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The Action of Alkali Metals on Phenylgermanium Halides[1]

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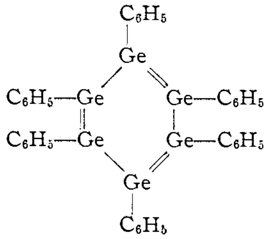
RECEIVED JANUARY 15, 1960

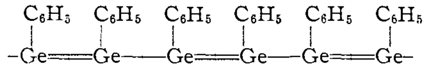
An amorphous polymer consisting of phenylgermanium units is obtained by the action of potassium on trichlorophenylgermane. Brominative degradation of this polymeric material yields a new crystalline organogermanium compound, *sym*-tetrabromodiphenyldigermane in addition to tribromophenylgermane and dibromodiphenylgermane Unequivocal syntheses of the *sym*-tetrabromodiphenyldigermane from tribromophenylgermane, of *sym*-dibromotetraphenyldigermane from dibromodiphenylgermane and the formation of the phenylgermanium polymer from trichlorophenylgermane by means of lithium amalgam are also reported.

The synthesis of organometallic compounds containing atoms of the fourth main group of the periodic system by the action of the alkali metals on the corresponding metal halides of this group is well known. In the case of germanium, this general reaction has been described many times in the literature.[2,3] The treatment of dichlorodiphenylgermane with sodium in boiling xylene, for example, leads to a substance for which a four-membered germanium ring has been proposed.[4] Of particular interest to us, however, is the report by Schwarz, *et al.*,[5,6] in which either sodium or, better, potassium in boiling xylene is used to convert trichlorophenylgermane into hexaphenylhexagermane, an amorphous substance which these authors formulated either as structure A or B, the latter preferred, on the basis of carbon-hydrogen analyses, color, molecular weight determination and halogenation reactions. Collected reference sources[1] and monographs[2,7-12] repeat these structures and conclusions, although the material does not appear to have been characterized as a pure substance. However, G. E. Coates[13] writes of it as an obscure compound of unknown structure.

$$2\ R_3GeX + 2\ Me \longrightarrow R_3Ge{-}GeR_3 + 2\ MeX$$



A



$$-\overset{\overset{C_6H_5}{|}}{Ge}{=}\overset{\overset{C_6H_5}{|}}{Ge}-\overset{\overset{C_6H_5}{|}}{Ge}{=}\overset{\overset{C_6H_5}{|}}{Ge}-\overset{\overset{C_6H_5}{|}}{Ge}{=}\overset{\overset{C_6H_5}{|}}{Ge}-$$

B

The literature concerning the dehalogenation of trichlorophenylsilane is of relevant interest here. Thus, Benkeser and Foster[14] describe the formation of a xylene-insoluble material when this trichloride is treated with a large excess of alkali metal under conditions of strong agitation; whereas Kipping, *et al.*,[15] using a limited amount of metal and less vigorous dispersing conditions, obtain products whose analyses correspond to a phenyl/silicon ratio of 1:1. However, these latter authors state that, although analysis points to the phenyl–silicon formula, C_6H_5Si, their later results showed that this product is a mixture containing considerable amounts of combined oxygen. Our study of the action of potassium and lithium on trichlorophenylgermane coincides with the results and conclusions reached by both of these groups.

In the present work, the reaction between trichlorophenylgermane and potassium was carried out initially under conditions as close as possible to those employed by Schwarz, *et al.*,[5,6] including the use of pea-sized (*linsengrossen*) pieces of potassium and carbon dioxide as the reaction atmosphere. In no case could satisfactory yields of a higher molecular weight compound be obtained and unchanged trichlorophenylgermane was recovered. However, when a vibrating agitator (cf. Experimental) was employed for the dispersion of the molten potassium metal (in a nitrogen atmosphere), the reaction rate was accelerated considerably; and when a 50% excess of potassium *in toluene* was used with very vigorous agitation, an insoluble precipitate similar to that observed by Benkeser and Foster,[14] was formed after several hours. This intractable, dark brown powder containing 28% germanium was not studied further.

After many attempts to avoid excessive as well as incomplete reaction it proved possible to interrupt the dehalogenation at a stage at which the solution did not undergo color change when exposed to air and from which a product could be precipitated containing no more than 1–5% chlorine. This solid, deposited from the toluene solution with petroleum ether, analyzed as a compound in which the phenyl/germanium ratio was 1:1 and resembled the material described by Schwarz, *et al.*[5,6] However, an oxygen content of 5–10% was appar-

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[1] A portion of this paper was presented in Boston, April, 1959; *cf.* Abstracts, 135th Meeting, Amer. Chem. Soc., p. 70-O.

[2] O. H. Johnson, *Chem. Revs.*, **48**, 259 (1951).

[3] M. P. Brown and G. W. A. Fowles, *J. Chem. Soc.*, 2811 (1958).

[4] C. A. Kraus and C. L. Brown, THIS JOURNAL, **52**, 4031 (1930).

[5] R. Schwarz and M. Lewinsohn, *Ber.*, **64**, 2352 (1931).

[6] R. Schwarz and M. Schmeisser, *ibid.*, **69**, 579 (1939).

[7] E. Gastinger, *Fortschr. chem. Forsch.*, **3**, 633 (1955).

[8] E. Krause and A. von Grosse, "Die Chemie der metallorganischen Verbindungen," Bornträger Verlag, Berlin, 1937, p. 306.

[9] F. Runge, "Organo-metallverbindungen," Wissenschaftliche Verlagsges., Stuttgart, 1932, p. 241.

[10] Gmelin, "Handbuch der Anorganischen Chemie," System No. 45, Germanium, 8th Ed. Suppl., Verlag Chemie, Weinneim/Bergstr., 1958, p. 548.

[11] N. V. Sidgwick, "Chemical Elements and Their Compounds," Vol. I, Oxford Univ. Press, 1950, p. 574. .

[12] E. G. Rochow, "Chemistry of Organometallic Compounds," J. Wiley & Sons, New York, 1957, p. 178.

[13] G. E. Coates, "Organo-metallic Compounds," Methuen-J. Wiley and Sons, London–New York, 1956, p. 115.

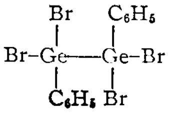
[14] R. A. Benkeser and D. J. Foster, THIS JOURNAL, **74**, 5314 (1952).

[15] F. S. Kipping, A. G. Murray, and (in part) J. G. Maltby, *J. Chem. Soc.*, 1180 (1929).

ent from analysis and a strong infrared absorption between 800–900 cm.$^{-1}$, a characteristic band of germanium oxides.[16] Molecular weight determinations of different samples of this material gave values ranging from 805 to 1280, corresponding to 5–8 phenylgermane units. Attempts to obtain a homogeneous, crystalline specimen of the product were uniformly unsuccessful, and so the polymer was degraded to less intractable units.

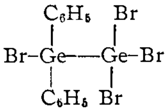
This oxygenated phenylgermane polymer was cleaved with bromine in carbon tetrachloride, a process requiring the consumption of 1.3 to 1.4 atoms of bromine per "phenylgermane unit" *by addition reaction* in the cold as reported by Schwarz and Schmeisser.[5] This experimental result permits the conclusion that both materials are essentially of the same composition. During the bromination period of twelve hours, a small amount of white, amorphous solid was deposited which was found to be rich in oxygen and germanium content but poor in bromine and was identified after hydrolysis as a mixture consisting chiefly of germanoic acid and a small amount of phenylgermanoic acid.

Concentration of the brominating solution yielded the new organogermanium derivative, tetrabromodiphenyldigermane, m.p. 115–119°, as a white, crystalline substance which proved to be thermally unstable, decomposing to tribromophenylgermane either after standing in solution for a period of time or more rapidly on heating. The mother liquor remaining after separation of the tetrabromide contained dibromodiphenylgermane in addition to tribromophenylgermane. A decision between the two possible structures, Ia and Ib, for the tetrabromide was reached unequivocally by synthesis.



$$\begin{array}{ccc} & Br & C_6H_5 \\ & | & | \\ Br- & Ge & —Ge-Br \\ & | & | \\ & C_6H_5 & Br \end{array}$$

Ia



$$\begin{array}{ccc} & C_6H_5 & Br \\ & | & | \\ Br- & Ge & —Ge-Br \\ & | & | \\ & C_6H_5 & Br \end{array}$$

Ib

The action of lithium amalgam on tribromophenylgermane in ether solution at room temperature provided the *sym*-tetrabromodiphenyldigermane, Ia, which was found to be the same as the tetrabromide isolated from the brominative degradation.[17] The effectiveness of this method in synthesizing germanium–germanium bonds was exploited further in preparing *sym*-dibromotetraphenyldigermane[5] from dibromodiphenylgermane. Finally, the method was also applicable to the dehalogenation of trichlorophenylgermane and subsequent formation of the oxygenated phenylgermane polymer having the same appearance and behavior as the product previously obtained with potassium.

The polymeric material is shown by brominative degradation to be composed of phenylgermanium, diphenylgermanium, phenylgermanium–oxygen, and germanium–oxygen units. However, owing to the fact that this dehalogenation product could not be isolated as a pure compound, an exact formulation of its structure is not possible. As expected, therefore, the results of the dehalogenation of trichlorophenylgermane parallel the experiences of Kipping, *et al.*,[15] with the silicon analogs.

Experimental[18]

Reaction of Trichlorophenylgermane with Potassium.—In a typical run, 4 g. (0.015 mole) of trichlorophenylgermane[19] was dissolved in 80 ml. of toluene under an atmosphere of nitrogen[20] and then heated with 2.6 g. (0.07 g. atom, 42% excess) of potassium metal in an oil bath maintained at 125°. The potassium was dispersed by means of a Vibro-Mischer[21] over a total reaction period of 12 hours, following which the deep brown solution did not decolorize rapidly on exposure to air. This solution was now removed from the sludge of potassium chloride and unreacted potassium by decantation and filtration, then concentrated and diluted with a small amount of petroleum ether. This caused the precipitation of a minor amount of a dark solid which was discarded. Addition of a large volume of petroleum ether to the yellow liquid precipitated a bright yellow, flocculent material which, after drying, averaged about 1.7 g. per run. This amorphous product had a softening point of *ca.* 240°.

Anal. Calcd. for C_6H_5Ge: C, 48.2; H, 3.3; Ge, 48.5; and for C_6H_5OGe: C, 43.4; H, 3.1; O, 9.7; Ge, 43.8. Found: C, 46.5–48.4; H, 3.4–3.6; O (by difference), 5.7–9.7; Ge, 37.1–41.5; Cl, 1.2–4.9; mol. wt. (Signer-Barger), 805–1280.

This material showed broad infrared absorption of strong intensity at 850 cm.$^{-1}$, the characteristic band of germanium–oxygen bonding.[16] The resistivity of the yellow powder was found to be 10^{15} ohm-cm. at 150° ($\epsilon = 5.5$). On decomposition in a sublimation tube at *ca.* 250°/0.2 mm. the powder gave a small amount of almost pure chlorotriphenylgermane as the sole volatile product.

Bromination of Phenylgermane Polymer.—Optimal conditions for the complete bromination of phenylgermane polymers and highest yields of the crystalline tetrabromodiphenyldigermane required the immediate addition of a concentrated brominating solution. In a typical run, 6 g. of the yellow *phenylgermane polymer* was dissolved in 50 ml. of carbon tetrachloride and treated at room temperature with 50 ml. of a solution of bromine (5.05 g.) in carbon tetrachloride. The mixture warmed to *ca.* 50° and then was left standing for 12–18 hours at room temperature. At the end of this period, the reaction solution contained 0.55 g. of excess bromine as determined by titration, from which it was *calculated that* 1.37 atoms of bromine had been consumed per "phenylgermane unit."

During bromination, 0.7 g. of a white, amorphous solid, rich in Ge and O, precipitated. This was filtered and washed with carbon tetrachloride, and the filtrate (A) was put aside for further examination (*vide infra*).

Anal. Found: C, 10.4; H, 1.2; O (by difference), 30.2; Br, 6.9; Ge, 51.3.

This precipitate after hydrolysis consisted mainly of germanoic acid and a small amount of phenylgermanoic acid, both of which were completely soluble in 10% cold, aqueous potassium hydroxide, from which 0.4 g. of white flocks was precipitated with carbon dioxide.

Anal. Found: C, 12.9; H, 1.9; O (by difference), 25.9; Ge, 59.2, corresponding to $C_{1.32}H_{2.36}O_2Ge$.

Treatment of this material with hydriodic acid according to standard procedure for *hydrohalogenation* of germanium oxides[2] gave mainly tetraiodogermane, m.p. 145°, after crystallization from dichloromethane, plus a small amount of triiodophenylgermane, m.p. 45–47°, in a weight ratio of 5:1.

Filtrate A from the preceding operation was evaporated *in vacuo* in order to remove excess bromine and part of the carbon tetrachloride. After standing in the cold overnight,

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[16] These and other spectral data concerning germanium compounds have been determined by Messrs. D. Beasecker, R. B. Coffey, and J. V. Pustinger of the Instrumental Analytical Department and will be published separately.

[17] We wish to acknowledge our indebtedness to Professor G. Wittig, Heidelberg, for his suggestion of this method of synthetic approach during a fruitful discussion of this problem.

[18] Melting points were determined on a Kofler hot stage. Molecular weights and analyses were performed by the Schwarzkopf Microanalytical Laboratory, Woodside 77, New York.

[19] Prepared according to R. Schwarz and M. Schmeisser, *Ber.*, **69**, 579 (1936), b.p. 100–102°/12 mm., $n^{25}D$ 1.5522 ± 0.0005.

[20] G. E. lamp-grade nitrogen used through this work.

[21] Ab. für. Chemie Apparatebau, Zürich.

the crude, crystalline mass which had formed was filtered and washed with cold *n*-hexane: m.p. 100–115°. Mother liquor (B) was set aside. After two recrystallizations from hexane, 1.85 g. of **tetrabromodiphenyldigermane**, m.p. 115–119°, was obtained.

Anal. Calcd. for $C_{12}H_{10}Br_4Ge_2$: C, 23.2; H, 1.6; Br, 51.6; Ge, 23.5; mol. wt., 619. Found: C, 23.55; H, 1.62; Br, 51.42; Ge, 22.91; mol. wt., 569.[22]

The instability of the tetrabromide was observed in its slow decomposition in solution and during an attempt to sublime the solid at 105°/0.1 mm. In both cases, partial transformation of the tetrabromide to the liquid tribromophenylgermane occurred. The 4° m.p. range is undoubtedly due to the same process. The infrared, ultraviolet, Raman, and nuclear magnetic spectra of this tetrabromodiphenyldigermane are consistent with the symmetrical structure, **1,1,2,2-tetrabromo-1,2-diphenyldigermane**.

Mother liquor B, resulting from the separation of the crystalline tetrabromide above, was now fractionally distilled in a small bulb column. Between 93–123°/1 mm., 2.50 g. of a colorless liquid was collected which, on repeated distillation between 78–85°/0.1 mm., gave 1.4 g. of **tribromophenylgermane**.

Anal. Calcd. for $C_6H_5Br_3Ge$: C, 18.5; H, 1.3; Br, 61.6; Ge, 18.6. Found: C, 19.9; H, 1.38; Br, 60.4; Ge, 17.8.

The identity of the main portion of this fraction was established chemically by hydrolyzing 0.7 g. of the fraction with methanolic potassium hydroxide on the water bath. A white flocculent precipitate (0.4 g.) of the phenylgermanoic acid was then obtained by passing carbon dioxide through the clear, alkaline solution. This solid was treated with hydriodic acid (d = 1.7) on the water bath in a sealed tube for several hours. The resulting brown oil was disssolved in hot acetic acid which, on cooling, deposited crystalline triiodophenylgermane, m.p. 45–47°. A mixed m.p. of this substance with an authentic sample of the triiodide, m.p. 47–48°, prepared in the same way from trichlorophenylgermane, showed no depression.

Anal. Calcd. for $C_6H_5I_3Ge$: C, 13.6; H, 0.94; I, 71.8; Ge, 13.7. Found: C, 13.8; H, 1.20; I, 72.01; Ge, 13.92.

The second, or middle, fraction (1.0 g.) in the distillation came over between 125–145°/1 mm. and was found to consist of tribromophenylgermane and dibromodiphenylgermane.

The third and final fraction (2.20 g.) was collected between 135–150°/0.1 mm., and this, on redistillation, between 140–145°/0.1 mm., gave 1.5 g. of the liquid **dibromodiphenylgermane**.

Anal. Calcd. for $C_{12}H_{10}Br_2Ge$: C, 37.2; H, 2.6; Br, 41.3; Ge, 18.9. Found: C, 37.56; H, 2.99; Br, 41.61; Ge, 18.24.

A pot residue of 0.7 g. was discarded.

The dibromide was chemically identified by conversion to the crystalline diiododiphenylgermane in the following manner. A sample of the liquid bromide (0.31 g.) was treated with methanolic potassium hydroxide, giving 0.18 g. (95% based on diphenylgermanium oxide) of insoluble, white flocks which were collected on the filter. Carbon dioxide saturation of the mother liquor produced no precipitation. The insoluble substance, diphenylgermanium oxide (0.10 g.), was treated with 2 ml. of hydriodic acid in a sealed tube on the water bath for 3 hours. On cooling, the resultant dark oil solidified, permitting easy removal of excess hydriodic acid by decantation. Crystallization of the solid from nitromethane gave crystalline diiododiphenylgermane, m.p. 70–71°, which melted undepressed with an authentic sample of the iodide prepared by Johnson and Harris.[23]

Synthesis of *sym*-Tetrabromodiphenylgermane.—Tribromophenylgermane (8.5 g., 0.02 mole) was dissolved in 45 ml. of anhydrous ether and then added under nitrogen to lithium amalgam prepared from 0.16 g. (0.02 g. atom) of lithium metal and 50 g. of mercury under hydrogen according to the procedure described by Witting and Pohmer.[24] After shaking at room temperature in a Schlenk tube for 70 hours, the ether solution was separated from ether-insoluble yellow flocks (polymer) and mercury by decantation and filtration. Evaporation of the solvent ether and extraction of the residue with benzene served to remove lithium bromide from the reaction product. Removal of benzene from the extract left a partially crystalline mass which was extracted into *n*-hexane and crystallized by concentration. In this manner, 1.35 g. (20%) of **1,1,2,2-tetrabromo-1,2-diphenyldigermane**, m.p. 113–117°, was obtained.

Synthesis of sym-Dibromotetraphenylgermane.—Dibromodiphenylgermane (5.00 g.) dissolved in 20 ml. of ether was shaken for 40 hours with lithium amalgam prepared from 0.09 g. of lithium and 90 g. of mercury.[24] After removing mercury, lithium bromide, and ether as described in the preceding paragraph, the crystalline **1,2-dibromo-1,1,2,2-tetraphenyldigermane** was isolated, which, after recrystallization from benzene, melted between 167–169°, 2.4 g. (60%).

Anal. Calcd. for $C_{24}H_{20}Br_2Ge_2$: C, 46.9; H, 3.3; Br, 26.1; Ge, 23.7. Found: C, 47.02; H, 3.48; Br, 25.81; Ge, 23.92.

Reaction of Trichlorophenylgermane with Lithium Amalgam.—Trichlorophenylgermane (11 g., 0.04 mole) was dissolved in 150 ml. of absolute ether and added under nitrogen to lithium amalgam prepared from 1.4 g. (0.20 g. atom) of lithium and 235 g. of mercury.[24] Exothermic reaction commenced at once and was completed by shaking the mixture for 80 hours in a Schlenk tube. During this time, a green-brown, amorphous material separated and was removed ultimately by filtration, together with mercury. The ether filtrate was discarded since it no longer contained germanium compounds. The insoluble amorphous material was now extracted into benzene giving an orange solution which was filtered from the mercury, centrifuged, concentrated, and then diluted with *n*-hexane. Precipitation of 4 g. of yellow flocks ensued, and this material appeared to be very similar to that obtained when trichlorophenylgermane was treated with potassium in toluene. This phenylgermane polymer showed germanium–oxygen absorption also and softened at about 240°.

Anal. Calcd. for C_6H_5OGe: C, 43.4; H, 3.1; O, 9.7; Ge, 43.8. Found: C, 44.2; H, 3.3; O (by difference), 8.6; Ge, 40.3; and Cl, 3.6.

The yellow, amorphous product (3.65 g.) was brominated rapidly in 30 ml. of carbon tetrachloride with 30 ml. of a 2 N solution of bromine in the same solvent with evolution of heat and a bromine uptake of 2.65 g. of bromine, or 1.35 bromine atoms per "phenylgermane unit." After standing for 20 hours, the solution and bromination precipitate were separated, and the filtrate was then treated as described in the first experiment in this Section.

The bromination precipitate (0.35 g.) was found as before to be rich in germanium and oxygen.

Anal. Found: C, 5.98; H, 1.7; O (by difference), 37.7; Br, 6.6; Ge, 48.0.

Crude, crystalline *sym*-tetrabromodiphenyldigermane, 2.15 g., was isolated and recrystallized from *n*-hexane, m.p. 112–115° (1.9 g.).

Distillation of the mother liquor resulting from the tetrabromide isolation, between 100–200° (bath temperatures)/ 0.3 mm. gave 2.50 g. of a colorless liquid mixture which was found by vapor-phase chromatographic analysis to consist of dibromodiphenyl-germane and tribromophenylgermane in a mole ratio of 1:4. Identification of the components was made by alkaline hydrolysis of the bromides to alkali-insoluble diphenylgermanium oxide and soluble phenylgermanoic acid, respectively. The oxide was crystallized from acetic acid and subjected to mixed melting with an authentic specimen, m.p. 218–222°, with no depression.[25] The acid was precipitated from the alkaline solution by carbon dioxide, then converted to the crystalline triiodophenylgermane with hydriodic acid as described previously and identified by mixed m.p.

The 1.0 g. of a pot residue was discarded.

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[22] The molecular weight was measured cryoscopically by Dr. A. Neckel, I. Chemisches Institut, Universität Wien.

[23] O. H. Johnson and D. M. Harris, THIS JOURNAL, **72**, 5564 (1950).

[24] G. Wittig and L. Pohmer, *Chem. Ber.*, **89**, 1334 (1956).

[25] W. Metlesics and H. Zeiss, THIS JOURNAL, **82**, 3324 (1960).