>
<td>-0.2</td>
</tr>
<tr>
<td>liquid</td>
<td>59.7</td>
<td>6.9</td>
<td>+0.7</td>
</tr>
</tbody>
</table>

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 Ge₂Cl₆ at 29.7°

<table>
<thead>
<tr>
<th>Time after immersion into bath, min.</th>
<th>Pressure, min.</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>1.1</td>
</tr>
<tr>
<td>4</td>
<td>1.1</td>
</tr>
<tr>
<td>5</td>
<td>1.0</td>
</tr>
<tr>
<td>7</td>
<td>1.2</td>
</tr>
<tr>
<td>9</td>
<td>1.3</td>
</tr>
<tr>
<td>11</td>
<td>1.5</td>
</tr>
<tr>
<td>15</td>
<td>1.7</td>
</tr>
</tbody>
</table>

The rise in pressure, starting at about 9 minutes, is believed due to decomposition of the Ge₂Cl₆ to the more volatile GeCl₄. 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 \( \Delta H^0 \) 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° - 42.0°.

The infrared spectrum of Ge₂Cl₆ was taken in CCl₄ solution and in CS₂ solution. Both the NaCl and KBr regions were observed. See Figs. 5 and 6. A known amount of doubly distilled Ge₂Cl₆ was distilled into an ampule with a constricted neck. The solvent was then condensed onto it and the ampule warmed to room temperature. The Ge₂Cl₆ 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 Ge₂Cl₆.
FIG. 5. INFRARED SPECTRA OF 0.3 M GeCl₄ IN CC1₄ SOLUTION
FIG. 6. INFRARED SPECTRA OF 0.25 M Ge₂Cl₆ IN CS₂ SOLUTION.
IV. CHEMICAL PROPERTIES

A. Reaction with NaBH₄

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 CaH₂, then distilled, the fraction boiling between 161° and 162° being collected. Even with this procedure, some slight reaction of the solvent with the NaBH₄ dissolved in it was observed.

After Ge₂Cl₆ 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 NaBH₄ 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 N₂. Pumping and stirring were continued for at least one hour after the last of
bo~ohydride solution had been added. The flask was then isolated from the line. The content of the -78° 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° (Dry-Ice-acetone), -112° (carbon disulfide slush), and -196° (liquid nitrogen), respectively.

2. Results and Discussion

The -78° trap was found to contain mainly solvent that had passed through the original -78° 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° 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° 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 Ge₂Cl₆ With NaBH₄

<table>
<thead>
<tr>
<th>conc. Ge₂Cl₆, moles/liter</th>
<th>conc. BH₄⁻, moles/liter</th>
<th>BH₄⁻, Ge₂Cl₆</th>
<th>%Ge as GeH₄</th>
<th>%Ge as Ge₂H₆</th>
<th>%B recovered as B₂H₆</th>
<th>rate of addition, ml/min</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.10</td>
<td>0.63</td>
<td>6.5</td>
<td>15.5</td>
<td>trace</td>
<td>27.3</td>
<td>5</td>
</tr>
<tr>
<td>0.04</td>
<td>0.27</td>
<td>7.1</td>
<td>29.9</td>
<td>trace</td>
<td>5.6</td>
<td>5</td>
</tr>
<tr>
<td>0.13</td>
<td>0.09</td>
<td>6.6</td>
<td>41.1</td>
<td>8</td>
<td>3.3</td>
<td>0.5</td>
</tr>
<tr>
<td>0.19</td>
<td>0.10</td>
<td>7.5</td>
<td>41.6*</td>
<td>5</td>
<td>3.1</td>
<td>1</td>
</tr>
</tbody>
</table>

* 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 digermane, and 43.2% more germane.

As shown in Table VI, germane was always obtained as the major product. The yields of digermane 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 digermane, 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:

\[
\text{Ge}_2\text{Cl}_6 + 6 \text{NaBH}_4 \rightarrow \text{GeH}_4 + \text{GeH}_2 + 3 \text{B}_2\text{H}_6 + 6 \text{NaCl}
\]

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 germate. Secondly, much less than the expected diborane was recovered.

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

\[
\text{Ge}_2\text{H}_6 + \text{BH}_4^- \rightarrow \text{H}_3\text{Ge-GeH}_3 \rightarrow \text{H}_3\text{Ge-BH}_3^- + \text{GeH}_4
\]

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

\[
\text{H}_3\text{Ge-BH}_3^- + 3 \text{H}_2\text{O} + \text{H}^+ \rightarrow \text{GeH}_4 + \text{H}_3\text{BO}_3 + 3\text{H}_2
\]

One might then write the reaction in diglyme solution as:

\[
\text{Ge}_2\text{Cl}_6 + 7 \text{NaBH}_4 \rightarrow \text{GeH}_4 + 6 \text{NaCl} + \text{Na}^+\text{(H}_3\text{GeBH}_3^-) + 3 \text{B}_2\text{H}_6
\]

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 Apiezon 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 noncondensible 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 Ge₂Cl₆ with H₂O

<table>
<thead>
<tr>
<th>mmole Ge₂Cl₆</th>
<th>Solution added</th>
<th>Normality of final solution</th>
<th>Conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.26</td>
<td>0.5 ml distilled H₂O</td>
<td>3N HCl</td>
<td>room temp. 24 hrs.</td>
</tr>
<tr>
<td>0.34</td>
<td>0.2 ml 0.1N NaOH</td>
<td>10N HCl</td>
<td>room temp. 30 hrs.</td>
</tr>
<tr>
<td>0.17</td>
<td>2.0 ml 1N NaOH</td>
<td>0.5N NaOH</td>
<td>room temp. 48 hrs.</td>
</tr>
<tr>
<td>0.22</td>
<td>0.2 ml 0.1N NaOH</td>
<td>6.5N HCl</td>
<td>room temp. 24 hrs.</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>50°, 1 hr.</td>
</tr>
<tr>
<td>0.39</td>
<td>0.2 ml 0.1N NaOH</td>
<td>11.6N HCl</td>
<td>room temp. 24 hrs.</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>70°-100° overnight</td>
</tr>
</tbody>
</table>

* based on 6 moles HCl forming from each mole Ge₂Cl₆.
In no case was hydrogen evolved, even in the basic solution. This differs sharply from the analogous reaction of Si$_2$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: GeO is yellow to brown and is insoluble in water. 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 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 "germano-oxalic acid" is formed according to the reaction:

$$\text{Ge}_2\text{Cl}_6 + 4\text{H}_2\text{O} \rightarrow (\text{GeOOH})_2 + 6\text{HCl}$$

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

\[(\text{GeOCl}_2)_2 \rightarrow \text{GeO} + \text{GeO}_2 + \text{H}_2\text{O}\]

C. Reaction with \(\text{NH}_3\)

1. Solid-Vapor Reaction

a. Apparatus and Experimental Procedure

Two different methods were used to study the reaction of \(\text{Ge}_2\text{Cl}_6\) with ammonia. In the first, a known amount of sodium-dried vapor was allowed to come in contact with a known amount of \(\text{Ge}_2\text{Cl}_6\). 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 \(\text{Ge}_2\text{Cl}_6\) with \(\text{NH}_3\)

<table>
<thead>
<tr>
<th>mmole (\text{Ge}_2\text{Cl}_6):</th>
<th>1.</th>
<th>2.</th>
</tr>
</thead>
<tbody>
<tr>
<td>mmole (\text{NH}_3) added:</td>
<td>0.197</td>
<td>0.228</td>
</tr>
<tr>
<td>mmole (\text{NH}_3) recovered:</td>
<td>3.05</td>
<td>3.31</td>
</tr>
<tr>
<td>mmole (\text{NH}_3) reacted:</td>
<td>1.81</td>
<td>1.73</td>
</tr>
<tr>
<td>(\text{NH}_3/\text{Ge}_2\text{Cl}_6):</td>
<td>6.3</td>
<td>6.9</td>
</tr>
<tr>
<td>reaction time, hrs.:</td>
<td>30</td>
<td>9</td>
</tr>
<tr>
<td>temperature:</td>
<td>0° to 25°</td>
<td>-63°</td>
</tr>
</tbody>
</table>
Reaction of Si₂Cl₆ with ammonia proceeds by the following equation:

\[ \text{Si}_2\text{Cl}_6 + 9 \text{NH}_3 \rightarrow \text{Si}_2(\text{NH})_3 + 6 \text{NH}_4\text{Cl} \]

If this is in fact the reaction which Ge₂Cl₆ 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 H₂O except that it had a diameter of 10 mm. About 2 ml of sodium-dried ammonia was condensed onto a known quantity of Ge₂Cl₆ in a tube cooled with liquid nitrogen. The tube was sealed and allowed to warm to 0°C. After 24 hours its contents were frozen with liquid nitrogen and the tube was opened under vacuum. It was then warmed to -63°C whereupon the excess ammonia distilled off. Finally the tube was allowed to warm to room temperature while the pumping continued to ensure 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

mmol Ge₂Cl₆: 0.102

mmol 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:

\[ \text{Ge}_2\text{Cl}_6 + 9 \text{NH}_3 \rightarrow \text{Ge}_2(\text{NH})_3 + 6 \text{NH}_4\text{Cl} \]

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 Ge_2Cl_6 with HCl

<table>
<thead>
<tr>
<th>mmole Ge_2Cl_6</th>
<th>0.168</th>
</tr>
</thead>
<tbody>
<tr>
<td>mmole HCl added</td>
<td>1.35</td>
</tr>
<tr>
<td>mmole HCl recovered</td>
<td>1.19</td>
</tr>
<tr>
<td>mmole HCl reacted</td>
<td>0.16</td>
</tr>
<tr>
<td>HCl/Ge_2Cl_6</td>
<td>0.95</td>
</tr>
</tbody>
</table>

The results above indicate that the following reaction took place.

\[ \text{Ge}_2\text{Cl}_6 + \text{HCl} \rightarrow \text{GeHCl}_3 + \text{GeCl}_4 \]

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 GeHCl_3 and the possible existence of GeCl_4.
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 GeCl₂ which resulted from the following reaction:

\[
\text{GeHCl}_3 \rightarrow \text{GeCl}_2 + \text{HCl}
\]
FIG. 8. INFRARED SPECTRUM OF VAPORS OVER PRODUCTS OF REACTION OF Ge₂Cl₆ WITH HCl.
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\(^9\) 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 germananes have also been obtained\(^{10}\) from the reaction of ammonium bromide with magnesium germanide in liquid ammonia. Recently\(^{11}\) 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.

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

$$\text{CaH}_2 + \text{Ge} \rightarrow \text{CaGe} + \text{H}_2$$

$$\text{CaGe} + 2\text{HCl aq.} \rightarrow \text{CaCl}_2 + (\text{GeH}_2)_x$$

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 $\text{Ge}_3\text{H}_8$.\(^{13}\)

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.\(^{14}\) 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 organodigermanes 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 \((\text{C}_6\text{H}_5)_6\text{Ge}_2\) was used to make a known reagent, such as \((\text{C}_6\text{H}_5)_3\text{GeK}\), for further study have been omitted when repetitive. References to work prior to January, 1950 are from Johnson.\(^{15}\)

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, \(R_3\text{GeX}\), with an alkali-metal, generally sodium, at elevated temperatures. The following have been reported:

\[
2(\text{C}_6\text{H}_5)_3\text{GeBr} + 2\text{Na} \rightarrow (\text{C}_6\text{H}_5)_6\text{Ge}_2 + 2\text{NaBr}
\]

This was the reaction of Morgan and Drew\(^ {14}\) 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, \((\text{C}_2\text{H}_5)_3\text{GeBr}\), to form hexaethyl digermane, \((\text{C}_2\text{H}_5)_6\text{Ge}_2\).\(^ {16}\) A 30% yield of this compound was realized, however, by the direct action of sodium at elevated temperatures.

Hexamethyldigermane, \((\text{CH}_3)_6\text{Ge}_2\), was first synthesized by refluxing bromotrimethylgermane, \((\text{CH}_3)_3\text{GeBr}\), with an excess of potassium under nitrogen.\(^ {17}\) 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 \((\text{CH}_3)_6\text{Ge}_2\).

Hexabenzyldigermane, \((\text{C}_6\text{H}_5\text{CH}_2)_6\text{Ge}_2\), has been obtained, in unreported yield, from the reaction of bromotribenzylgermane, \((\text{C}_6\text{H}_5\text{CH}_2)_3\text{GeBr}\), with sodium in refluxing xylene.\(^ {18}\)
An 85% yield of hexacyclohexyldigermane, \((\text{C}_6\text{H}_{11})_6\text{Ge}_2\), was realized when the appropriate bromo compound was refluxed with an excess of sodium in toluene.\(^{19}\)

A very interesting reaction, worthy of further investigation, has been reported by Kraus and Brown.\(^{20}\) Dichlorodiphenylgermane, \((\text{C}_6\text{H}_5)_2\text{GeCl}_2\), with sodium in boiling xylene formed a compound with the empirical formula \((\text{C}_6\text{H}_5)_2\text{Ge}\).

\[
(\text{C}_6\text{H}_5)_2\text{GeCl}_2 + 2\text{Na} \rightarrow (\text{C}_6\text{H}_5)_2\text{Ge} + 2\text{NaCl}
\]

Only about 10-20% of the theoretical amount of \((\text{C}_6\text{H}_5)_2\text{Ge}\) was obtained in the form of crystals. However, a considerable amount of resinous material approximating in composition \((\text{C}_6\text{H}_5)_2\text{Ge}\), 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 \(((\text{C}_6\text{H}_5)_2\text{Ge})_4\), molecular weight 907). It has been suggested\(^{15}\) that this might consist of a four-membered germanium ring.

\[
\begin{align*}
(\text{C}_6\text{H}_5)_2\text{Ge} & \rightarrow \text{Ge}(\text{C}_6\text{H}_5)_2 \\
(\text{C}_6\text{H}_5)_2\text{Ge} & \rightarrow \text{Ge}(\text{C}_6\text{H}_5)_2 \\
\end{align*}
\]

An even more fascinating compound has been prepared in boiling xylene by the reaction of either sodium\(^{21}\) (refluxed 8 hrs.) or potassium\(^{22}\) (refluxed 12 hrs.) with phenyltrichlorogermane.

\[
6 \text{C}_6\text{H}_5\text{GeCl}_3 + 18 \text{Na} \rightarrow (\text{C}_6\text{H}_5\text{Ge})_6 + 18 \text{NaCl}.
\]
It was suggested by the authors that this was an open chain molecule rather than a benzene-type ring.

\[
\text{Ge} = \text{Ge} - \text{Ge} = \text{Ge} - \text{Ge} = \text{Ge} - \\
C_6H_5 \quad C_6H_5 \quad C_6H_5 \quad C_6H_5 \quad C_6H_5 \quad C_6H_5 
\]

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-tolyldigermane, \((\text{p-CH}_3\text{C}_6\text{H}_9)_6\text{Ge}_2\). 

b. Grignard Reactions

Morgan and Drew detected no hexaphenyldigermane 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 GeCl\(_4\), Bauer and Burschkies were able to isolate some hexaphenyldigermane, although their main product was still tetraphenyldigermane, \((\text{C}_6\text{H}_5)_4\text{Ge}\). Reaction
with GeBr$_4$ gave lower, but still significant amounts of the digermane.

In addition, under the same conditions, hexa-p-tolyldigermane was obtained from 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, for the phenyl derivative, to give hexaphenyldigermane as the major product. Using a ten-to-one mole ratio of Grignard reagent to 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, tetraphenyldigermane is the major product.

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

$$4\text{GeCl}_4 + 14\text{C}_6\text{H}_5\text{MgBr} \rightarrow 2(\text{C}_6\text{H}_5)_6\text{Ge}_2 + 2\text{C}_6\text{H}_5\text{Cl} + 7\text{MgBr}_2 + 7\text{MgCl}_2$$

No evidence to support the formation of chlorobenzene is given.

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

$$2\text{GeCl}_4 + 8\text{CH}_2\text{CHMgBr} \rightarrow (\text{CH}=\text{CH})_6\text{Ge}_2 + (\text{CH}=\text{CH})_2 + 4\text{MgBr}_2 + 4\text{MgCl}_2$$

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 GeCl$_4$ to GeCl$_2$ by the Grignard reagent, producing the butadiene. GeCl$_2$ was then vinylated and the Grignard added to it. Finally, reaction of this latter compound with partially vinylated GeCl$_4$ would give
the desired product:

\[
\begin{align*}
&\text{GeCl}_4 + 2 \text{CH}_2\text{CHMgBr} \rightarrow \text{GeCl}_2 + (\text{CH}_2\text{CH})_2 + \text{MgCl}_2 + \text{MgBr}_2 \\
&\text{GeCl}_2 + 2 \text{CH}_2\text{CHMgBr} \rightarrow (\text{CH}_2\text{CH})_2 \text{Ge} + \text{MgCl}_2 + \text{MgBr}_2 \\
&(\text{CH}_2\text{CH})_2 \text{Ge} + \text{CH}_2\text{CHMgBr} \rightarrow (\text{CH}_2\text{CH})_3 \text{GeMgBr} \\
&(\text{CH}_2\text{CH})_3 \text{GeMgBr} + (\text{CH}_2\text{CH})_3 \text{GeCl} \rightarrow (\text{CH}_2\text{CH})_6 \text{Ge}_2 + \frac{1}{2} \text{MgCl}_2 + \frac{1}{2} \text{MgBr}_2
\end{align*}
\]

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 that up to 8% hexaethyldigermane could be obtained in the preparation of tetraethylgermane by the reaction of ethylmagnesiumbromide with GeCl₄ or GeBr₄ in ether. Kraus and Flood, 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, R₃GeM, with a halotriorganogermane, R₃GeX, may cause a coupling of the germanium atoms to occur. Kraus and Sherman showed this with the following reaction.

\[
(\text{C}_6\text{H}_5)_3\text{GeNa} + (\text{C}_2\text{H}_5)_3\text{GeBr} \rightarrow (\text{C}_6\text{H}_5)_3\text{GeGe(C}_2\text{H}_5)_3 + \text{NaBr}
\]

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.20

\[ 2(C_6H_5)_3GeNa + (C_6H_5)_2GeCl_2 \rightarrow (C_6H_5)_6Ge_3 + 2NaCl \]

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

This method of preparing organodigermes, 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 triphenylgermyllithium with bromine in ethylene glycol dimethyl ether for form 78\% hexaphenyldigermane.27

\[ 2(C_6H_5)_3GeLi + Br_2 \rightarrow (C_6H_5)_6Ge_2 + 2LiBr \]

The fact that up to 12\% \((C_6H_5)_3GeBr\) 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 Harris23a found that by adding an excess of an ether solution of phenyllithium, \(C_6H_5Li\), dropwise into a refluxing ether solution of triphenylgermane, \((C_6H_5)_3GeH\), up to 60\% of the germane was converted to hexaphenyldigermane.

\[ 2(C_6H_5)_3GeH + C_6H_5Li \rightarrow (C_6H_5)_6Ge_2 + C_6H_6 + LiH \]

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.

\[
(C_6H_5)_3GeH + C_6H_5Li \rightarrow (C_6H_5)_3GeLi + C_6H_6
\]

\[
(C_6H_5)_3GeH + (C_6H_5)_3GeLi \rightarrow (C_6H_5)_6Ge_2 + LiH
\]

Gilman and Gerow\textsuperscript{23} 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\% \((C_6H_5)_6Ge_2\) 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, \((C_6H_5)_3GeCOOH\), which was weighed.

\[
C_6H_5Li + (C_6H_5)_3GeH \rightarrow C_6H_6 + (C_6H_5)_3GeLi \rightarrow 1.0\text{CO} \quad 2.0\text{H}_2O
\]

\[
(C_6H_5)_3GeCOOH
\]

It is noteworthy that the reaction of methylolithium 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 germene initially produced.
It has also been found\(^\text{25}\) that the reaction of ethyllithium with GeBr\(_4\) in ether solution produced 8.5% hexaethyldigermane 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 organodigermane, several more unusual reactions have resulted, surprisingly, in the formation of hexaphenyldigermane 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, (C\(_{6}\)H\(_5\))\(_3\)GeCOOCH\(_3\).\(^{29}\) Instead of the expected bis(triphenylgermyl) ketone or tris (triphenylgermyl) carbinol, carbon monoxide was vigorously evolved and hexaphenyldigermane was obtained in 75% yield (based on triphenylgermanecarboxylate).

\[
(C_{6}H_{5})_{3}GeLi + (C_{6}H_{5})_{3}GeCOOCH_{3} \rightarrow (C_{6}H_{5})_{6}Ge_{2} + CO + LiOCH_{3}
\]

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.

\[
(C_{6}H_{5})_{3}Ge^{-} + (C_{6}H_{5})_{3}GeCOOCH_{3} \rightarrow (C_{6}H_{5})_{6}Ge \cdots Ge \cdots C \cdots OCH_{3} \rightarrow
\]

\[
(C_{6}H_{5})_{6}Ge_{2} + CO + OCH_{3}^{-}
\]

To ascertain the origin of each germanium atom in the product, methyl triphenylgermanecarboxylate was reacted with triphenylsililyl lithium, (C\(_{6}\)H\(_5\))\(_3\)SiLi. The only product isolated was (triphenylgermyl) triphenylsilane,
indicating that in the formation of hexaphenyldigermane, one germanium atom came from the triphenylgermyl lithium, the other from the ester.

Reaction of triphenylgermyl lithium with diethylcarbonate, \((\text{C}_2\text{H}_5\text{O})_2\text{CO}\), also resulted in the evolution of carbon monoxide and the isolation of hexaphenyldigermane 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.

\[
(\text{C}_6\text{H}_5)_3\text{GeLi} + (\text{C}_2\text{H}_5\text{O})_2\text{CO} \rightarrow (\text{C}_6\text{H}_5)_3\text{GeCOOC}_2\text{H}_5 + \text{LiOC}_2\text{H}_5
\]

\[
(\text{C}_6\text{H}_5)_3\text{Ge}^- + (\text{C}_6\text{H}_5)_3\text{GeCOOC}_2\text{H}_5 \rightarrow (\text{C}_6\text{H}_5)_6\text{Ge}_2 + \text{CO} + \text{OC}_2\text{H}_5^-
\]

Smith and Kraus,\(^{30}\) 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 hexaphenyldigermane. The amount of hexaphenyldigermane 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 hexaphenyldigermane. 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% hexaphenyldigermane. Bis(triphenylgermyl)methane, \([(\text{C}_6\text{H}_5)_3\text{Ge}]_2\text{CH}_2\), was obtained in 9% yield, but the source of the second hydrogen was left unexplained.
Acetylene dichloride, ethylene dibromide, and β-butylene bromide gave 63%, 87%, and 91% hexaphenyldigermane, 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% hexaphenyldigermane 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-diodotetraethyldigermane, \((C_4H_9)_2I\)GeGeI\((C_4H_9)_2\). It is obtained in the reaction of germanium diiodide, GeI\(_2\), with excess dibutylmercury, \(Bu_2Hg\), in acetone. It is the only haloorganodigermane known.

\[
2\text{GeI}_2 + 3(C_4H_9)_2Hg \rightarrow (C_4H_9)_2\text{IGeGeI}(C_4H_9)_2 + 2C_4H_9\text{HgI} + \text{Hg}
\]

2. Properties

No reactions of the polygermanes or their derivatives are known which retain the Ge-Ge bond. With the exception of hexaphenyldigermane, 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 bromotriorganogermane. When a solution of bromine in ethylbromide is added to hexaethyldigermane, bromotriethylgermane is quantitatively produced.\(^{16}\)

\[
(C_2H_5)_6\text{Ge}_2 + \text{Br}_2 \rightarrow 2(C_2H_5)_3\text{GeBr}
\]

A boiling carbon tetrachloride solution is needed to affect cleavage of hexaphenyldigermane by bromine.\(^{14}\) Octaphenyltrigermane reacts incompletely with bromine in a carbon tetrachloride solution at room temperature to give bromotriphenylgermane and dibromodiphenylgermane.\(^{20}\)
\[(\text{C}_6\text{H}_5)_6\text{Ge}_2 + 2\text{Br}_2 \rightarrow 2(\text{C}_6\text{H}_5)_3\text{GeBr} + (\text{C}_6\text{H}_5)_2\text{GeBr}_2\]

The cleavage of the metal-metal bond by halogens was used by Seyforth\(^{24}\) in his identification of hexavinyldigermane. 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 hexaethyldigermane to triethylgermilyl lithium.\(^{16}\)

\[(\text{C}_2\text{H}_5)_6\text{Ge}_2 + 2\text{Li} \rightarrow 2(\text{C}_2\text{H}_5)_3\text{GeLi}\]

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

Refluxing potassium does not react with hexamethyldigermane.\(^{17}\) Even with sodium-potassium alloy in ethylene glycol dimethyl ether, after three days, almost 50% of the hexamethyldigermane was recovered and no yellow color, characteristic of the potassium salt, was observed.

A suspension of hexaphenyldigermane in a sodium-liquid ammonia solution reacts only very slowly, but again this may partially be due to its insolubility in this solvent.\(^{32}\)

Gilman and Gerow\(^{33}\) studied the cleavage of hexaphenyldigermane in various solvents in an attempt to prepare triphenylgermilyl 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% tetraphenyldigermane. 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.

\[
(C_6H_5)_6Ge_2 + Li \rightarrow 2(C_6H_5)_3GeLi
\]

It is believed\(^{34}\) that in this case conversion is complete.

Diphenylgermanium tetramer, \((C_6H_5)_2Ge\)_4, in liquid ammonia, adds two sodium atoms for each germanium atom, giving a red solution characteristic of \((C_6H_5)_2GeNa_2\).\(^{20}\)

Of all the organic compounds containing a Ge-Ge bond only hexavinyl-digermane is reported to be air-sensitive.\(^{24}\) 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, $\text{Si}_4\text{H}_{10}$. 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. The authors were able to identify $\text{n-Si}_4\text{H}_{10}$, another $\text{Si}_4\text{H}_{10}$ of undetermined structure, $\text{n-Si}_5\text{H}_{12}$, $\text{iso-Si}_5\text{H}_{12}$, and tentatively to identify hexa-, hepta-, and octasilanes.

Disilane has also been obtained by reaction of lithium aluminum hydride with hexachlorodisilane.

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. The passage of silicon tetrachloride over silicon at temperatures exceeding 1000° 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.

$\text{Si}_{10}\text{Cl}_{22}$ and $\text{Si}_{10}\text{Cl}_{20}\text{H}_2$ 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 $\text{Si}_{18}\text{Cl}_{30}$. 
Friedel and Ladenburg prepared hexaiododisilane from silicon tetraiodide and silver metal.\(^1\)

\[ 2 \text{SiI}_4 + 2 \text{Ag} \rightarrow 2 \text{AgI} + \text{Si}_2\text{I}_6 \]

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

\[ \text{Si}_2\text{I}_6 + 3 \text{Br}_2 \rightarrow \text{Si}_2\text{Br}_6 + 3 \text{I}_2 \]

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.\(^2\)

Disilane does not react with pure water in quartz vessels.\(^3\) 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.\(^4\) Hexafluorodisilane reacted with ice water to give a compound probably analogous to oxalic acid.

\[ \text{Si}_2\text{I}_6 + 4 \text{H}_2\text{O} \rightarrow (\text{SiOOH})_2 + 6 \text{H}_2\text{I} \]

Alkaline solution caused the Si-Si bond to break.

\[ (\text{SiOOH})_2 + 4 \text{KOH} \rightarrow 2 \text{K}_2\text{SiO}_3 + 2 \text{H}_2\text{O} + \text{H}_2 \]

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.\(^5\)
The reaction of hexachlorodisilane with ammonia has recently been studied by Billy.\textsuperscript{17} At -79°, 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:

\[
\text{Si}_2\text{Cl}_6 + 27\text{NH}_3 \rightarrow \text{Si}_2\text{N}_3\text{H}_3 + 6\text{NH}_4\text{Cl} \cdot 3\text{NH}_3
\]

The author proposed that the compound is polymeric, corresponding to

\[
\text{Si} - \text{Si} - \text{NH} - \text{Si}\text{NH} - \text{NH}
\]

rather than individual molecular units such as \(\text{HN} = \text{Si} - \text{Si} = \text{NH}\), as was previously proposed.\textsuperscript{48} \(\text{Si}_2(\text{NH})_3\) 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.\textsuperscript{49}

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 \(\{(\text{C}_6\text{H}_5)_3\text{Si}\}_4\) and \(\{(p-\text{CH}_3\text{C}_6\text{H}_4)_3\text{Si}\}_4\) from dichlorodiphenylsilane, \((\text{C}_6\text{H}_5)_2\text{SiCl}_2\) and dichlorodi-p-tolylsilane, \((p-\text{CH}_3\text{C}_6\text{H}_4)_3\text{SiCl}_2\) respectively. These compounds are also believed to be cyclic. Dichlorodimethylsilane, \((\text{CH}_3)_2\text{SiCl}_2\), gives primarily \(\{(\text{CH}_3)_3\text{Si}\}_6\) 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

\[ R_3SiX + R_3SiM = R_6Si_2 + MX \]

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

\[ (C_6H_5)_3SiK + SiCl_4 = (C_6H_5)_3SiSiCl_3 + KCl \]

Reaction of organometallic reagents with halodisilanes, yet to be attempted for hexachlorodigermane, has successfully produced organodi-germanes.

\[ Si_2X_6 + 6 MW = R_6Si_2 + 6 MX \]

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.

\[ 2 RSiR_3' + H_2 \rightarrow 2 RH + R'SiR_3' \]

High temperatures and pressures are essential. Hexamethyldisilane, hexaethylsilane, 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 hexaphenyldigermane, 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 organodigermes, 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 effective-
ly produced by sodium-potassium alloy in ether and by lithium in tetrahydro-
furan.

Hexaaryldisilanes show no tendency to dissociate into free radicals.
Even hexa-p-biphenyldisilane is unaffected by prolonged treatment with
oxygen and iodine,\(^50\) as in hexaphenyldisilane.\(^51\)

D. Comparison to Compounds Containing Sn-Sn Bond

The chemistry of distannane compounds is at about the same stage as
that of the digermene 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.\(^52\) It is very unstable, decomposing com-
pletely 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.\(^53\)

As with germanium and silicon, the most commonly used method of pre-
paring compounds of the type \(R_6Sn_2\) has been the reaction of sodium with a
halotriorganostannane.

\[
{2R_3SnX + 2Na \rightarrow R_6Sn_2 + 2NaX}
\]
A great variety of other methods of synthesis have proven successful. For instance, tin alloy reactions with ethyliodide and with phenyl mercuric chloride form, among their products, hexaethyldistannane, \((\text{C}_2\text{H}_5)_6\text{Sn}_2\), and hexaphenyldistannane \((\text{C}_6\text{H}_5)_6\text{Sn}_2\), 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-tolyldistannane.

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.
ACKNOWLEDGEMENTS

The author wishes to thank Dr. H. L. Jolly for his guidance throughout the course of this work.

This work was performed under the auspices of the United States Atomic Energy Commission.
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