[Contribution from the Chemical Laboratory of Brown University]

STUDIES RELATING TO ORGANIC GERMANIUM DERIVATIVES. II. SOME TRIPHENYL GERMANIUM DERIVATIVES AND THEIR REACTIONS

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In the development of the chemistry of germanium, certain simple triphenyl germanium derivatives have been prepared and some of their reactions have been studied. A comparison of the properties of such compounds with those of corresponding compounds of carbon presents interesting contrasts. Thus triphenyl germanium amine is extremely susceptible to hydrolysis, while the analogous organic amines are comparatively stable. Triphenyl germanium amine results from the action of gaseous ammonia upon solutions of triphenyl germanium bromide or other halides in organic solvents. The product is so sensitive toward moisture that it is largely hydrolyzed in the operations incident to its separation unless extreme precautions are taken. Even then this method does not serve in preparing a strictly pure compound.

Since the amine upon hydrolysis yields triphenyl germanium oxide and ammonia, the process, as a whole, is expressed by the equations

$$(C_6H_5)_3GeBr + 2NH_3 = NH_4Br + (C_6H_5)_3GeNH_2 \qquad (1)$$
$$2(C_6H_5)_3GeNH_2 + H_2O = 2NH_3 + [(C_6H_5)_3Ge]_2O \qquad (2)$$

Triphenyl germanium amine may also be prepared by the action of potassium amide on triphenyl germanium bromide in ammonia solution. In this case, reaction is facilitated by an excess of potassium amide, which forms a monopotassium salt of the amine. This behavior is similar to that of the simpler aromatic amines;[1] triphenylmethylamine, however, does not react with potassium amide.[2] The following equations represent the reactions

$$(C_6H_5)_3GeBr + KNH_2 = (C_6H_5)_3GeNH_2 + KBr \qquad (3)$$
$$(C_6H_5)_3GeNH_2 + KNH_2 = (C_6H_5)_3GeNHK + NH_3 \qquad (4)$$

The amine may be liberated from its salt by means of ammonium bromide. It appears as a fine white crystalline precipitate. The following reaction is involved

$$(C_6H_5)_3GeNHK + NH_4Br = KBr + NH_3 + (C_6H_5)_3GeNH_2 \qquad (5)$$

The amine is further distinguished from its organic analogs by its marked tendency to lose ammonia with the formation of the imine, $[(C_6H_5)_3Ge]_2NH$. This sometimes occurs immediately upon precipitation. Attempts to recrystallize the amine invariably yielded mixtures of triphenyl germanium amine and imine and, perhaps, also the nitride.

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[1] White, Morrison and Anderson, This Journal, **46**, 967 (1924).

[2] Kraus and Rosen, *ibid.*, **47**, 2739 (1925).

This tendency of the amine to lose ammonia is paralleled by that of the corresponding hydroxide, triphenyl germanol, to lose water. On hydrolyzing triphenyl germanium halides, the oxide is invariably obtained. Kraus and Foster[3] have shown that the germanol may be obtained indirectly from sodium triphenyl germanide by oxidation of this salt to the germanolate and subsequent hydrolysis of this compound. Although triphenyl germanol loses water at higher temperatures, it is comparatively stable under ordinary conditions, much more so, in fact, than the corresponding amine.

Complete conversion of the amide to the nitride may be effected by heating the primary amine above 200° under atmospheric pressure and then evacuating the containing tube. The nitride may be purified by fractional sublimation *in vacuo* or by recrystallization from dry petroleum ether. From the latter solvent it crystallizes in colorless needles which melt at 163–164° (corr.).

Analysis of the amine was first carried out by decomposing the compound with hydrochloric acid and separating the ammonium chloride from the triphenyl germanium chloride[4] formed in this reaction. The latter compound, which was also prepared from the oxide, was found to melt at 116° (corr.). It is interesting to note that neither a nitrate nor a sulfate could be prepared by a similar method. The triphenyl germanium oxide was recovered unchanged, showing that it is much more resistant to hydrolysis than its structural analog, *bis*-triphenylmethyl ether.[5] The oxide is readily attacked by sodium in liquid ammonia solution. Apparently the primary products of this reaction are sodium triphenyl germanide, $(C_6H_5)_3GeNa$, and sodium triphenyl germanolate, $(C_6H_5)_3GeONa$. These products are analogous to those obtained by the cleavage of aromatic ethers with sodium–potassium alloy.[6]

It is evident that the compounds of germanium with electronegative elements show a somewhat greater reactivity than do their carbon analogs.

Experimental Part

Action of Ammonia on Triphenyl Germanium Bromide.—Triphenyl germanium bromide was treated with liquid ammonia at its boiling point, −33.5°. Solutions of triphenyl germanium bromide in ether, petroleum ether and benzene were also treated with gaseous ammonia at ordinary temperatures. The reactions were carried out in tubes similar to those described by White[7] but ground-glass joints were employed throughout in place of rubber stoppers and inlet and outlet tubes were provided with

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

[4] Subsequent to the completion of the present investigation, Orndorff, Tabern and Dennis, *ibid.*, **49**, 2513 (1927), have reported the preparation of the chloride by a similar method. They give its melting point as 117–118°.

[5] Gomberg, *ibid.*, **35**, 200 (1913); *Ber.*, **46**, 225 (1913).

[6] Ziegler and Thielmann, *ibid.*, **56**, 1740 (1923).

[7] White, THIS JOURNAL, **45**, 779 (1923).

stopcocks so that the tube could readily be evacuated. The entire tube length was 40 cm. and it could be weighed on a 2-kilo balance.

When ammonia was passed through a solution of triphenyl germanium bromide in an organic solvent, a precipitate was formed immediately which, upon separation and analysis, proved to be ammonium bromide.

Anal. Subs., 0.2970, 0.3959: AgBr, 0.5694, 0.7527. NH_4Br recovered, 100.14, 99.11%.

The organic residue was soluble in benzene and was crystallized therefrom and identified as triphenyl germanium oxide, m. p. 183–184° (corr.).[8]

The molecular weight of the oxide was determined in benzene at its boiling point by a modification of the Cottrell[9] method.

Mol. wt. Solvent, 32.57, 31.55; solute, 1.370, 2.197; Δt, 0.183°, 0.302°. Calcd. for $[(C_6H_5)_3Ge]_2$: mol. wt., 623.4. Found: 620.6, 622.6, mean, 621.6.

The molecular weight of the oxide in benzene appears to be normal.

On treating the bromide with liquid ammonia, some unchanged triphenyl germanium bromide was usually recovered at the end of the experiment. The amount of ammonia absorbed in the reaction, as determined by weight increase, varied from 1.72 to 1.96 moles per mole of bromide. This indicates the preliminary formation of triphenyl germanium amine, but it was found impossible to obtain both a complete reaction and an oxide-free product.

Action of Potassium Amide on Triphenyl Germanium Bromide in Liquid Ammonia.—A quantity of metallic potassium more than equivalent to the triphenyl germanium bromide to be treated was converted to potassium amide in liquid ammonia solution by means of a bit of rusty iron as a catalyst. This catalyst was removed when the reaction was complete. The ammonia was then evaporated and the reaction tube evacuated. The tube was next filled with pure dry nitrogen and triphenyl germanium bromide (1.302 g.) was introduced. This procedure was necessary, since ammonia vapor causes the bromide to cake on the walls of the reaction tube. The nitrogen was removed by means of a pump and ammonia was condensed on the materials in the tube. Reaction took place at once. It was accompanied by a decrease in the weight of the non-volatile contents of the tube amounting to 0.0605 g., which is equivalent to 1.113 moles of ammonia per mole of the original bromide used. The ammonia used in this reaction was dried by means of sodium in an auxiliary tube; the reaction tube was pre-dried by heating to 200°.

The product obtained under these conditions was completely soluble in liquid ammonia and insoluble in ether. Upon hydrolysis the product became partially soluble in petroleum ether. When ammonium bromide was added equivalent to the excess of potassium amide, a precipitate was formed in the liquid ammonia solution. After evaporating the ammonia and exhausting the reaction tube, the gain in weight in two experiments corresponded to 15.42 and 16.92 g. per mole of the original bromide, while 16.00 g. is required for the formation of the amine, $(C_6H_5)_3GeNH_2$. Evidently triphenyl germanium bromide reacts with potassium amide according to Equation 3.

The amount of free potassium amide was approximated by titrating the solution with ammonium bromide until a permanent precipitate began to appear. In two experiments the amount of potassium amide reacting with the bromide was found to be 1.842 and 1.879 moles, respectively. For the formation of the monopotassium salt two

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[8] This oxide separates from benzene in the form of characteristic crystals containing two molecules of solvent which are slowly lost upon standing in the air at ordinary temperature. The benzene may be removed readily by heating the compound to 100° in an oven.

[9] Cottrell, This Journal, **41**, 721 (1919).

moles of potassium amide is required. The method of titration is not a precise one, since it is possible that the amine is appreciably soluble in liquid ammonia.

Triphenyl Germanium Nitride.—In order to obtain the amine, or its de-ammoniation products, in a pure state, reactions were carried out in a two-legged tube, which permitted the recrystallization of the products of reaction from petroleum ether in absence of air and moisture. When the initial reaction was completed, the ammonia was evaporated, the tube exhausted and petroleum ether introduced. The organic residue, being soluble in the ether, was decanted into the second leg, after which the solvent was recondensed in the first leg and the process repeated until the organic material was completely separated from the inorganic salts. Analysis of the product indicated that the amine lost ammonia during recrystallization. Accordingly, in later experiments, the product was heated to 200° and the tube was evacuated to facilitate the loss of ammonia. Under these conditions the product sublimed to the colder parts of the tube immediately above the bath. These crystals were then analyzed for nitrogen by dissolving in warm alcohol acidified with hydrochloric acid. The resulting solution was diluted with water and separated from precipitated triphenyl germanium chloride by filtration. Sodium hydroxide was added to the filtrate to liberate the ammonia, which was distilled and titrated with standard acid.

Anal. Subs., 0.3535, 0.6040, 0.3063: cc. of 0.0999 *N* HCl, 3.78, 7.28, 3.48. Calcd. for $[(C_6H_5)_3Ge]_3N$: N, 1.98. Found: N, 1.82, 2.05, 1.93; mean, 1.94.

Action of Sodium on Triphenyl Germanium Oxide in Liquid Ammonia.—A known weight of triphenyl germanium oxide was treated with metallic sodium in liquid ammonia. The first two equivalents of sodium, which were added slowly, reacted fairly rapidly. Thereafter reaction was quite slow and the reaction mixture was left for fifteen hours with a considerable excess of metal. At the end of that time the free metal was titrated back with ammonium bromide until the blue color, due to sodium, just disappeared. The solution exhibited a yellow color and a considerable quantity of a white precipitate was present. The yellow color was doubtless due to sodium triphenyl germanide, while the precipitate was taken to be sodium triphenyl germanolate. In three experiments, 2.42, 2.60 and 2.46 equivalents of metal reacted per mole of triphenyl germanium oxide. It was inferred that reaction takes place as follows

$$[(C_6H_5)_3Ge]_2O + 2Na = (C_6H_5)_3GeNa + (C_6H_5)_3GeONa \qquad (6)$$

While the sodium is capable of breaking down readily the first of the germanium–oxygen bonds, it attacks the second only with difficulty if at all. If the second bond had been completely broken down, four atoms of sodium should have been used up in the reaction.

The values found for the amount of sodium used are somewhat higher than required according to Equation 6. It is of course possible that a slow reduction of sodium triphenyl germanolate may have occurred. On the other hand, the reaction between the solvent and the metal may have been catalyzed by the presence of the germanium compounds. In the second experiment some sodium triphenyl germanide was evidently further reduced to disodium diphenyl germanide, as was indicated by the red color of the solution. In any case the reaction must have taken place initially according to Equation 6.

On passing dry air through the ammonia solution, on the completion of the initial reaction, the solution was decolorized and the amount of precipitate was increased. This was due to the oxidation of sodium triphenyl germanide to the corresponding germanolate, a reaction which is known to occur according to Kraus and Foster.

Summary

Ammonia reacts with triphenyl germanium bromide with the formation of ammonium bromide and triphenyl germanium amine. The amine

hydrolyzes with great ease in the presence of traces of moisture and loses ammonia readily, even at ordinary temperatures, with the formation of an imine and possibly some nitride.

Triphenyl germanium bromide is immediately and quantitatively ammonolyzed by potassium amide in liquid ammonia. In the presence of excess amide, the monopotassium salt, $(C_6H_5)_3GeNHK$, is formed. The amine is re-formed from the potassium salt on the addition of ammonium bromide.

Tritriphenyl germanium nitride was prepared by heating triphenyl germanium amine to 200° *in vacuo.* It crystallizes in the form of needles melting at 163–164°. It is soluble in petroleum ether and other common organic solvents and may be sublimed *in vacuo.*

Metallic sodium reacts with triphenyl germanium oxide in liquid ammonia with the formation of sodium triphenyl germanide and sodium triphenyl germanolate.

It is pointed out that the compounds of germanium are generally more reactive than are the analogous compounds of carbon.

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THE REACTION BETWEEN ALKALI METAL ALKYLS AND QUATERNARY ARSONIUM COMPOUNDS

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In some of the early work on organic arsenic compounds Cahours[1] reported the preparation of pentamethylarsine by the action of zinc dimethyl on tetramethylarsonium iodide. The evidence for the existence of this penta-alkylarsine was slight and the work has never been confirmed. Previous attempts in this Laboratory to prepare the analogous penta-alkyl nitrogen[2] and phosphorus[3] compounds by the action of alkali metal alkyls on the corresponding -onium salts have not been successful. In view of Cahour's claim for the existence of pentamethylarsine, the work has been extended to the arsonium salts.

The methods used in the study of the reactions of alkali metal alkyls and arsonium salts were very similar to those used in the earlier work on nitrogen and phosphorus compounds. Lithium ethyl and lithium *n*-butyl were used in most of the experiments.

The first reaction studied was that between lithium *n*-butyl and tetraethylarsonium bromide. Low-boiling petroleum ether was used as a sol-

[1] Cahours, *Ann.*, **122**, 337 (1862).

[2] Hager with Marvel, THIS JOURNAL, **48**, 2689 (1926).

[3] Coffman and Marvel, *ibid.*, **51**, 3496 (1929).