that in the preparation of hexaphenyldigermane the ether is not removed immediately after the addition of the toluene solution of germanium tetrachloride. This change in conditions, with the attendant lower refluxing temperature, is sufficient to cause the major change in the principal products.

Preparation of Diphenylgermane from Hexaphenyldigermane.—Using the procedure described in the preparation of diphenylgermane from tetraphenylgermane, 73 g. (0.12 mole) of hexaphenyldigermane was brominated with 60 g. (0.325 mole) of bromine, the resultant bromides reduced by 25 g. of lithium aluminum hydride and the diphenylgermane separated by fractional distillation; yield, 37.5 g. (67%) of diphenylgermane, $n^{25}\text{D}$ 1.5918, from distillate and 7.5 g. (10%) of triphenylgermane from residue.

Conversion of Diphenylgermane to Diiododiphenylgermane.—A solution of 1.6 g. (0.007 mole) of freshly distilled diphenylgermane in 20 ml. of chloroform was placed in a flask cooled in ice water and was brominated with 2.4 g. (0.015 mole) of bromine. The addition of bromine was accompanied by the evolution of hydrogen bromide. When bromination was complete, the solvent and any excess bromine were distilled off under a pressure of 1 mm., the last traces being removed by heating over a steam-bath. The resulting dibromodiphenylgermane was dissolved in ethanol and treated with concentrated ammonium hydroxide while heated on the steam-bath. The dibromo compound is converted to the oxide[6] which, after several recrystallizations from nitromethane, gave a white crystalline substance sintering at 145° and melting with a range from 180 to 210°. The purified hydrolysis product was covered with 47% HI and warmed on the steam-bath until the solid changed to an oil. The oil was dissolved in benzene and separated from the excess hydriodic acid. The benzene was removed under reduced pressure giving an oil which crystallized on scratching the walls of the container. The crystals of diiododiphenylgermane are soluble in many solvents but are recrystallized most readily from nitromethane, m. p. 70.0–71.0° (cor.).

Anal. Calcd.: C, 30.00; H, 2.10. Found: C, 30.11; H, 2.13.

Some solvents, such as methanol and acetic acid, seem to promote the decomposition of the diiododiphenylgermane to a greater extent than other solvents. Some decomposition also occurs in nitromethane solution although to a much lesser degree than in the other solvents used. Discoloration within a few days indicates that the diiodo compound is only moderately stable.

Iodination of Diphenylgermane.—To 1 g. (0.0044 mole) of diphenylgermane ($n^{20}\text{D}$ 1.5938) dissolved in 2 ml. of chloroform was added portionwise 2.22 g. (0.0088 mole) of iodine. The first iodine crystals disappeared rapidly but by the time 1.11 g. had been added there was no evidence of a reaction. The reaction mixture was heated to 70° at which temperature a vigorous reaction occurred with the evolution of a gas and disappearance of the iodine color. The remainder of the iodine (1.11 g.) was added while the reaction mixture was at 100°. After the addition of the iodine the volatile material was distilled out by heating the container on the steam-bath under a pressure of 1 mm. The residue gave orange crystals on cooling which were recrystallized from acetic acid. This material (0.9 g.) had a melting point of 144 to 145° (cor.) indicating the formation of germanium tetraiodide.

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Summary

1. Two new compounds, diphenylgermane and diiododiphenylgermane, have been prepared and some properties described.

2. Reduction of mixed bromophenylgermanes with lithium aluminum hydride gave the corresponding phenylgermanes readily separated by fractionation.

3. Dibromodiphenylgermane is easily prepared by the bromination of diphenylgermane.

4. Diiododiphenylgermane is formed by bromination of diphenylgermane at relatively low temperatures followed by the replacement of the bromine by iodine from hydriodic acid.

5. Attempts to iodinate diphenylgermane directly yielded principally germanium tetraiodide.

6. A convenient method of preparing hexaphenyldigermane is described.

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[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

Some Reactions of Triphenylgermane

BY OTTO H. JOHNSON AND DARREL M. HARRIS[1]

I. The Reaction between Triphenylgermane and Phenyllithium.—When triphenylgermane and phenyllithium are allowed to react in ether solution, the products are found to be either practically pure tetraphenylgermane or a mixture of tetraphenylgermane and hexaphenyldigermane depending upon the conditions under which the reaction is carried out.

If phenyllithium is present in large excess, as in the case of the addition of a dilute solution of triphenylgermane in ether to a refluxing ether solution of phenyllithium, the reaction favors almost quantitative conversion of the triphenylgermane to tetraphenylgermane. Hexaphenyldigermane is formed in negligible amounts if at all. The over-all main reaction is represented by the equation

$$\text{Ph}_3\text{GeH} + \text{PhLi} \longrightarrow \text{Ph}_4\text{Ge} + \text{LiH} \qquad \text{(a)}$$

Gilman and Massie[2] and Meals[3] have shown that this is a general reaction for similar silicon compounds. The lithium hydride separates out as a white precipitate during the course of the reaction.

When the procedure for mixing the two reactants is reversed so that the triphenylgermane is present in large excess, that is, when the ether

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(1) Part II from a thesis to be submitted by Darrel M. Harris to the Graduate School of the University of Minnesota in partial fulfillment of the requirements for the degree for Doctor of Philosophy.

(2) Gilman and Massie, THIS JOURNAL, **68**, 1128 (1946).

(3) Meals, *ibid.*, **68**, 1880 (1946).

solution of phenyllithium is added to a refluxing concentrated solution of triphenylgermane in ether, the main reaction is quite different and the principal germanium product resulting from the reaction is hexaphenyldigermane. Similar results are obtained using Grignard reagents in place of phenyllithium. Bauer and Burschkies[4] have reported the presence of hexaphenyldigermane as a by-product in the preparation of tetraphenylgermane by the addition of a benzene solution of germanium tetrachloride to an ether solution of phenylmagnesium bromide. By controlling the conditions as described in the experimental part of this paper, the action of phenylmagnesium bromide on germanium tetrachloride in ether–toluene solution will yield a product containing as much as 60% hexaphenyldigermane, the remainder being principally tetraphenylgermane. The physical characteristics of the latter two germanium compounds are such that they are easily separated by fractional sublimation. During the addition of phenyllithium solution, a white precipitate, presumably lithium hydride, is formed, and then the solution turns a brick red hue. The precipitate and color disappears on subsequent acidification with acetic acid. The color is interesting as a possible indication of free triphenylgermyl.

The formation of the hexaphenyldigermane may indicate the presence of triphenylgermyllithium. A possible mechanism to account for the formation of the hexaphenyldigermane is indicated in equations b and c.

$$\mathrm{Ph_3GeH + PhLi \longrightarrow Ph_3GeLi + PhH} \qquad \text{(b)}$$

$$\mathrm{Ph_3GeH + Ph_3GeLi \longrightarrow Ph_3GeGePh_3 + LiH} \qquad \text{(c)}$$

The results cited are not proof that these reactions occur but are advanced as a plausible explanation.

The possible formation of some triphenylgermyllithium in the presence of a large excess of triphenylgermane is of special interest since nothing has yet been reported to indicate the formation of comparable silicon compounds as a result of the action of organolithium compounds on substituted silanes. If the conditions described actually cause the formation of $\mathrm{Ph_3GeLi}$, then in this particular reaction germanium may be acting more like carbon than like silicon.

Triphenylgermane reacts with iodine to give iodotriphenylgermane and with benzoyl chloride to give chlorotriphenylgermane.

II. Disproportionation of Triphenylgermane.—The observation that the distillation of relatively pure triphenylgermane yields considerably larger quantities of tetraphenylgermane than would be expected as an impurity, led to the suspicion that triphenylgermane disproportionates into tetraphenylgermane and diphenylgermane and possibly other products. Heating pure triphenylgermane, under controlled conditions, results in a mixture of products from which triphenylgermane, tetraphenylgermane and diphenylgermane can be separated and identified.

Experimental

Preparation of Triphenylgermane.—A solution of 58.4 g. (0.15 mole) of tetraphenylgermane[5] in 400 ml. of ethylene bromide was placed in a three-necked, one-liter flask fitted with the usual reflux condenser, motor-stirrer and dropping funnel. The solution was heated to boiling and 25.6 g. (0.16 mole) of bromine added dropwise and refluxing continued until there was only slight evidence of bromine vapor, usually for about one-half an hour after the last addition of bromine. The solvent and unreacted bromine were then distilled off under reduced pressure, leaving a residue from which bromotriphenylgermane crystallized on cooling. The crude bromotriphenylgermane was recrystallized from low-boiling petroleum ether, distilled and recrystallized twice from acetic acid; yield 44.5 g. (75.5%) m. p. 137–138° (cor.).

Reduction of Bromotriphenylgermane.[6]—To a one-liter, three-necked flask, fitted with a reflux condenser and motor-driven stirrer was added 400 ml. of anhydrous ether and 10 g. of lithium aluminum hydride. While the contents of the flask were protected by dry helium, 32.5 g. of bromotriphenylgermane was added to the flask portionwise. The solution was refluxed for one hour after the last addition of bromotriphenylgermane and then the ethyl ether displaced by 60–68° petroleum ether. The petroleum ether was removed by filtering under pressure through a No. 39533 coarse Corning fritted glass filter tube and the solid residue washed several times with petroleum ether.[5] After removal of the petroleum ether by distillation the triphenylgermane was distilled,[7] yield 20.5 g. (79%), m. p. 40–41°.

Triphenylgermane prepared by this procedure always showed traces of tetraphenylgermane which were removed by recrystallization from methanol. Recrystallization from methanol gave translucent, flaky crystals of triphenylgermane, m. p. 41.0–41.5° (cor.). Kraus and Foster[7] reported a melting point of 47° for the α-form of triphenylgermane and 27° for the β-form. Johnson and Nebergall[6] reported 27° for what was obviously the β-form.

Reaction between Triphenylgermane and Phenyllithium.—A quantity of lithium metal shot slightly in excess of 0.26 mole was placed in 200 ml. of anhydrous ether and 41.0 g. (0.26 mole) of redistilled bromobenzene added dropwise. When the reaction was complete and the precipitate had settled, the straw-colored phenyllithium solution was filtered off by carefully inserting a No. 39533 coarse Corning fritted glass filter tube into the supernatant liquid and forcing the filtrate through it by dry helium under pressure. The filtrate was then made to a volume of 250 ml. with anhydrous ether and divided into two equal portions for duplicate runs. One of the 125-ml. portions of phenyllithium solution was placed in a 500-ml. flask fitted with a refluxing condenser and a dropping funnel and so arranged that the reaction was carried out in an atmosphere of dry helium. The flask was heated to refluxing temperature and a solution of 5 g. (0.016 mole) of triphenylgermane in 75 ml. of anhydrous ether was added dropwise and with constant stirring over a period of 45 minutes. A white precipitate, presumably lithium hydride, began to form after about one-third of the triphenylgermane had been added.

After all of the triphenylgermane solution had been added, the mixture was refluxed for twelve hours, then 300 ml. of benzene was added and the solution distilled until practically all of the ether had been removed as evidenced by the boiling point of the residual liquid. The excess phenyllithium was destroyed with 50% acetic acid solution and the benzene layer washed with hot water. The volume of the benzene solution was reduced to approximately

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[4] Bauer and Burschkies, *Ber.*, **67B**, 1041 (1934).

[5] Johnson and Harris, THIS JOURNAL, **72**, 5564 (1950).

[6] Johnson and Nebergall, *ibid.*, **71**, 1720 (1949).

[7] Kraus and Foster, *ibid.*, **49**, 457 (1927).

50 ml. by distillation which also removed any water left in the benzene layer. Upon cooling, crystals appeared and were filtered off and washed with cold, low-boiling petroleum ether; yield for duplicate preparations 4.5 g., 4.4 g. (70%) m. p. 224–225° (cor.) and 226–228° (cor.), respectively. The crystals were found to consist chiefly of tetraphenylgermane with a very small quantity of hexaphenyldigermane.

Separation of Tetraphenylgermane and Hexaphenyldigermane.—These two compounds can be quantitatively separated by fractional sublimation. A sample of the crystals from the preceding experiment weighing approximately 0.2 g. was placed in a platinum boat which was placed in the closed end of a horizontal tube approximately 1 cm. in diameter and 30 cm. long. Uniform heating was obtained by placing the closed end of the tube loosely in a hole in a large iron block fitted with a thermometer well. At 210° and a pressure of approximately 1 mm., the tetraphenylgermane sublimed leaving a residue of hexaphenyldigermane in the boat corresponding to 1.4% of the sample. The sublimate had a m. p. of 225 to 227°. After resublimation and recrystallization from acetic acid the crystals melted at 230–231° (cor.). Mixing with known tetraphenylgermane gave no depression of this melting point.

The hexaphenyldigermane residue in the boat had a m. p. of 325 to 328°. Sublimation at 270–280° at 1 mm. pressure and recrystallization from chloroform yielded crystals melting at 330–331° (cor.). Mixing with known hexaphenyldigermane gave no lowering of this melting point.

Conditions Yielding Hexaphenyldigermane.—The relative concentrations of triphenylgermane and phenyllithium affects the composition of the products to a considerable degree. When the sequence of mixing is reversed, that is, when the phenyllithium solution is added to the triphenylgermane the formation of hexaphenyldigermane over tetraphenylgermane is favored. The reaction was carried out in exactly the same manner except that the 125 ml. of phenyllithium solution, prepared as described above, was now added to the refluxing triphenylgermane solution. The product was extracted and crystallized from benzene in exactly the same manner as before. The character of the crystalline mass is entirely different, however, and it filtered with so much difficulty and with such large mechanical losses that no attempt was made to obtain accurate yield figures. Representative samples from two runs had melting points ranging from 250 to 296° for the one sample and 245 to 290° for the other. These analyzed, respectively, 60 and 54% hexaphenyldigermane by the method described above, as compared to the 1.4% obtained when the triphenylgermane solution was added to the phenyllithium solution.

Reaction of Triphenylgermane with Benzoyl Chloride.—A solution of 1 g. of triphenylgermane in 5 ml. of benzoyl chloride was refluxed for 45 minutes using a Wood's metal-bath at 210°. The excess benzoyl chloride was then removed by distillation under reduced pressure while the flask was heated in boiling water. The contents crystallized on cooling. Recrystallization from acetic acid gave 0.5 g. of a white crystalline material melting at approximately 110°. Distillation and recrystallization from absolute ethanol gave chlorotriphenylgermane, m. p. 114–115° (cor.). This is slightly lower than the m. p. of 117–118° previously reported.[8]

Iodination of Triphenylgermane.—A solution of 0.3 g. (0.001 mole) of triphenylgermane with 0.25 g. (0.001 mole) of iodine in 1 ml. of carbon tetrachloride was refluxed until most of the color had disappeared. The solvent and the excess iodine were removed by distillation and sublimation at 100° under reduced pressure, giving a crop of crystals upon cooling. Recrystallization from acetic acid gave 0.1 g. of white crystalline iodotriphenylgermane, m. p. 156–157°.[7]

Disproportionation of Triphenylgermane.—Triphenylgermane was subjected to higher temperatures by placing 2.6 g. in a 25-ml. Claisen flask fitted with a reflux condenser and heating to 300° for one-half hour in a dry helium atmosphere. At the end of this time the pressure was reduced until a product, principally triphenylgermane and diphenylgermane, distilled over at 240°; yield 1.2 g. This product was refractionated yielding 0.4 g. of material distilling over at approximately 90° and 1 mm. pressure, which proved to be diphenylgermane, and 0.7 g. of unchanged triphenylgermane, m. p. 40.0–41.0°. The diphenylgermane was identified by conversion to diiododiphenylgermane, m. p. 70.0–71.0° (cor.), and running a mixed melting point with known diiododiphenylgermane.

The residue in the Claisen flask was washed with hot methanol and the residual solid material filtered off and recrystallized from acetic acid. This was identified as tetraphenylgermane; yield 0.6 g., m. p. 230–231° (cor.).

Summary

1. When dilute triphenylgermane solution is added to phenyllithium solution, the principal product is tetraphenylgermane with a very small fraction of hexaphenyldigermane being formed. When the triphenylgermane is present in large excess, over half of the resulting product is hexaphenyldigermane with the tetraphenyl compound present in lesser quantity.

2. The possibility is advanced that triphenylgermyllithium is present in the solution.

3. Triphenylgermane gives iodotriphenylgermane with iodine and chlorotriphenylgermane with benzoyl chloride.

4. At higher temperatures triphenylgermane was found to disproportionate rapidly yielding tetraphenylgermane, triphenylgermane and diphenylgermane.

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(8) Orndorff, Tabern and Dennis, THIS JOURNAL, **49**, 2512 (1927).