[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE COLLEGE]

Analogs of Hexaphenylethane. V. Triphenylsilyltriphenylgermane[1]

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Triphenylsilyltriphenylgermane shows no tendency to dissociate into free radicals. It is inert toward oxygen in refluxing xylene, toward iodine in refluxing chloroform and is largely unaffected by iodine in refluxing xylene. It is cleaved by sodium–potassium alloy in diethyl ether to form triphenylgermylpotassium and triphenylsilylpotassium, which on carbonation form triphenylgermanecarboxylic acid and triphenylsilanecarboxylic acid, respectively, with the latter acid decarbonylizing to give triphenylsilanol. Triphenylsilyltriphenylgermane is prepared from the reaction of triphenylsilylpotassium on either triphenylchlorogermane or triphenylbromogermane.

The analogs of hexaphenylethane containing two dissimilar group IVB elements which have been reported are triphenylmethyltriphenylsilane,[2] triphenylmethyltriphenylgermane,[3] triphenylmethyltriphenyltin,[4] triphenylmethyltriphenyllead[4] and triphenylsilyltriphenyltin.[5] This list has been extended to include triphenylsilyltriphenylgermane, the topic of this paper, and triphenylgermyltriphenyltin, which will be reported at a later date.

Because of the similarity between germanium and silicon it was not surprising to learn that triphenylsilyltriphenylgermane, like hexaphenyldisilane[6] and hexaphenyldigermane[1] and unlike hexaphenylethane, showed no tendency to dissociate into free radicals. It was unaffected by oxygen in refluxing xylene and by iodine in refluxing chloroform. With iodine in refluxing xylene no triphenyliodogermane or triphenyliodosilane or their hydrolysis products were isolated. Under similar conditions hexaphenylethane forms triphenylmethyl iodide or peroxide.

Triphenylsilyltriphenylgermane is a white, difficultly soluble solid melting at 357–359° and volatilizing at about 500° with some decomposition. It is easily cleaved by sodium–potassium alloy in diethyl ether to form triphenylsilylpotassium and triphenylgermylpotassium, which on carbonation from triphenylsilanecarboxylic acid and triphenylgermanecarboxylic acid.

$$(C_6H_5)_3SiGe(C_6H_5)_3 \xrightarrow[\text{ether}]{\text{Na/K}} (C_6H_5)_3SiK + (C_6H_5)_3GeK \xrightarrow[\text{2, H}_2\text{O}]{\text{1, CO}_2} (C_6H_5)_3SiCOOH + (C_6H_5)_3GeCOOH \quad (1)$$

The triphenylsilanecarboxylic acid decarbonylates[7,8] more easily than triphenylgermanecarboxylic acid[3] and is not isolated as such, but as triphenylsilanol, which is the product of this decarbonylation. It is interesting to note that hexaphenyldisilane[9] and triphenylsilyltriphenylgermane are easily cleaved by sodium–potassium alloy in diethyl ether while triphenylmethyltriphenylgermane[3] requires long stirring before cleavage begins and hexaphenyldigermane[1] does not react at all under the same conditions. Comparisons of this sort are not always valid, however, due to the fact that conditions may not be duplicated exactly in all of the instances. It has been found in this Laboratory, for example, that the amount of solvent added initially plays a very important part in the length of time required for a given cleavage to begin. Indeed, cleavage may not take place at all if the amount of solvent added initially is too great.

$$(C_6H_5)_3SiCOOH \longrightarrow CO + (C_6H_5)_3SiOH \quad (2)$$

Triphenylsilyltriphenylgermane has been prepared in 63% yield from the reaction of triphenylsilylpotassium with triphenylbromogermane, in 43% yield from the reaction of triphenylsilylpotassium with triphenylchlorogermane and in 87% yield from the reaction of triphenylsilyllithium[10] with methyl triphenylgermanecarboxylate.[11] An attempt to prepare this compound by the reaction of triphenylgermylpotassium with triphenylchlorosilane yielded a mixture which could not be separated into its components. It is believed that a mixture of hexaphenyldigermane, hexaphenyldisilane and triphenylsilyltriphenylgermane is present and because of their similar solubility characteristics or isostructural relationship complete separation is not possible. This mixture is probably formed by means of a halogen–metal interconversion reaction followed by coupling of the various species present.

$$\begin{aligned}
&(a)\quad (C_6H_5)_4Ge + Na/K \xrightarrow{\text{ether}} (C_6H_5)_3GeK + C_6H_5K\\
&(b)\quad (C_6H_5)_3GeK + (C_6H_5)_3SiCl \longrightarrow\\
&\qquad (C_6H_5)_3GeSi(C_6H_5)_3 + (C_6H_5)_3GeCl + (C_6H_5)_3SiK \quad (3)\\
&(c)\quad (C_6H_5)_3GeCl + (C_6H_5)_3SiK \longrightarrow (C_6H_5)_3GeSi(C_6H_5)_3\\
&(d)\quad (C_6H_5)_3GeCl + (C_6H_5)_3GeK \longrightarrow (C_6H_5)_3GeGe(C_6H_5)_3\\
&(e)\quad (C_6H_5)_3SiCl + (C_6H_5)_3SiK \longrightarrow (C_6H_5)_3SiSi(C_6H_5)_3
\end{aligned}$$

The fact that a mixture is not obtained in the reaction of triphenylsilylpotassium with triphenylchlorogermane or triphenylbromogermane indicates that halogermanes do not undergo halogen–metal interconversion reactions as readily as halosilanes. This is substantiated by the fact that when triphenylbromogermane was allowed to react with triphenylmethylsodium[3] no product other than the simple coupling product was found or indicated. However, when triphenylmethylsodium was allowed to react with triphenylbromosilane[2] a variable amount of hexaphenyldisilane was formed

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[1] For paper IV of this series see H. Gilman and C. W. Gerow, THIS JOURNAL, **77**, 5509 (1955).

[2] A. G. Brook, H. Gilman and L. S. Miller, *ibid.*, **75**, 4759 (1953).

[3] A. G. Brook and H. Gilman, *ibid.*, **76**, 77 (1954).

[4] J. C. Bailie, *Iowa State Coll. J. Sci.*, **14**, 8 (1939) [*C. A.*, **34**, 6241 (1940)].

[5] H. Gilman and S. D. Rosenberg, THIS JOURNAL, **74**, 531 (1952).

[6] W. Schlenk, J. Renning and G. Rackey, *Ber.*, **44**, 1178 (1911).

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

[8] A. G. Brook and H. Gilman, *ibid.*, **77**, 2322 (1955).

[9] H. Gilman and T. C. Wu, *ibid.*, **73**, 4031 (1951).

[10] A. G. Brook and H. Gilman, *ibid.*, **76**, 278 (1954).

[11] H. Gilman and C. W. Gerow, *ibid.*, **77**, 4675 (1955).

which could not be separated completely from the triphenylmethyltriphenylsilane. The same authors[2] also observed that a halogen–metal interconversion reaction took place when triphenylsilylpotassium was allowed to react with triphenylchloromethane, because on carbonation triphenylacetic acid was isolated along with hexaphenyldisilane and hexaphenylethane. It should be noted that no halogen–metal interconversion reaction was indicated when triphenylgermylpotassium was allowed to react with triethylchlorosilane,[1] for only triphenylgermyltriethylsilane was isolated.

Experimental[12]

Preparation of Triphenylsilyltriphenylgermane. From Triphenylsilylpotassium and Triphenylbromogermane.—A suspension of triphenylsilylpotassium was prepared from 3.5 g. (0.0068 mole) of hexaphenyldisilane and 1 ml. (0.02 g. atom of potassium) of sodium–potassium alloy (1:5) in diethyl ether according to recent directions.[13] The excess alloy was amalgamated and the suspension transferred to another flask. To this stirring mixture was added 5.0 g. (0.013 mole) of triphenylbromogermane suspended in about 25 ml. of diethyl ether. After stirring 2.5 hours the mixture was hydrolyzed by the slow addition of 100 ml. of water. Filtration then yielded 6.7 g. of a solid melting over the range 302–323°. The ether layer was separated and the aqueous layer washed three times with ether. The combined ether portions were dried over anhydrous sodium sulfate and the solvent distilled to leave a small amount of solid which was combined with the 6.7 g. and crystallized from toluene to give 5.6 g. of solid melting over the range 313–320°. Another crystallization from toluene and one from benzene gave 3.5 g. of product melting at 352–353°. Recrystallization of the residues gave an additional 0.8 g. of product melting at 351.5–353°. The combined yield of triphenylsilyltriphenylgermane was 4.3 g. (63%).

Anal. Calcd. for $C_{36}H_{30}GeSi$: C, 76.76; H, 5.40; GeSi, 17.84. Found: C, 77.26, 77.19; H, 5.51, 5.46; GeSi, 17.83, 17.91.

From Triphenylsilylpotassium and Triphenylchlorogermane.—To a suspension of triphenylsilylpotassium prepared as above from 10 g. (0.0193 mole) of hexaphenyldisilane and 1.3 ml. (0.026 g. atom of potassium) of 1:5 sodium–potassium alloy in diethyl ether was added dropwise 13.1 g. (0.0386 mole) of triphenylchlorogermane suspended in about 50 ml. of ether. After stirring 1 hour the mixture was hydrolyzed with 100 ml. of water and worked up as previously to give 14.1 g. of insoluble material melting over the range 345–355°. From the ether layer there was obtained 8.4 g. of solid melting over the range 93–130°. Attempted purification of the 8.4 g. of solid was unsuccessful. It is believed a mixture of triphenylsilanol and hexaphenyldigermoxane was present. The 14.1 g. was crystallized from benzene to give 11.5 g. (43%) of product melting at 354–355°.

From Triphenylgermylpotassium and Triphenylchlorosilane (Attempted).—A suspension of triphenylgermylpotassium was prepared by the cleavage of 16.9 g. (0.044 mole) of tetraphenylgermane with 2.5 ml. (0.05 g. atom of potassium) of 1:5 sodium–potassium alloy in diethyl ether in accordance with recent directions. The excess alloy was amalgamated and the mixture was transferred to another flask in a stream of nitrogen. To this stirring mixture was added dropwise 26.2 g. (0.088 mole) of triphenylchlorosilane suspended in 100 ml. of ether. After stirring one-half hour the mixture was hydrolyzed by the addition of 100 ml. of water. Working up as previously gave 20.7 g. of ether-insoluble solid melting over the range 240–285°. From the ether layer there was obtained 18.3 g. of solid melting over the range 105–135°. The 18.3 g. was refluxed in petroleum ether (b.p. 60–70°) and filtered hot to give 5.2 g. of insoluble triphenylsilanol (mixed melting point) melting at 150.5–153.5°. Recrystallization of the remainder of the ether soluble material from petroleum ether (b.p. 60–70°) gave an additional 4.5 g. of triphenylsilanol melting at 150.5–153°. The total yield of this product was 9.7 g. (39.5%). The ether insoluble portion was recrystallized repeatedly from benzene; however the only isoluble product was tetraphenylgermane (10.5 g., m.p. 237–240°). The impure solids melted over the range 300–350°.

Dissociation Experiments with Triphenylsilyltriphenylgermane. With Oxygen in Refluxing Xylene.—To a 100-ml. flask was added 1.0 g. of triphenylsilyltriphenylgermane and 50 ml. of xylene. Dry air was bubbled rapidly through the refluxing solution for 48 hours. Cooling the solution crystallized 0.6 g. of starting material melting at 354–355°. Removal of the solvent left 0.4 g. of starting material melting at 352–353°. Mixed melting points of both of these fractions with starting material showed no depression. Total yield of starting material recovered was 1.0 g. (100%).

With Iodine in Refluxing Chloroform.—To a 100-ml. flask was added 0.3 g. of triphenylsilyltriphenylgermane, 50 ml. of chloroform and enough iodine to impart a pink color to the solution. The solution was refluxed 22 hours after which time the pink color persisted. Removal of the chloroform by distillation left 0.3 g. (100%) of starting material (mixed melting point) melting at 353.5–354.5°.

With Iodine in Refluxing Xylene.—To a 100-ml. flask was added 1.0 g. of triphenylsilyltriphenylgermane, 0.5 g. of iodine, 3 drops of quinoline and 50 ml. of xylene. This solution was refluxed 24 hours then allowed to cool. There precipitated 0.7 g. (70%) of starting material (mixed melting point) melting at 345–350°. The brown solution was decolorized by shaking with an aqueous solution of sodium sulfite. The xylene layer was separated and the solvent distilled to leave 0.2 g. of an infusible solid. The 0.7 g. was recrystallized from benzene to give 0.6 g. of starting material melting at 354–355°.

Reaction of Triphenylsilyltriphenylgermane with Sodium–Potassium Alloy in Diethyl Ether.—To a 250-ml. flask was added 5.6 g. (0.01 mole) of triphenylsilyltriphenylgermane, 1.2 ml. (0.24 g. atom of potassium) of sodium–potassium alloy and enough ether to make a paste. After stirring about a minute reaction began as was evidenced by a greenish color. After 5 minutes the color had changed to tan. After stirring 30 minutes an additional 30 ml. of ether was added and the mixture was stirred for a total of 29.5 hours. The excess alloy was then amalgamated by the addition of mercury and the suspension was poured in a stream of nitrogen into a slurry of Dry-ice and ether. When the mixture warmed to room temperature water was added and the ether layer separated. The basic solution was extracted twice with ether and the combined ether portions were dried over anhydrous sodium sulfate and the solvent distilled to leave 2.9 g. of solid melting over the range 150–157°. This was recrystallized from petroleum ether (b.p. 60–70°) to give 2.4 g. (86%) of triphenylsilanol (mixed melting point) melting at 154–156°. The basic aqueous layer was made acidic by the addition of concentrated hydrochloric acid, precipitating 2.6 g. (74%) of triphenylgermanecarboxylic acid melting at 178–180° with the evolution of carbon monoxide.[2] Recrystallization of the acid from ethanol gave 2.05 g. of acid melting at 189–193° with the evolution of carbon monoxide.

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[12] All melting points are uncorrected. Reactions involving alkali metals were carried out in an atmosphere of dry, oxygen-free nitrogen.

[13] H. Gilman and T. C. Wu, *J. Org. Chem.*, **18**, 753 (1953).