[Contribution from Research and Engineering Division, Monsanto Chemical Co.]

Diphenylgermanium Oxide

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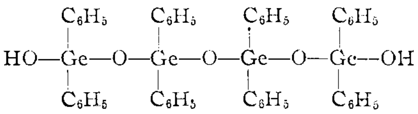
Three pure polymeric forms of diphenylgermanium oxide have been obtained in high yield from tetraphenylgermane. The interconvertibility of these oxides is also described. Since it is known that these oxides are readily transformed into diphenylgermanium dihalides, this method serves as the most convenient route to the latter compounds.

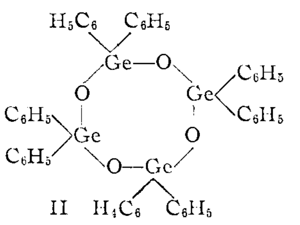
In the course of an investigation into the behavior of phenylgermanium halides in the presence of alkali metals,[1] it became necessary to deal with the dihalides and oxides of diphenylgermanium(IV). By drawing on the literature concerned with the synthesis of phenylgermanium halides and by introducing several modifications, a simpler method than those already recorded for the preparation of the halides has been devised. At the same time, a reinvestigation of the different forms of diphenylgermanium oxide as intermediates in the synthesis was undertaken, and this work is now reported also.

The reaction of germanium tetrabromide and an excess of phenylmagnesium bromide has been described by Morgan and Drew,[2] yielding tetraphenylgermane, $(C_6H_5)_4Ge$, bromotriphenylgermane, $(C_6H_5)_3GeBr$, and the less phenylated bromogermanes, dibromodiphenylgermane and tribromophenylgermane. Whereas the former pair was reported to be easily separable as solids, the latter two liquid bromides required identification by the isolation of their hydrolytic products. The hydrolysis of tribromophenylgermane by Morgan and Drew led to phenylgermanoic acid, an amorphous substance of variable composition ranging between C_6H_5GeOOH and the anhydride structure, $(C_6H_5GeO)_2O$, and having complete solubility in aqueous alkali. On the other hand, hydrolysis of dibromodiphenylgermane with silver nitrate gave two crystalline substances whose formulas could be based on the dehydration products of the hypothetical *gem*-diol, dihydroxydiphenylgermane. The first of these, m.p. 149°, was formulated as trianhydro-tetrakis-diphenylgermane-diol (I), the second, m.p. 218°, as tetraanhydro-tetrakis-diphenylgermane-diol (II), and both as tetrameric forms of the diphenylgermanium oxide unit. A third higher melting (260°), amorphous, insoluble oxide was also reported by Morgan and Drew without structural assignment.



$$HO-\underset{C_6H_5}{\overset{C_6H_5}{Ge}}-O-\underset{C_6H_5}{\overset{C_6H_5}{Ge}}-O-\underset{C_6H_5}{\overset{C_6H_5}{Ge}}-O-\underset{C_6H_5}{\overset{C_6H_5}{Ge}}-OH$$

I



II

The action of bromine on tetraphenylgermane in carbon tetrachloride likewise did not allow the direct isolation of dibromodiphenylgermane owing to product contamination.[3] Hydrolysis of the bromination mixture gave, in addition to triphenylgermanium oxide, two substances, m.p. 147° and 210°, which apparently were the same as the dehydration products of dihydroxydiphenylgermane described previously.[2] The reaction was abandoned by the authors as an unsatisfactory route to dibromodiphenylgermane.

Since Morgan and Drew had obtained two diphenylgermanium oxides by hydrolyzing a mixture of bromides containing dibromodiphenylgermane, Kraus and Brown[4] undertook the hydrolysis of the pure dihalide with the result that the oxide which they isolated was found to have no definite melting point. However, by means of boiling benzene and ethanol extractions they did recover small amounts of material melting between 133–150° from the first solvent and between 140–185° and 149–300° from the second. They concluded that the hydrolysis of diphenylgermanium dihalides produced a mixture of complex oxides and that it was doubtful whether the simple, monomeric diphenylgermanium oxide could be obtained.

In another series of reactions leading from diphenylgermane to diiododiphenylgermane, Johnson and Harris[5] hydrolyzed an unisolated sample of dibromodiphenylgermane with aqueous ammonia and reported without discussion a crystalline diphenylgermanium oxide which, after several crystallizations from nitromethane, sintered at 145° and then melted between 180–210°.

In the present work, it is found that the cleavage of tetraphenylgermane with excess bromine in dibromoethane and subsequent hydrolysis give a crude insoluble diphenylgermanium oxide, m.p. 230–295°, similar to the higher melting oxide reported by Morgan and Drew. However, when boiled in acetic acid for a prolonged period, it can be brought into solution and then crystallized in nearly quantitative yield as the soluble oxide, m.p. 219–221°, probably the same as that described by Morgan and Drew[2] as the tetrameric form II. The oxide exhibits characteristic germanium-oxygen absorption by a strong, broad (in solution)[6] band at 850 cm.$^{-1}$ in its infrared spectrum. The absence of hydroxyl absorption supports structure

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[1] W. Metlesics and H. Zeiss, This Journal, **82**, 3321 (1960).

[2] G. T. Morgan and H. D. K. Drew, *J. Chem. Soc.*, **127**, 1760 (1925).

[3] W. R. Orndorff, D. L. Tabern and L. M. Dennis, This Journal, **49**, 2512 (1927).

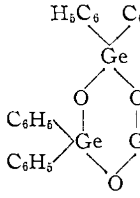
[4] C. A. Kraus and C. L. Brown, *ibid.*, **52**, 3690 (1930).

[5] O. H. Johnson and D. M. Harris, *ibid.*, **72**, 5564 (1950).

[6] In its solid form (Nujol mull) this peak is split into two bands, 860, 818 cm.$^{-1}$.

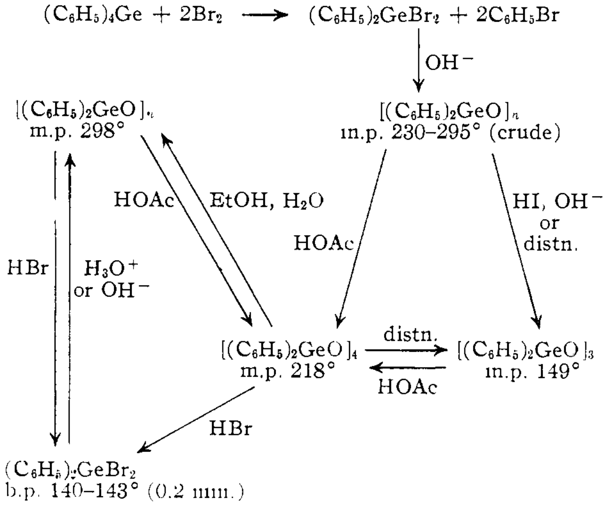
II. Treatment of this oxide with concentrated hydrohalogenic acids converts it in essentially quantitative fashion into the dihalodiphenylgermanes.[7]

Hydrolysis of pure dibromodiphenylgermane under acidic or alkaline conditions gives a microcrystalline diphenylgermanium oxide, m.p. 290–295°, which appears to be a purer form of the crude oxide isolated from the bromination of tetraphenylgermane and hydrolysis steps described above. This oxide is converted into diiododiphenylgermane with hydriodic acid and then hydrolyzed to the crystalline oxide, m.p. 147–149°, this presumably being the other oxide described by Morgan and Drew in terms of structure I. However, it is now found that the 149°-oxide is in fact a pure *trimeric* form of diphenylgermanium oxide. This assignment (structure III) is based chiefly on an accurate determination of molecular weight[8] and the absence of hydroxyl absorption in its infrared spectrum. The trimeric form may be obtained also by distillation of either the 218°- or 295°-oxide.



III

Conversely, the trimer may be transformed into the 218°-oxide by refluxing in acetic acid and into the 295°-oxide by boiling in aqueous ethanol. The scheme of interconversions (see diagram) is completed by the conversion of the 218°-oxide into the 295°-oxide by boiling aqueous ethanol and its regeneration from the high melting oxide in refluxing acetic acid.[9]



The data gathered from the insoluble 295°-oxide do not permit any structural conclusion to be reached other than that it is a polymeric form of diphenylgermanium oxide. This phenomenon of oxide multiplicity has also been demonstrated with the dialkylgermanium oxides.[10]

Experimental[11]

Diphenylgermanium Oxide (218°).[12]—Tetraphenylgermane (10 g., 0.026 mole) in 70 ml. of boiling dibromoethane was treated over a period of several hours with 10.5 g. (0.066 mole, 27% excess)[13] of bromine dissolved in 20 ml. of the same solvent. After an additional reflux period of 15 hours, the main amount of the solvent was removed *in vacuo* on the steam-bath. The residue was hydrolyzed with aqueous potassium hydroxide and then subjected to steam distillation whereby all volatile material including bromobenzene was removed. The pot residue[13] consisted of a white solid, crude diphenylgermanium oxide, m.p. 230–295°. This oxide is sparingly soluble in common organic solvents, but after prolonged digestion with boiling acetic acid, it could be brought into solution. On very slight dilution with water and cooling, the acid deposited a white, crystalline diphenylgermanium oxide, m.p. 215–218°, in total yield of 91% (5.75 g.) This substance is most probably the oxide isolated by Morgan and Drew (m.p. 218°, indefinite) and reported by them to be in a tetrameric form.[2] This oxide is soluble in and recrystallizable from ether. The purest specimen melted between 219–221° and exhibited in carbon disulfide a strong infrared absorption band at 850 cm.$^{-1}$, a characteristic of the germanium–oxygen linkage.

Anal. Calcd. for $C_{12}H_{10}OGe$: C, 59.4; H, 4.2; Ge, 30.0. Found: C, 59.5; H, 4.2; Ge, 30.0.

On boiling briefly in aqueous ethanol (40:60), the oxide is converted to the higher melting oxide, m.p. 295–298°.

Trimeric Diphenylgermanium Oxide (149°).—A sample (1.5 g.) of the high melting diphenylgermanium oxide, m.p. 290–295°, was heated at 100° in a sealed tube with 15 ml. of hydriodic acid (d. 1.7). Within 30 minutes its transformation to diiododiphenylgermane was complete, and the tube was then cooled. Ether was added to the tube contents and then water, after which the ether layer was washed several times with water and then with an aqueous solution of sodium thiosulfate and bicarbonate. The ether solution was now concentrated and on addition of petroleum ether deposited crystalline diphenylgermanium oxide, m.p. 142–148°. After several crystallizations from benzene–hexane ether–hexane, a constant m.p. of 147–149° was attained with the pure trimeric oxide.

Anal. Calcd. for $(C_{12}H_{10}OGe)_3$: C, 59.4; H, 4.2; Ge, 30.0; mol. wt., 728; active H, 0.00. Found: C, 59.7; H, 4.3; Ge, 30.2; mol. wt., 727; active H, 0.03.

The infrared spectrum of the trimeric oxide in carbon disulfide confirmed germanium–oxygen by exhibiting a strong band at 850 cm.$^{-1}$. A comparison of its spectrum with that of the 218°-oxide showed a very close structural relationship. However, a mixed m.p. of the two oxides gave a definite depression to 142°.

The trimeric oxide may be distilled at 300° (bath temperature) and 0.2 mm. as a colorless glass which crystallizes again when scratched.

Diphenylgermanium Oxide Interconversions. (a) To Trimeric Diphenylgermanium Oxide.—All diphenylgermanium oxides can be converted into the trimeric oxide, m.p. 149°, *via* the diiododiphenylgermane method described above. Also, high temperature (300°) distillation of either the 218° or 295°-oxide yields mainly the trimeric form as the distillate.

(b) To 218°-Diphenylgermane Oxide.—All diphenylgermanium oxides on prolonged refluxing in acetic acid are converted to the 218°-oxide which is crystallized from the acid solution by limited addition of water and cooling.

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[7] O. H. Johnson, *Chem. Revs.*, **48**, 259 (1951); *cf.* also ref. 4.

[8] We are indebted to Dr. A. Neckel, 1. Chemisches Institut, University of Vienna, for this measurement.

[9] A sample of the diphenylgermanium oxide prepared by Johnson and Harris (ref. 5) was kindly made available to us by Dr. D. M. Harris. This material was found to be interconvertible with the other oxides also.

[10] E. A. Flood, This Journal, **54**, 1663 (1932); H. H. Anderson, *ibid.*, **72**, 194 (1950); **74**, 2370 (1952).

[11] Melting points were determined on a Kofler hot-stage. The analyses were performed by the Schwarzkopf Microanalytical Laboratories, Woodside 77, N. Y.

[12] The bromination procedure used by Johnson and Harris (ref. 5) in preparing dibromodiphenylgermane from diphenylgermane was followed in the present bromination of tetraphenylgermane.

[13] If less bromine was employed in this step, the residue remaining after hydrolysis and steam distillation (*vide infra*) remained semi-solid, and the yield of diphenylgermanium oxide was low.

(c) **To 295°-Diphenylgermanium Oxide.**—All diphenylgermanium oxides are transformed into the 295°-oxide when refluxed briefly in a 40:60 mixture of water–ethanol.

When pure dibromodiphenylgermane is hydrolyzed under acidic (water) as well as alkaline conditions, it gives a white, microcrystalline solid, the high melting (290–295°) diphenyl germanium oxide.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF KANSAS]

Anodic Reductions. VI. Electrolysis of Benzophenone in Pyridine Solutions between Aluminum Electrodes

BY TSU TZU TSAI, WILLIAM E. MCEWEN AND JACOB KLEINBERG

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The anodic oxidation of aluminum in pyridine solutions of sodium iodide or lithium chloride in the presence of benzophenone gives initial mean valence numbers significantly lower than 3. Reduction products, namely benzhydrol and benzopinacol, are isolated from the anolyte hydrolysate in amounts corresponding to oxidation of aluminum from its measured initial mean valence state to the familiar tripositive state. The ratio of the two reduction products shows a dependence on the nature of the cation of the electrolyte. The same reduction products are obtained from the catholyte hydrolysate when lithium chloride is used as electrolyte and aluminum as cathode. Mechanisms are proposed to account for both anolyte and catholyte products.

It was noted over one hundred years ago by Wöhler and Buff[1] that during the electrolysis of aqueous sodium chloride between aluminum electrodes hydrogen was evolved at the anode and aluminum dissolved with a current efficiency significantly greater than 100% on the assumption of oxidation to the tripositive state. Turrentine[2] also observed the anodic evolution of hydrogen, and proposed that the hydrogen arose from reaction of the solvent water with lower valent (+1 or +2, or both) aluminum formed as a primary anodic oxidation product. Substantial evidence for the anodic generation of lower valent aluminum in anhydrous acetic acid,[3,4] liquid ammonia,[5,6] acetone[7] and ethanol,[4] has also been obtained. Moreover, compelling additional electrochemical evidence for the formation of lower valent aluminum in aqueous salt solutions has recently been reported.[8] Thus, it was shown that when a flowing anolyte consisting of aqueous sodium chloride or nitrate was caused to pass over an aluminum rod serving as anode and then into a solution of an oxidizing agent, *e.g.*, MnO_4^- or Ag^+, contained in a separate vessel, reduction of the oxidant occurred, MnO_4^- to MnO_2 and Ag^+ to Ag°. The occurrence of reduction at a distance from the anode can best be interpreted in terms of a primary anodic oxidation of aluminum to a lower valent state. In none of the investigations cited above could a salt of lower valent aluminum be isolated from solution following electrolysis. However, in every instance in which the anodic current efficiency exceeded 100%, either the solvent itself or some oxidant present in the solvent was reduced.

In view of the fact that in previous work[9–14] reduction of a variety of organic compounds was effected in pyridine solution by unipositive magnesium anodically generated, and in view of the evidence for lower valent aluminum given above, we decided to investigate the possibility of "anodic reductions" of organic compounds in pyridine solution during the course of electrolysis between aluminum electrodes. The present paper describes the reduction of benzophenone. This compound was chosen because a thorough study has been made of its reduction during electrolysis between magnesium electrodes in pyridine solution.[9] Moreover, it has been shown[15] that the ketyl radical-ion formed as the primary anolyte reduction product in electrolyses between magnesium electrodes is capable of corroding massive magnesium.

Experimental

Materials.—The 10-mm. aluminum rod from which all electrodes were cut was of 99.98% purity and was furnished by the Aluminum Company of America. The sodium iodide was Merck reagent grade, and it was dried at 110° before use. The lithium chloride employed as electrolyte was Baker and Adamson reagent grade. Pyridine, Fisher analytical reagent, was fractionally distilled from sodium and stored over barium oxide. The benzophenone, m.p. 46°, was obtained from Eastman.

Apparatus and Procedure.—The source of direct current was a full-wave mercury tube rectifier, capable of supplying up to 1000 volts. The quantity of electricity passed through the circuit was determined by means of a silver coulometer placed in series with the electrolytic cell. The electrolyses were carried out in a 2-compartment cell with a sintered glass disk separating anode and cathode compartments. The cell was maintained in a constant temperature bath kept at 39.5 ± 0.5°.

The aluminum electrodes were cleaned in 10% sodium hydroxide solution, then washed with distilled water and dried in an oven at 110°. The sodium iodide–pyridine solution

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[1] F. Wöhler and H. Buff, *Ann.*, **103**, 218 (1857).

[2] J. W. Turrentine, *J. Phys. Chem.*, **12**, 448 (1908).

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[4] P. Brouillet, I. Epelboin and F. Froment, *Compt. rend.*, **239**, 1795 (1954).

[5] M. C. del Boca, *Helv. Chem. Acta*, **16**, 565 (1933).

[6] W. E. Bennett, A. W. Davidson and J. Kleinberg, THIS JOURNAL, **74**, 732 (1952).

[7] U. Sborgi and P. Marchetti, *Nuovo Cimento*, **22**, 151 (1921).

[8] E. Raijola and A. W. Davidson, THIS JOURNAL, **78**, 556 (1956).

[9] M. D. Rausch, W. E. McEwen and J. Kleinberg, *ibid.*, **76**, 3622 (1954).

[10] M. D. Rausch, F. D. Popp, W. E. McEwen and J. Kleinberg, *J. Org. Chem.*, **21**, 212 (1956).

[11] W. E. McEwen, J. Kleinberg, D. L. Burdick, W. D. Hoffman and J. Y. Yang, THIS JOURNAL, **78**, 4587 (1956).

[12] M. D. Rausch, W. E. McEwen and J. Kleinberg, *Chem. Revs.*, **57**, 417 (1957).

[13] J. Y. Yang, W. E. McEwen and J. Kleinberg, THIS JOURNAL, **80**, 4300 (1958).

[14] W. D. Hoffman, W. E. McEwen and J. Kleinberg, *Tetrahedron*, **5**, 293 (1959).

[15] D. L. Burdick, A. V. Santoro, W. E. McEwen and J. Kleinberg, THIS JOURNAL, **79**, 5467 (1957).