[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE COLLEGE]

Analogs of Hexaphenylethane. III. Triphenylmethyltriphenylgermane, Triphenylgermanecarboxylic Acid and Some of Its Derivatives[1]

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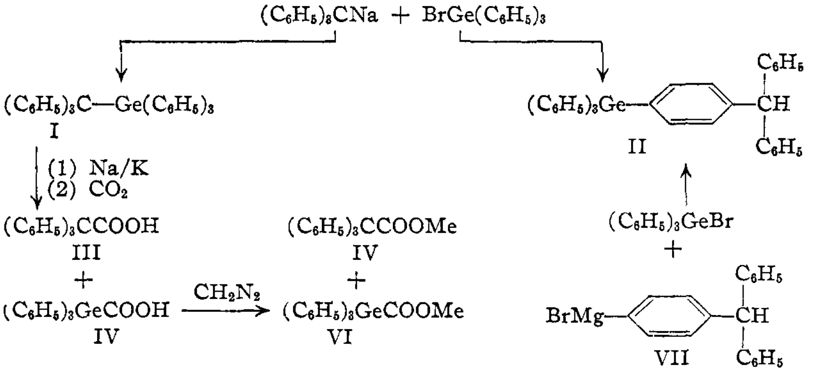
Triphenylmethyltriphenylgermane, prepared from the reaction of triphenylmethylsodium with triphenylbromogermane, is shown not to dissociate to any detectable extent. Also isolated from the reaction mixture is *p*-triphenylgermylphenyldiphenylmethane. Cleavage of triphenylmethyltriphenylgermane with sodium-potassium alloy, followed by carbonation, yields triphenylacetic acid and triphenylgermanecarboxylic acid, also prepared by a similar cleavage of hexaphenyldigermane. This latter acid eliminates carbon monoxide and water on heating to the melting point, forming triphenylgermyl triphenylgermanecarboxylate, identified by an independent synthesis, and by saponification to triphenylgermanecarboxylic acid and triphenylgermanol. Triphenylgermanol was prepared by hydrolysis of triphenylbromogermane with aqueous alcoholic alkali.

A project of this Laboratory is the preparation of analogs of hexaphenylethane containing group IVb elements other than carbon, in order to study the tendency of these compounds to dissociate into free radicals. Paper II of this series described the preparation of triphenylmethyltriphenylsilane, a very stable compound which showed no tendency to dissociate into free radicals under conditions where the dissociation of hexaphenylethane is readily detected. In view of the general similarity of organogermanium and organosilicon compounds, it was therefore not unexpected to find that triphenylmethyltriphenylgermane was a similarly unreactive and stable compound showing no tendency to dissociate.

Triphenylmethyltriphenylgermane (I) has been prepared in about 50% yield from the reaction of triphenylmethylsodium with triphenylbromogermane in ether. As with the silicon analog, its preparation is accompanied by the formation, in about 25% yield, of the isomeric *p*-triphenylgermylphenyldiphenylmethane (II).



In contrast to the formation of the analogous silicon compound from triphenylmethylsodium and triphenylbromosilane, which requires 48 hours of refluxing in ether for completion of the reaction, the reaction of triphenylmethylsodium with triphenylbromogermane is essentially instantaneous, the product precipitating immediately from the reaction mixture. Actually, it is possible to titrate an ethereal solution of triphenylbromogermane with ethereal triphenylmethylsodium to a clearly defined end-point, indicated by the lack of discharge of the intense red color of the triphenylmethylsodium. This behavior indicates that triphenylbromogermane is considerably more reactive toward triphenylmethylsodium than is triphenylbromosilane, although one might have expected the reverse to be the case, since from the available data Sidgwick[2] has concluded that the trisubstituted halogermanes hydrolyze more slowly with water or alkali than do the corresponding silanes.

Triphenylmethyltriphenylgermane is a white, almost insoluble solid melting at 342–344°. No reaction occurs when the compound, in refluxing xylene, is treated over several hours with iodine or with air. These tests indicate that triphenylmethyltriphenylgermane does not dissociate appreciably into free radicals, since under similar conditions hexaarylethanes form triaryliodomethanes and triarylmethyl peroxides in high yields.

The infrared spectrum[3] of triphenylmethyltriphenylgermane is qualitatively identical with that of triphenylmethyltriphenylsilane except for small shifts in the frequency of the absorption bands due to the substitution of germanium for silicon.

The identification of triphenylmethyltriphenyl-germane (I) was accomplished by its cleavage with sodium-potassium alloy, a slow reaction requiring 1 to 2 days stirring before the cleavage began. The reaction mixture was carbonated and on working up, a mixture of triphenylacetic acid (III) and triphenylgermanecarboxylic acid (IV) was isolated. This latter compound has not been previously reported and is discussed in detail later in this paper. This mixture of acids could not be separated by fractional crystallization from ethanol, and appeared to form mixed crystals, since the solid melted midway between the melting points of the pure acids. The mixed acids were converted to their methyl esters with diazomethane, and the esters were then successfully separated by fractional crystallization to yield pure methyl triphenylacetate (V) and methyl

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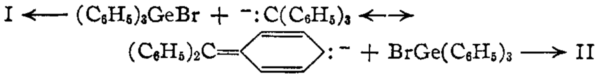
[1] (a) For paper I of this series see T. C. Wu and H. Gilman, THIS JOURNAL, **75**, 3762 (1953). (b) For paper II of this series see A. G. Brook, H. Gilman and L. S. Miller, *ibid.*, **75**, 4759 (1953).

[2] N. Sidgwick, "Chemical Elements and their Compounds," Vol. I, Oxford Press, New York, N. Y., 1950, pp. 558, 573.

[3] We are indebted to Dr. V. A. Fassel and Mr. M. Margoshes for the infrared absorption spectra of this and other compounds. Complete data will be published elsewhere by these authors.

triphenylgermanecarboxylate (VI). These products could have arisen only from triphenylmethyltriphenylgermane.

The second product from the reaction of triphenylmethylsodium with triphenylbromogermane, recovered from the ether layer after hydrolysis with water, was identified as *p*-triphenylgermylphenyldiphenylmethane (II) by an unambiguous synthesis from triphenylbromogermane and the Grignard reagent of *p*-bromophenyldiphenylmethane (VII). The analogous silicon compound has been reported[1b] from the reaction of triphenylhalosilanes with triphenylmethylsodium, and the probable mechanism of formation suggested there, involving nucleophilic attack of the mesomeric triphenylmethyl anion on triphenylbromosilane, applies equally well in the present case.



Triphenylgermanecarboxylic acid (IV), derived from the cleavage of triphenylmethyltriphenylgermane with sodium-potassium alloy followed by carbonation, has not previously been reported in the literature, and its synthesis, for purposes of structure proof, became necessary. Mr. C. W. Gerow of this Laboratory has recently succeeded in cleaving hexaphenyldigermane with sodium-potassium alloy, to yield triphenylgermylpotassium. Although the analogous sodium compound has been previously prepared by treatment of tetraphenylgermane with sodium in liquid ammonia,[4] hexaphenyldigermane has not been reported to be cleaved by metals in the absence of ammonia under any conditions. The cleavage succeeds by employing a minimum of ether as a medium for the reaction, and by using a small amount of tetrahydrofuran as an initiator or catalyst.[5]

When hexaphenyldigermane is treated under the above conditions, essentially quantitative cleavage is obtained in 24 hours, for when the heterogeneous system is carbonated, and then hydrolyzed, no hexaphenyldigermane is recovered. Acidification of the aqueous layer gives after recrystallization from ethanol an 82.5% yield of an acid, melting at 189–190° with evolution of a gas, having the correct analysis and neutralization equivalent for triphenylgermanecarboxylic acid (IV). This compound can be converted to its methyl ester (VI) with diazomethane.

$$\begin{tikzcd}
(C_6H_5)_3Ge{-}Ge(C_6H_5)_3 \arrow[r, "(1)\ \text{Na/K}", "(2)\ CO_2"'] & \underset{\text{IV}}{(C_6H_5)_3GeCOOH} \arrow[r, "\text{heat}", "-CO"'] \arrow[d, "\text{NaOH}"] \arrow[dl, "CH_2N_2"'] & (C_6H_5)_3GeOH + (C_6H_5)_3GeCOOH \arrow[d, shift left, "\substack{\text{heat}\\ -H_2O}"] \\
\underset{\text{VI}}{(C_6H_5)_3GeCOOMe} & (C_6H_5)_3GeCOONa + BrGe(C_6H_5)_3 \arrow[r] & \underset{\text{VIII}}{(C_6H_5)_3GeCOOGe(C_6H_5)_3} \arrow[u, shift left, "\substack{(1)\ KOH\\ (2)\ H^+}"]
\end{tikzcd}$$

The behavior of triphenylgermanecarboxylic acid on melting is most interesting. Like its silicon analog,[6] it liberates carbon monoxide on melting, but instead of yielding the silanol and the disiloxane as triphenylsilanecarboxylic acid is reported to do,[6] it gives rise to water and a high yield of triphenylgermyl triphenylgermanecarboxylate (VIII) identical with a sample prepared from the sodium salt of triphenylgermanecarboxylic acid and triphenylbromogermane. The identity of the two materials was established by a mixed melting point determination, by the identity of their infrared spectra, and by the fact that the authentic triphenylgermyl triphenylgermanecarboxylate could be saponified to yield triphenylgermanecarboxylic acid and triphenylgermanol.

The formation of triphenylgermyl triphenylgermanecarboxylate (VIII) from the acid by heating is best explained by loss of carbon monoxide by a part of the acid to give triphenylgermanol (IX) which at the elevated temperature (190°) must esterify with the remaining acid, eliminating water, as rapidly as the germanol is formed, since the 86% yield of the ester (VIII) obtained indicates that the reaction proceeds almost quantitatively under these conditions.

The isolation of triphenylgermanol (IX) from saponification of the ester (VIII) required the preparation of an authentic specimen. Although this compound has been prepared by hydrolysis of the corresponding sodium salt, obtained from oxidation of triphenylgermylsodium,[4] it has been reported[4,7] that the alkaline hydrolysis of triphenylbromogermane gives rise to hexaphenyldigermoxane. Under our conditions, it has been found possible to prepare this compound in excess of 80% yield by brief refluxing of triphenylbromogermane in 10% aqueous alcoholic alkali.

Experimental[8]

Reaction of Triphenylmethylsodium with Triphenylbromogermane.—To 10.7 g. (0.028 mole) of triphenylbromogermane, m.p. 137–138°, prepared by bromination of tetraphenylgermane in 76.5% yield,[9] in 40 ml. of ether was added an ethereal solution of triphenylmethylsodium, prepared from 14 g. (0.05 mole) of triphenylchloromethane and 110 g. of 3% sodium amalgam in 280 ml. of ether.[10] Analysis of the triphenylmethylsodium solution[11] indicated the concentration of the reagent to be 0.159 *M*. The blood-red color of the triphenylmethylsodium solution was immediately discharged on addition to the reaction flask, and a white precipitate formed. The triphenylmethylsodium solution was titrated in until a permanent red color remained in the flask and the reaction was then stirred overnight. An additional few drops of the triphenylmethylsodium solution were required the next day to restore the red color to the flask. A total of 165 ml. (104% based on triphenylbromogermane) of triphenylmethylsodium solution was required. The re-

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[4] C. A. Kraus and L. S. Foster, THIS JOURNAL, **49**, 457 (1927).

[5] This work will be reported in greater detail in a forthcoming paper by H. Gilman and C. W. Gerow.

[6] R. A. Benkeser and R. G. Severson, THIS JOURNAL, **73**, 1424 (1951).

[7] G. T. Morgan and H. D. K. Drew, *J. Chem. Soc.*, **127**, 1760 (1925); O. H. Johnson and W. H. Nebergall, THIS JOURNAL, **71**, 1720 (1950).

[8] All melting points are uncorrected. Reactions involving organometallic compounds were carried out in an atmosphere of dry oxygen-free nitrogen.

[9] O. H. Johnson and D. M. Harris, THIS JOURNAL, **72**, 5566 (1950).

[10] W. B. Renfrow, Jr., and C. R. Hauser, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 607.

[11] H. Gilman and A. H. Haubein, THIS JOURNAL, **66**, 1515 (1944).

action mixture was hydrolyzed with water and the insoluble material filtered off. This triphenylmethyltriphenylgermane weighed 8.3 g. (56.5%) and melted crudely from 327–333°. It could be recrystallized with difficulty from dioxane or pyridine and then melted at 342–344°. The purified yield was 41%. The mixed melting point with hexaphenyldigermane (m.p. 337–338°) was not depressed but melted at 340–342°.

Anal.[12] Calcd. for $C_{37}H_{30}Ge$: C, 81.05; H, 5.49; Ge, 13.3. Found: C, 80.6; H, 5.45; Ge, 13.1.

The ether layer from the above filtration was dried with sodium sulfate and the ether was then removed under reduced pressure to yield 8.3 g. of a sticky yellow solid. This material was refluxed with 100 ml. of petroleum ether (b.p. 60–70°) and filtered hot. The 1.8 g. of yellow-white powder thus obtained melted at 196–206°. The yellow impurity was removed by dissoving the material in benzene, and then adding glacial acetic acid, which precipitated 1.7 g. (11%) of pure *p*-triphenylgermylphenyldiphenylmethane, m.p. 207–209°.

The petroleum ether filtrate from above deposited additional white-yellow solid which was similarly freed of its yellow impurity. After recrystallization from a benzene–petroleum ether (b.p. 60–70°) solution an additional 3.7 g. (24%) of *p*-triphenylgermylphenyldiphenylmethane was obtained which melted at 208–209°. The mixed melting point with *p*-triphenylsilylphenyldiphenylmethane (m.p. 213–215°) melted from 209–213°.

The mixed melting point of this compound with authentic *p*-triphenylgermylphenyldiphenylmethane, described below, was not depressed, and the infrared spectra of these compounds were identical.

Anal. Calcd. for $C_{37}H_{30}Ge$: C, 81.05; H, 5.49; Ge, 13.3. Found: C, 80.75; H, 5.49; Ge, 12.9.

A second run similar to the above gave a 51% yield of pure triphenylmethyltriphenylgermane and a 26% yield of pure *p*-triphenylgermylphenyldiphenylmethane.

Cleavage of Triphenylmethyltriphenylgermane with Sodium–Potassium Alloy.—To 1.4 g. (0.00256 mole) of triphenylmethyltriphenylgermane in 10 ml. of ether was added 1 ml. of 1:5 sodium–potassium alloy. After stirring for 2 days the suspension acquired an orange-red color. An additional 5 ml. of ether was added and the suspension was stirred an additional 4 days and then was carbonated with a Dry Ice–ether slurry, and then hydrolyzed with water. The ether layer, after drying and removal of the ether under reduced pressure, yielded a trace of gum, which after recrystallization from ethanol gave 0.05 g. (8%) of white solid melting at 86–89° which did not depress the mixed melting point with authentic triphenylmethane.

The slightly cloudy aqueous layer was filtered, and then acidified precipitating 1.1 g. of acidic material which softened at 168° and melted over the range 203–209° with evolution of a gas. It was recrystallized from ethanol to give lustrous crystals melting from 203–220°, again with the evolution of a gas. The second crop from the mother liquors melted from 190–195° with gas evolution. Successive crystallizations from ethanol or benzene failed to materially alter the melting points, or to eliminate the evolution of gas upon melting. An infrared spectrum of the crude material possessed all the absorption bands found in the individual spectra of triphenylacetic acid and triphenylgermanecarboxylic acid.

A sample (0.45 g.) of the crude mixture of acids was dissolved in ether and treated with excess diazomethane. The ether was removed under reduced pressure and the crude ester mixture was fractionally crystallized from a 1:3 mixture of benzene and petroleum ether (b.p. 60–70°). The first fraction (0.2 g.) melted at 175–181° and was essentially pure methyl triphenylacetate, for after one additional crystallization from 1:3 benzene–petroleum ether (b.p. 60–70°) it melted at 185–187°, and failed to depress the mixed melting point with authentic methyl triphenylacetate, m.p. 186–188°. The infrared spectrum was identical with that of methyl triphenylacetate. The pure methyl triphenylacetate isolated represented a yield of about 48%.

The second fraction (0.15 g.) melted from 157–171°, and the third (0.1 g.) melted from 105–108°. This latter material was recrystallized from petroleum ether (b.p. 60–70°) and then melted at 99–104°. The mixed melting point with authentic methyl triphenylgermanecarboxylate (m.p. 107–108°) was not depressed but melted at 102–105°. The material was again crystallized from petroleum ether (b.p. 60–70°) and melted at 105–107°. The mixed melting point was 106–108°. The infrared spectrum of this compound was identical with that of authentic methyl triphenylgermanecarboxylate. The pure methyl triphenylgermanecarboxylate isolated represented a yield of about 26%.

Dissociation Experiments with Triphenylmethyltriphenylgermane.—When 0.3 g. (0.00055 mole) of triphenylmethyltriphenylgermane, 0.1 g. of iodine and 3 drops of quinoline were refluxed in 50 ml. of xylene for 12 hours, no consumption of iodine was observed. The solution was cooled, causing crystallization of a solid. The iodine was removed with aqueous sodium sulfite, and the solid filtered off and dried. The material recovered weighed 0.27 g. (90% recovery), melted at 335–340°, and did not depress a mixed melting point with the starting material.

Similarly, when 0.3 g. of triphenylmethyltriphenylgermane, and 3 drops of an approximately 0.001 *M* solution of iodine in chloroform were refluxed with 50 ml. of chloroform for 11 hours, no consumption of iodine was observed, and the 0.29 g. of material recovered after evaporation of the solvent under reduced pressure melted from 320–328°. After recrystallization from dioxane, it melted at 339–341°, and did not depress a mixed melting point with the starting material.

When a stream of dry air was bubbled through a mixture of 0.3 g. of triphenylmethyltriphenylgermane in refluxing xylene for 35 hours, the solution gradually became yellow. When the solution was cooled, 0.27 g. (90%) of material crystallized out which melted at 333–337°. The mixed melting point with the starting material was 338–341°.

***p*-Triphenylgermylphenyldiphenylmethane.**—The Grignard reagent of *p*-bromophenyldiphenylmethane was prepared from 10 g. (0.031 mole) of the halide and 0.96 g. (0.04 g. atom) of magnesium in 100 ml. of ether. The reaction failed to start when the dried magnesium was treated with a small portion of the halide solution. The reaction was initiated by the addition of 0.2 ml. of ethyl bromide, and the magnesium was then slowly consumed, and the reaction mixture slowly turned dark red during the 24 hours it was refluxed. At the end of this time a strong Color Test I[13] was obtained, and a 5-ml. aliquot when hydrolyzed and titrated with standard acid, indicated a 62% yield of the Grignard reagent. To 2.85 g. (0.0074 mole) of triphenylbromogermane in 10 ml. of ether was added 50 ml. (0.0074 mole) of the above Grignard reagent. The material was refluxed for 24 hours at which time a strong positive Color Test I was obtained. The ether was then allowed to distil off until a paste remained which was stirred at about 100° for 2 hours. The paste was then treated with 50 ml. of benzene and stirred at room temperature overnight. The reaction was then hydrolyzed with water and dilute acid, the benzene layer dried, and the solvent removed under reduced pressure. To the resulting gummy solid was added 20 ml. of petroleum ether (b.p. 60–70°) which precipitated 2.3 g. (57%) of *p*-triphenylgermylphenyldiphenylmethane, m.p. 207–209°. Recrystallization from benzene–petroleum ether (b.p. 60–70°) raised the melting point to 208–210°, and a mixed melting point with the lower melting (208–209°) material obtained from the reaction of triphenylmethylsodium with triphenylbromogermane was not depressed. The infrared spectra of the two compounds were identical. Additional material isolated from the petroleum ether extract raised the total yield to 65%.

Cleavage of Hexaphenyldigermane. Triphenylgermanecarboxylic Acid.—To a slowly stirred suspension of 5.0 g. (0.0082 mole) of hexaphenyldigermane in 10 ml. of ether, was added 2.5 ml. of 1:5 sodium–potassium alloy, followed by 25 drops of tetrahydrofuran. A green-blue coloration occurred where the tetrahydrofuran came in contact with the alloy. After stirring for from five to ten minutes, the suspension acquired on one occasion a yellow-brown color,

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(12) Mr. C. W. Gerow has found that germanium can be analyzed by following the procedure described for the analysis of silicon by H. Gilman, B. Hofferth, H. W. Melvin and G. E. Dunn, *ibid.*, **72**, 5767 (1950), except that "Vycor" crucibles are used. The results have been found to be generally slightly low, probably due to loss of germanium as the volatile monoxide. The loss can be minimized by very slow ignition of the sample.

(13) H. Gilman and F. Schulze, THIS JOURNAL, **47**, 2002 (1925).

and on a second occasion a green-gray color. The material was stirred a total of 24 hours after the addition of 25 ml. of ether. The suspension was then carbonated with a Dry Ice–ether slurry, and then hydrolyzed with water to give two clear layers with almost no undissolved material. The layers were separated, the ether layer was dried and the solvent was removed to give only a trace of gum. The aqueous layer was acidified, precipitating a white solid. This material was recrystallized from ethanol to yield a total of 4.75 g. (83%) of triphenylgermanecarboxylic acid, which softened at 187° and which rapidly evolved a gas at 189–190° as the material melted. The infrared spectrum was similar to that of triphenylacetic acid except that the positions of the absorption bands were shifted.

Anal. Calcd. for $C_{19}H_{16}O_2Ge$: C, 65.38; H, 4.61; Ge, 20.85; neut. equiv., 349. Found: C, 65.39; H, 4.59; Ge, 21.07; neut. equiv., 351, 352.

Methyl Triphenylgermanecarboxylate.—To 0.55 g. (0.00155 mole) of triphenylgermanecarboxylic acid in 10 ml. of ether was added excess diazomethane in ether. Gas was evolved briskly. The ether was removed under reduced pressure and the white crystalline solid was crystallized from petroleum ether (b.p. 60–70°). The 0.5 g. (87%) of methyl triphenylgermanecarboxylate isolated melted sharply at 107–108°. Recrystallization did not alter the melting point. The infrared spectrum was qualitatively similar to that of methyl triphenylacetate, with some shift in the positions of the absorption bands.

Anal. Calcd. for $C_{20}H_{18}O_2Ge$: C, 66.17; H, 4.99. Found: C, 65.97; H, 5.13.

Thermal Decomposition of Triphenylgermanecarboxylic Acid.—A 15-cm. length of 6-mm. diameter glass tubing, sealed at one end, was packed with 0.5 g. (0.00143 mole) of finely powdered triphenylgermanecarboxylic acid. The tube was then bent at right angles about 6 cm. from the open end, and placed in a melting point bath. The open end of the tube was lightly packed with filter paper moistened with a dilute aqueous solution of palladium chloride. The bath temperature was slowly raised to 190°, at which temperature the material in the tube softened and melted with the evolution of gas. The temperature was maintained between 190° and 210° for about 5 minutes, until bubbling and gas evolution had virtually ceased, and a clear colorless liquid remained in the tube. During the evolution of the gas, the filter paper in the open end of the tube became black, indicating the gas evolved was carbon monoxide.[14] A similar result had previously been observed with carbon monoxide generated from formic acid and warm concentrated sulfuric acid. The blackened filter paper was replaced with fresh material which also turned black. During the heating period, a colorless liquid also collected just above the bend of the tube. When bubbling in the liquid and gas evolution had ceased, and the material in the tube was a clear colorless liquid, the glass tube was removed from the bath, cooled, and cut into pieces. The colorless liquid which formed at the bend in the tube turned white anhydrous copper sulfate blue, indicating that the liquid was water.

The viscous liquid in the bottom of the tube was removed by expelling it with air. It formed a gummy solid which was crystallized from a 1:1 mixture of chloroform and petroleum ether (b.p. 60–70°). The 0.4 g. (86%) of triphenylgermyl triphenylgermanecarboxylate isolated, melted at 157–159°. Further recrystallization from the same solvent mixture raised the melting point to 163–164°. The mixed melting point with authentic triphenylgermyl triphenylgermanecarboxylate, described below, was not depressed, and the infrared spectra of the two compounds were identical.

Anal. Calcd. for $C_{37}H_{30}O_2Ge_2$: C, 68.15; H, 4.63; Ge, 22.3. Found: C, 67.50; H, 4.67; Ge, 20.5.

Triphenylgermyl Triphenylgermanecarboxylate.—To 0.5 g. (0.00143 mole) of triphenylgermanecarboxylic acid was added 14.1 ml. of 0.1015 *M* sodium hydroxide (0.00143 mole) with gentle heating to effect solution. The water was removed under reduced pressure. To the white solid formed were added 20 ml. of benzene and 0.57 g. (0.0015 mole) of triphenylbromogermane. The material was refluxed for 2 hours, filtered, and the benzene removed under reduced pressure. The white solid isolated was recrystallized from a mixture of benzene and petroleum ether (b.p. 60–70°). A total of 0.75 g. (81%) of triphenylgermyl triphenylgermanecarboxylate, m.p. 160–161°, was isolated which after one additional crystallization melted 163–164°, and which did not depress the mixed melting point with the material described above. The infrared spectrum was characteristic of an ester, except that the absorption bands were slightly displaced, due to the substitution of germanium for carbon.

This compound was also synthesized in 53% yield from the silver salt, prepared by dissolving the acid in excess aqueous ammonium hydroxide, removing most of the excess ammonia under reduced pressure, and treating the aqueous solution with excess silver nitrate. A white precipitate formed which rapidly turned brown. The material was filtered, washed with water, then with methanol in which it seemed to be slightly soluble, and then with ether in which it again appeared to be slightly soluble. A 0.8-g. (0.0018 mole if pure silver salt) portion of this brown solid was refluxed with 0.69 g. (0.0018 mole) of triphenylbromogermane in 10 ml. of benzene for 2 hours, and was then filtered. The benzene was removed under reduced pressure, and the white solid, m.p. 131–150°, was recrystallized from a benzene–petroleum ether (b.p. 60–70°) mixture to give 0.7 g. (53%) of compound melting at 162–164°. It did not depress the melting point when admixed with triphenylgermyl triphenylgermanecarboxylate, prepared from the sodium salt and triphenylbromogermane.

Saponification of Triphenylgermyl Triphenylgermanecarboxylate.—A 0.2-g. (0.00031 mole) sample of triphenylgermyl triphenylgermanecarboxylate was refluxed for 12 minutes with a solution of 8 ml. of 5% aqueous potassium hydroxide and 10 ml. of ethanol. The ethanol and part of the water were removed under reduced pressure, and the resulting material was diluted with water and ether-extracted. The ether layer was dried over sodium sulfate, and the ether removed under reduced pressure. The resulting white solid was recrystallized from petroleum ether (b.p. 60–70°) to yield 0.05 g. (51%) of triphenylgermanol, m.p. 129–133°, which after one further recrystallization melted at 132–134°, and which did not depress the mixed melting point of triphenylgermanol, m.p. 133–134°, prepared as described below. The infrared spectra of the two compounds were identical.

The aqueous, alkaline layer remaining after removal of the ether layer was acidified, precipitating a trace of white solid. The material was removed by ether extraction, and after the ether layer was dried with sodium sulfate, the ether was removed under reduced pressure to yield a white solid which melted from 182–187°, at which temperature gas was evolved. The material was recrystallized from ethanol to give 0.07 g. (65%) of triphenylgermanecarboxylic acid, m.p. 188–190° with evolution of gas, which did not depress the mixed melting point with an authentic sample.

Triphenylgermanol.—A solution of 0.5 g. of potassium hydroxide in 5 ml. of water, and 50 ml. of ethanol was refluxed with 2.0 g. (0.00522 mole) of triphenylbromogermane for 1 hour during which time all the material dissolved. The solution was cooled and poured into 200 ml. of water. The white solid (1.8 g.) which precipitated was filtered, dried and recrystallized from a 1:1 mixture of chloroform and petroleum ether (b.p. 60–70°) to yield a total of 1.4 g. (84%) of triphenylgermanol, m.p. 127–131°, which after one further recrystallization melted at 133–134°, (reported m.p. 134.2°[4]). The infrared spectrum was qualitatively identical to that of triphenylsilanol, except for a slight shift in the absorption bands due to substitution of germanium for silicon.

A repetition of the above run gave an 80% yield of identical material melting 132–134°.

Acknowledgment.—The authors are indebted to Mr. C. W. Gerow of this Laboratory for samples of tetraphenylgermane and hexaphenyldigermane.

AMES, IOWA

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[14] R. Nowicki, *Chem. Ztg.*, **35**, 1120 (1911).