[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, CORNELL UNIVERSITY]

GERMANIUM. XVIII. FURTHER ORGANIC COMPOUNDS OF GERMANIUM[1]

BY W. R. ORNDORFF, D. L. TABERN AND L. M. DENNIS

RECEIVED MARCH 25, 1927 PUBLISHED OCTOBER 5, 1927

Introduction

In previous papers[2] the authors have described the synthesis of some organic compounds of germanium. The study of these substances was undertaken not only to add to our knowledge of the rare element germanium, but also in the hope of being able to prepare organic compounds of either divalent or tetravalent germanium which would be soluble in water and which might be suitable for the treatment of pernicious anemia. It has been stated that an aqueous solution of germanium dioxide stimulates red cell formation[3] but the value of the substance for this purpose appears to have been disproved by Bodansky.[4]

The present investigation was not carried as far as had been contemplated but, because of the withdrawal of two of us (W. R. O. and D. L. T.) from the field, it seems desirable to place on record such results as were obtained.

Experimental

Triphenyl Germanium Bromide, $(C_6H_5)_3GeBr$.—This compound was first prepared by Morgan and Drew[5] by means of the Grignard reaction. Kraus and Foster[6] describe the preparation of this substance by the bromination of tetraphenyl germanium by boiling a solution of the latter substance and bromine in carbon tetrachloride for several hours. Before their article appeared we had found that when ethylene dibromide is employed as a solvent only a few minutes' warming is required and that a perfectly pure product results after removal of the solvent and a single recrystallization from petroleum ether containing hydrogen bromide. The melting point of the substances was found to be 134°, a somewhat lower value than reported in the two papers mentioned above.

Anal. Subs., 0.2774, 0.2882: AgBr, 0.1352, 0.1410. Calcd. for $C_{18}H_{15}GeBr$: Br, 20.8. Found: 20.8, 20.8.

---

[1] The investigation upon which this article is based was supported by a grant from the Heckscher Foundation for the Advancement of Research, established by August Heckscher at Cornell University.

[2] (a) Tabern, Orndorff and Dennis, THIS JOURNAL, **47**, 2039 (1925); (b) Dennis, Orndorff and Tabern, *J. Phys. Chem.*, **30**, 1049 (1926).

[3] (a) Hammett, Nowrey and Müller, *J. Exp. Med.*, **35**, 173 (1922); (b) Hammett and Nowrey, *ibid.*, 507; (c) Müller and Iszard, *Am. J. Med. Sci.*, **162**, 364 (1922).

[4] Bodansky, *Proc. Soc. Exp. Biol. Med.*, **20**, 534, 536 (1923).

[5] Morgan and Drew, *J. Chem. Soc.*, **127**, 1760 (1925).

Kraus and Foster, THIS JOURNAL, **49**, 457 (1927).

Treatment of an alcoholic solution of the bromide with silver nitrate, filtration and dilution of the filtrate with water yielded triphenyl germanium oxide reported by Morgan and Drew.

Triphenyl Germanium Chloride, $(C_6H_5)_3GeCl$.—When triphenyl germanium oxide is dissolved in dry petroleum ether and the solution is saturated with hydrogen chloride, triphenyl germanium chloride separates in large, colorless crystals resembling the corresponding bromide. It may also be made by saturating a solution of triphenyl germanium bromide with hydrogen chloride and cooling. A third method consists in dissolving triphenyl germanium oxide in boiling alcohol and adding concentrated hydrochloric acid. The products prepared by each of these methods were recrystallized from petroleum ether and were found to melt sharply at 117–118°.

Anal. Subs., 0.1830: AgCl, 0.0765. Calcd. for $C_{18}H_{15}GeCl$: Cl, 10.5. Found: 10.3.

The Action of Two Moles of Bromine on Tetraphenyl Germanium.—The removal of two phenyl groups from tetraphenyl germanium was found to proceed much less smoothly than the removal of one, the evolution of some hydrogen bromide indicating the existence of side reactions. Since the direct isolation of diphenyl germanium dibromide was not found possible, subsequent reaction products were hydrolyzed directly. In addition to some triphenyl germanium oxide, two substances melting at 147 and 210° were formed. In all probability these were the complex dehydration products of diphenyl germanic acid previously reported by Morgan and Drew. As this reaction did not seem to offer a satisfactory way of preparing diphenyl germanium dibromide, it was not investigated further.

Unsymmetrical Aryl and Alkyl Germanes

Triphenyl *p*-Tolyl Germanium, $(C_6H_5)_3GeC_6H_4CH_3$.—Triphenyl *p*-tolyl germanium was prepared by the action of a large excess of *p*-tolyl magnesium bromide upon triphenyl germanium bromide. To insure the completion of the reaction, the ether was replaced by dry benzene, and the flask was heated to boiling for eight hours. The reaction mass was decomposed by a dilute aqueous solution of ammonium chloride and was subjected to prolonged steam distillation to remove all ditolyl. The product is best recrystallized from petroleum ether and alcohol or from glacial acetic acid; m. p. 123–124°.

Anal. Subs., 0.2238, 0.1781: CO_2, 0.6209, 0.4960; H_2O, 0.1173, 0.0921. Subs., 0.2052, 0.2402: GeO_2, 0.0553, 0.0650. Calcd. for $C_{25}H_{22}Ge$: C, 76.02; H, 5.62; Ge, 18.36. Found: C, 75.69, 75.98; H, 5.87, 5.75; Ge, 18.70, 18.78.

Triphenylanisyl Germanium, $CH_3OC_6H_4Ge(C_6H_5)_3$.—When treated in the same way, anisyl magnesium bromide (but not the iodide) and triphenyl germanium bromide yielded triphenylanisyl germanium. The product was finally recrystallized twice from alcohol and four times from glacial acetic acid, in both of which it is fairly insoluble in the cold. It melts at 158–159° (uncorr.).

Anal. Subs., 0.1758, 0.1845: CO_2, 0.4720, 0.4945; H_2O, 0.0888, 0.0933. Subs., 0.2150, 0.1973: GeO_2, 0.0543, 0.0505. Calcd. for $C_{25}H_{22}OGe$: C, 73.02; H, 5.40; Ge, 17.68. Found: C, 73.24, 73.12; H, 5.65, 5.66; Ge, 17.53, 17.77.

Triphenylethyl Germanium, $(C_6H_5)_3GeC_2H_5$.—Triphenylethyl germanium was prepared, in good yield, in essentially the same manner from triphenyl germanium bromide and ethyl magnesium bromide; m. p. 75–76°.

Anal. Subs., 0.2254, 0.2130: CO_2, 0.5938, 0.5612; H_2O, 0.1239, 0.1122. Subs., 0.1812, 0.3982, 0.1493; GeO_2, 0.0571, 0.1251, 0.0465. Calcd. for $C_{20}H_{20}Ge$: C, 72.12; H, 6.06; Ge, 21.82. Found: C, 71.87, 71.86, H, 6.15, 5.89; Ge, 21.86, 21.81, 21.62.

Triphenyldimethylanilino Germanium, $(CH_3)_2NC_6H_4Ge(C_6H_5)_3$.—Specimens of triphenyl germanium bromide were refluxed with an excess of dry dimethylaniline under varying conditions but no interaction took place.

One mole of triphenyl germanium bromide and two moles of *p*-bromodimethylaniline were dissolved in xylene and the liquid was refluxed with an excess of sodium. Sodium bromide separated and after an hour the metal retained its fresh surface. The solvent was decanted and as much of it as possible removed under moderate diminished pressure. The addition of alcohol resulted in the separation of slightly brownish, crystalline nodules. After recrystallization from hot petroleum ether and alcohol the product melted at 138–140°. Purified through the hydrochloride, it melted at 140–141° and still retained a brownish tinge.

Anal. Subs., 0.2004, 0.1891: CO_2, 0.5423, 0.5117; H_2O, 0.1074, 0.1037. Subs. 0.2137, 0.2136: GeO_2, 0.0527, 0.0525. Calcd. for $C_{26}H_{25}NGe$: C, 73.64; H, 5.95; Ge, 17.11. Found: C, 73.82, 73.82; H, 5.997, 6.137; Ge, 17.12, 17.06.

Passage of hydrogen chloride through an ethereal solution of triphenyldimethylanilino germanium yields at once the solid, crystalline hydrochloride, which may be separated either by evaporation of the ether or by decantation. It is insoluble in water and in hydrochloric acid, but dissolves readily in absolute alcohol, from which it is precipitated by the addition of water. It melts with decomposition between 105 and 110°. From it pure triphenyldimethylanilino germanium may be secured by treatment with alkali.

Tetrabenzyl Germanium and Its Tetrasulfonic Acid

Tetrabenzyl Germanium, $(C_6H_5CH_2)_4Ge$.—Nine g. of magnesium turnings was suspended in ether and the formation of the Grignard reagent was initiated by the addition of about 5 g. of benzyl chloride. A mixture of 40 g. of benzyl chloride, 10 g. of germanium tetrachloride and five volumes of dry xylene was then added drop by drop with good mechanical stirring and gentle refluxing. Finally, sufficient xylene was added to form a thin paste and the ether was distilled off on a steam-bath. Heating on the steam-bath was continued for some hours and the mixture was allowed to stand for two days. On working it up in the usual manner, taking care to subject the organic product to a vigorous and prolonged steam distillation to insure the removal of all dibenzyl, a nearly quantitative yield of tetrabenzyl germanium was secured. The first product melted at 106–107°, and at 107–108° after repeated crystallization from several solvents, including alcohol and petroleum ether.

Anal. Subs., 0.2116, 0.2000: CO_2, 0.5991, 0.5660; H_2O, 0.1236, 0.1182. Subs., 0.2007, 0.1923: GeO_2, 0.0481, 0.0466. Calcd. for $C_{28}H_{28}Ge$: C, 76.92; H, 6.46; Ge, 16.62. Found: G, 77.24, 77.10; H, 6.54, 6.61; Ge, 16.64, 16.82.

Tetrabenzyl Germanium Tetrasulfonic Acid, $(SO_3HC_6H_4CH_2)_4Ge$.—The above germane is preferably sulfonated by slowly dissolving it in an excess of 25% fuming sulfuric acid, keeping the temperature below 35°. Rapid agitation is essential. After standing for half an hour at room temperature, the reaction mixture was poured upon ice and the excess of sulfuric acid was removed by barium carbonate. When alcohol was added to the decolorized and strongly concentrated filtrate, the barium salt separated as an oil which changed to a white, crystalline solid on the addition of more alcohol. The solid was ground in a mortar with anhydrous acetone and was dried, first at room temperature and then at 110°. This substance, the normal barium salt of tetrabenzyl germanium tetrasulfonic acid, dissolves readily and completely in cold water, but is insoluble in acetone, alcohol or ether.

For analysis for either barium or sulfur alone the sample was decomposed by fusion in a nickel crucible with a mixture of potassium hydroxide and potassium nitrate. Germanium was determined in other samples by dissolving them in boiling water and precipitating the barium by the addition of an excess of sulfuric acid. The filtrate was concentrated and finally heated to 120° in a platinum crucible. Fuming nitric acid was added and the determination of germanium was carried out as described by Tabern, Orndorff and Dennis.[2a]

Anal. Subs., 0.3615, 0.3730: $BaSO_4$, 0.1640, 0.1690. Subs., 0.2899, 0.3874: $BaSO_4$, 0.2618, 0.3442. Calcd. for $C_{28}H_{24}S_4O_{12}Ba_2Ge$: Ba, 26.75; S, 12.46; Ge, 7.06. Found: Ba, 26.62, 26.66; S, 12.40, 12.20.

Anal. Subs., 0.5433, 0.6897: $BaSO_4$, 0.2505, 0.3156; GeO_2, 0.0562, 0.0706. Found: Ba, 27.15, 26.92; Ge, 7.18, 7.10.

Simple and Substituted Germanic Acid Anhydrides

Phenyl Germanic Acid Anhydride, $(C_6H_5GeO)_2O$.—One mole (3.6 g.) of mercury diphenyl and one mole (2.1 g.) of germanium tetrachloride were dissolved in dry xylene and heated at 140° in a sealed Pyrex bulb for two days. The contents of the bulb was diluted with absolute ether and filtered. The solid residue was pure phenyl mercuric chloride. The filtrate was further diluted with benzene and was treated with water containing a few drops of ammonium hydroxide. On standing, a granular precipitate separated at the liquid interface. This was filtered off and dried at 115°. Although quite pure, the substance was dissolved in dilute sodium hydroxide and was precipitated hot by neutralization of the solution with acetic acid.

Anal. Subs., (A) 0.2149, (B) 0.1885: GeO_2, 0.1302, 0.1140. Calcd. for C_6H_5-GeOOH: Ge, 39.7; for $C_{12}H_{10}O_3Ge_2$: Ge, 41.8. Found: 41.9, 41.9.

These analytical results indicate that the product in hand approached quite closely to the anhydride in composition, though Morgan and Drew concluded that the acid secured by them in small amount as the end fraction from a Grignard reaction was the fully hydrated form.

The anhydride of phenyl germanic acid is a white, fluffy, amorphous solid, insoluble in water and organic solvents, but soluble in excess of alkali; from such solution it is precipitated in lustrous flakes by carbon dioxide. It has no definite melting point.

p-Tolyl Germanic Acid Anhydride, $(CH_3C_6H_4GeO)_2O$.—Mercury ditolyl and germanium tetrachloride when heated at 160–190° in xylene yielded p-tolyl germanic acid anhydride. The method of isolation was essentially the same as in the preceding instance.

Anal. Subs., 0.2100, 0.2309: GeO_2, 0.1175, 0.1285. Calcd. for C_7H_7GeOOH: Ge, 36.9; for $C_{14}H_{14}O_3Ge_2$: Ge, 38.65. Found: Ge, 38.9, 38.6.

Benzyl Germanic Acid Anhydride, $(C_6H_5CH_2GeO)_2O$.—Equimolecular quantities of mercury dibenzyl and germanium tetrachloride (4.2 g.) were dissolved in xylene and heated in a closed tube between 115 and 120° for two days. A higher temperature results in the decomposition of the mercury dibenzyl. The isolation of the benzyl germanic acid anhydride was carried out as in the case of the phenyl analog except that here, because of the marked solubility of the benzyl mercuric chloride, water was added directly to the xylene solution without filtration.

Benzyl germanic acid anhydride is a colorless, granular precipitate, soluble in alkalies, fairly soluble in boiling water and in pyridine, but insoluble in organic solvents.

Anal. Subs., 0.1958, 0.1269: GeO_2, 0.1074, 0.0690. Calcd. for C_7H_7GeOOH: Ge, 36.9; for $C_{14}H_{14}Ge_2O_3$: Ge, 38.65. Found: Ge, 38.1, 37.7.

Dimethylaminophenyl Germanic Acid Anhydride, $[(CH_3)_2NC_6H_4GeO]_2O$.—Ten grams of germanium tetrachloride and an excess of dry dimethylaniline were placed in a flask which was then sealed and heated to 100–110° for two days. The strongly fluorescent gelatinous product was made alkaline and was subjected to steam distillation. After filtration carbon dioxide was passed into the resultant clear solution until the acid anhydride was completely precipitated. Re-solution and reprecipitation were repeated until the filtrate contained no germanium dioxide. The product may also be purified by dissolving it in acid and precipitating it with dilute ammonium hydroxide.

Dimethylaminophenyl germanic acid anhydride is a pearly white, fluffy powder, soluble in very dilute mineral acids, and also in an excess of alkali. Like the preceding anhydrides it does not have a definite melting point.

Anal. Subs., 0.1896, 0.2581: CO_2, 0.3043, 0.4174; H_2O, 0.0825, 0.1134. Subs., 0.2068, 0.1985: GeO_2, 0.1006, 0.0955. Calcd. for $C_8H_{11}O_2NGe$: C, 42.53; H, 4.9; Ge, 32.17. Calcd. for $C_{16}H_{20}O_3N_2Ge_2$: C, 44.30; H, 4.65; Ge, 33.50. Found: C, 43.78, 44.12; H, 4.88, 4.92; Ge, 33.76, 33.40.

When a thin layer of the above anhydride is kept for some time in an atmosphere of dry hydrogen chloride, it is converted entirely into the hydrochloride of dimethylanilino germanium trichloride; $((CH_3)_2NC_6H_4GeO)_2O + 8HCl = 2HCl(CH_3)_2NC_6H_4GeCl_3 + 3H_2O$. The above hydrochloride melts with decomposition near 110°. It is readily and completely soluble in water and from such a solution ammonium hydroxide precipitates dimethylaminophenyl germanic acid anhydride.

Tetra-*n*-butyl Germanium, $(C_4H_9)_4Ge$.—Germanium tetrachloride was added to a large excess of butyl magnesium bromide, the reaction being carried out essentially in the manner described in a previous paper for the propyl analog. The desired product was thus secured in good yield as an almost odorless, oily liquid boiling between 178 and 180° at 733 mm. Unlike its lower homologs, it is ignited only with difficulty.

Anal. Subs., 0.2648, 0.1986: CO_2, 0.6178, 0.4590; H_2O, 0.2855, 0.2081. Subs., 0.2384, 0.2415: GeO_2, 0.0826, 0.0829. Calcd. for $C_{16}H_{36}Ge$: C, 63.81; H, 12.06; Ge, 24.13. Found: C, 63.65, 63.03; H, 12.07, 11.72; Ge, 24.05, 23.83.

Summary

A further study of the organic compounds of germanium—especially those containing potential solubilizing groups—has led to the synthesis and study of the following types of substances: (1) triphenyl germanium halides; (2) mixed aryl and alkyl derivatives, with and without a salt-forming group; (3) tetrabenzyl germanium and its tetrasulfonic acid; (4) simple and substituted phenyl germanic acid anhydrides; (5) tetra-*n*-butyl germanium.

ITHACA, NEW YORK