Hypochlorous Acid as the Absorbing Species.—A few experiments (*cf.* Table V) were performed with hypochlorous acid as the absorbing species and Mn(II) as the reducing agent. These results were useful in correcting for the contribution by this path to the change observed in the chlorine experiments.

Table V

Quantum Yield of the Photochemical Reaction of Hypochlorous Acid and Manganous Ion

λ 3650 Å.; pyrophosphate concn., 0.200 *M*; *p*H 2

No.	Temp.	Av. $(Mn^{++}) \times 10^3$	(HOCl)	Dark, % total	ϕ
1	24.6	4.57	0.1263	31.0	0.246
2	24.6	4.56	.0954	26.1	.242
3	2.5	4.54	.1519	22.5	.160

Although the data are much less complete than the chlorine system, it seems fairly safe to interpret the values of ϕ observed as measuring the primary efficiency for HOCl + $h\nu$. The value of 0.25 suggested by the data for 25° and λ 3650 Å. may be compared with the values obtained by Young and Allmand[12] for the quantum yield of the photodecomposition of HOCl under the same conditions. The variation of the quantum yield for the photodecomposition with concentration, and the fact that the quantum yield can rise above unity shows that secondary thermal processes are to some extent rate determining. At 37×10^{-3} *M* HOCl, $\phi_{\text{decomp.}}$ was observed to be 1.9. This value compared to the value of 0.25 suggested by our data for the primary efficiency, leads to the conclusion that the chain length for the photodecomposition is 8 under the indicated conditions.

Summary

The photochemical reactions: chlorine with manganous ion in the presence of pyrophosphate, chlorine with cerous ion, hypochlorous acid with manganous ion in the presence of pyrophosphate, have been studied in water solution and their quantum yields measured under a variety of conditions.

The quantum yield of the reaction of chlorine and manganous ion is independent, over a considerable range, of the concentration of manganous ion, chlorine, pyrophosphate ion and of the rate of light absorption. It increases as the chloride concentration increases, as the temperature increases, and as the energy per quantum increases. The quantum yield for the reaction of chlorine and cerous ion is within experimental error the same as that observed for the Cl_2–Mn(II) system.

The conclusion is reached that the observed quantum yields measure the primary efficiency for the production of chemically active species by the interaction of chlorine with a light quantum. This primary efficiency at λ 3650 Å. and 25° increases from 0.17 at low chloride to 0.62 in concentrated hydrochloric acid. At 3°, the values increase from 0.12 to 0.54 over the same range of chloride concentration.

For hypochlorous acid, a primary efficiency of 0.25 at 25° and λ 3650 Å. is indicated by the data.

Chicago, Illinois Received April 27, 1950

[12] Young and Allmand, *Can. J. Research*, **27B**, 318 (1949).

[Contribution from the School of Chemistry of the University of Minnesota]

Diphenylgermane and Dihalodiphenylgermane

By Otto H. Johnson and Darrel M. Harris[1]

The usual procedure for preparing halogen-substituted alkylgermanes has been to prepare the tetraalkyl compound and halogenate it under conditions that would yield the maximum amount of the particular halogermane desired. The resulting mixture of mono-, di-, tri- and tetrahalogermanes is then fractionated.

The separation of dibromodiphenylgermane from tribromophenylgermane by fractionation is difficult due to the similarity of their physical properties. The halogermanes are easily reduced and since triphenylgermane and diphenylgermane differ markedly in their boiling points it was decided to subject the mixture obtained after halogenation to a general reduction reducing all of the various alkyl halogermanes to the corresponding alkylgermanes which then should be easily fractionated. The procedure was surprisingly successful. Reduction was accomplished by the use of lithium aluminum hydride.[2] When the mixture was subjected to fractionation, it was found that almost pure diphenylgermane could be obtained from a single distillation by the use of a short fractionating column.

Since the diphenylgermane is readily converted to dibromodiphenylgermane by simple bromination, a relatively easy laboratory method for the preparation of this useful compound is now available.

Diphenylgermane has not been described in the literature. Kraus and Brown[3] attempted to prepare the compound by treatment of Ph_2GeNa

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[1] Part I 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 of Doctor of Philosophy. See following article for Part II.

[2] Johnson and Nebergall, This Journal, **71**, 1720 (1949).

[3] Kraus and Brown, *ibid.*, **52**, 4031 (1930).

with NH_4Br but the expected reaction did not occur, free hydrogen and "more complex derivatives" being formed instead.

Diphenylgermane is a colorless liquid with a pleasant initial odor which rapidly changes to a burning sensation in the nose and in the eyes. The compound seems to be fairly stable if kept at temperatures below zero. A sample with $n^{20}D$ 1.5935 showed only a slight change in index of refraction to $n^{20}D$ 1.5938 after being kept for one month at −15°. At room temperatures the compound is somewhat less stable. An analytical sample with $n^{25}D$ 1.5921 showed a change to $n^{25}D$ 1.5983 after four months storage at room temperatures. No reasons are advanced for this change at the present time. It may be disproportionation as in the case of triphenylgermane[4] or oxidation or both. Some tetraphenylgermane is observed after standing indicating that some of the change at least is due to redistribution. The decomposition is not rapid enough to prevent purification of the compound by fractional distillation. Iodination with two moles of iodine (4 g.-atoms) gave germanium tetraiodide.

Difficulty was encountered in obtaining an accurate analysis for germanium in diphenylgermane by any of the previously described methods. Accordingly, a study was made of disubstituted diphenylgermane derivatives that would be solid at room temperature and that could be identified by the usual mixed melting point procedures.

Diiododiphenylgermane (new) was selected as suitable for this purpose. To guard against possible redistribution at the higher temperatures required for direct iodination, the diphenylgermane was first brominated, a reaction that proceeds at relatively low temperatures. The dibromide was hydrolyzed yielding a product that seemed to be a mixture since the melting point had a wide range. The hydrolysis product was then treated with hydriodic acid, yielding diiodophenylgermane. This compound is relatively soluble in most organic solvents, being most easily crystallized from nitromethane which yields crystals with a melting point of 70.0–71.0° (cor.).

Diiododiphenylgermane has only moderate stability as evidenced by the brown discoloration formed after a few days standing.

Experimental

Preparation of Tetraphenylgermane.—A one-liter, three-necked flask was fitted with a reflux condenser, a motor-driven stirrer and a dropping funnel. In the flask was placed 24.3 g. (1 mole) of magnesium turnings, contained in 500 ml. of anhydrous ether, and 157 g. (1 mole) of redistilled bromobenzene was added dropwise. After refluxing for one hour, a solution of 21.4 g. (0.1 mole) of germanium tetrachloride in 250 ml. of toluene was added dropwise and the ether replaced immediately with toluene. After refluxing for two hours the excess phenylmagnesium bromide was destroyed by the addition of 50% acetic acid. The solution was heated to boiling and the toluene layer separated. The tetraphenylgermane crystallized out on cooling. Concentration of filtrate yields a second crop; yield 27.7 g. (72.5%), m. p. 225–228°.

Preparation of Diphenylgermane from Tetraphenylgermane.—In the apparatus described above for the preparation of tetraphenylgermane, 52.5 g. (0.137 mole) of tetraphenylgermane and 300 ml. of ethylene bromide were heated to reflux temperature. To the refluxing solution 46 g. (0.288 mole) of bromine were added dropwise and the refluxing continued until there was no visible evidence of bromine vapor or approximately for one-half hour after the last addition of bromine.[5,6,7,8] After bromination the ethylene bromide, bromobenzene and residual bromine were distilled off by heating the mixture on a water-bath under a pressure of 1 mm. The residue was diluted with 50 ml. of anhydrous ether and added dropwise by a separatory funnel to a mixture of 20 g. of lithium aluminum hydride in 450 ml. of ether contained in the same type of apparatus used for the preparation of tetraphenylgermane and protected from the atmosphere by a current of dry helium. The addition of the bromogermane mixture should be done carefully since it generates sufficient heat to cause refluxing. The refluxing was continued for two hours after the last addition of the bromogermane. At the end of this time the ethyl ether was distilled off until a volume of about 100 ml. remained. Then 100 ml. of petroleum ether was added and the solution again distilled to a volume of about 100 ml. The addition of petroleum ether with subsequent distillation was repeated several times until the boiling point indicated fairly complete removal of the ethyl ether. The resulting petroleum ether solution was filtered by pressure through a Corning no. 39533 coarse fritted glass filter tube, washing the remaining solids with additional petroleum ether. The petroleum ether in the filtrate was then removed by distillation and the residue subjected to fractional distillation. Distillation at 1 mm. pressure yields only a few drops of distillate below 93° and then distillation continues at 93° until practically all of the diphenylgermane is obtained. The temperature then rises sharply. Thus practically pure diphenylgermane is obtained by one distillation, the triphenylgermane present remaining in the distillation flask.

Anal. Calcd.: C, 62.99; H, 5.29. Found: C, 62.29; H, 5.33; $n^{25}D$ 1.5921; yield 17.5 g. (55%).

Preparation of Hexaphenyldigermane.—To one mole of phenylmagnesium bromide in 500 ml. of ether was added dropwise a solution of 21.4 g. (0.1 mole) of germanium tetrachloride in 225 ml. of toluene. After refluxing for three hours, 200 ml. of toluene was added and the volume reduced to about 600 ml. The excess Grignard reagent was destroyed with 50% acetic acid and the aqueous layer removed by means of a rubber-bulb pipet. The organic layer and residual solids were washed five times with hot water by the same procedure. Bringing the toluene solution to boiling resulted in the solution of the tetraphenylgermane leaving the insoluble hexaphenyldigermane. The latter was filtered from the hot toluene solution and a second quantity obtained by reducing the filtrate to a small volume and again filtering; yield for two preparations, 17.5 and 19.0 g. (57 and 62%). Increasing the refluxing time from three to ten hours gave yields of 55 and 65%, respectively, for two other preparations. The combined yields of hexaphenyldigermane from the four preparations had a m. p. of 325–327°. Purification by sublimation and recrystallization from chloroform gave a microcrystalline material, m. p. 330–331 (cor.). Mixing with a pure sample of known hexaphenyldigermane gave no depression of the melting point. The combined filtrates from the above four preparations yielded 30 g. (19%) of tetraphenylgermane, m. p. 225–229°.

This method for the preparation of hexaphenyldigermane is almost identical with the method described earlier for the preparation of tetraphenylgermane. The difference is

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[4] Johnson and Harris, THIS JOURNAL, **72**, 5566 (1950).

[5] Orndorff, Tabern and Dennis, *ibid.*, **49**, 2512 (1927).

[6] Kraus and Brown, *ibid.*, **52**, 3690 (1930).

[7] Schwarz and Lewinsohn, *Ber.*, **64B**, 2352 (1931).

[8] Trautman and Ambrose, U. S. Patent 2,416,360, *C. A.*, **42**, 2760d (1948).

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, $n^{25}D$ 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 ($n^{20}D$ 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.

Acknowledgment.—The helpful suggestions of Dr. William H. Nebergall and R. William Cummings, Jr., are acknowledged. The analyses were performed by Mr. Cummings.

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

$$Ph_3GeH + PhLi \longrightarrow Ph_4Ge + LiH \qquad (a)$$

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).