[Contribution from the Chemical Laboratory of Brown University]

STUDIES RELATING TO ORGANIC GERMANIUM DERIVATIVES. IV. DIPHENYL GERMANIUM AND OCTAPHENYL GERMANOPROPANE

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I. Diphenyl Germanium

It might be expected that diphenyl germanium could be prepared by the reduction of diphenyl germanium dihalides. The reduction of the corresponding tin[1] derivatives is readily effected by means of the alkali metals in liquid ammonia. In the case of germanium, however, a corresponding reduction cannot be accomplished because of the tendency of the dihalides to ammonolyze. However, since diphenyl germanium dichloride is not ammonolyzed in ethylamine, it was thought that reduction might be effected by means of lithium in that solvent. Lithium is used in preference to sodium or potassium since it is readily soluble in ethylamine.

The reduction of diphenyl germanium dichloride in ethylamine proved impractical as will be shown below. Accordingly, the attempt was made to reduce it by means of metallic sodium in xylene. Morgan and Drew[2] have effected the reduction of the triphenyl germanium halide by this means. This method proved successful although the yields obtained were disappointingly low.

Action of Ethylamine upon Diphenyl Germanium Dichloride.—In a preceding article of this series it was shown that diphenyl germanium dichloride is completely ammonolyzed in liquid ammonia.[3] It was thought, however, that the chloride might be dissolved in ethylamine without ammonolysis. Accordingly, a weighed quantity of the dichloride was treated with ethylamine in a weighed reaction tube. On initial addition of the amine, a solid was formed which dissolved readily in an excess of the solvent. A similar result was obtained when ethylamine was passed through a solution of the dichloride in dry benzene. A precipitate was initially formed which dissolved on further addition of amine.

On removing the ethylamine after solution of the dichloride, a definite compound could not be isolated. At 90 to 100°, at low pressures, the dichloride began to distil to the colder parts of the tube, although all the amine had not been removed. The amount of amine left in the reaction product varied with the conditions of the experiment. In one instance 0.94 millimole of the dichloride retained 5.17 millimoles of amine at 20°

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[1] Kraus and Greer, This Journal, **47**, 2568 (1925).

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

[3] Kraus and Brown, This Journal, **52**, 3690 (1930).

and 38 mm. pressure. After pumping for one hour at 20°, 3.0 millimoles were retained and, after pumping for two hours at 100°, 0.43 millimole.

It was not possible to separate the initial solid in pure condition. On evaporating the solution, a liquid remained which retained amine with great tenacity and from which a solid could not be separated. The small quantity of amine retained at 100° indicates that ammonolysis does not take place.

Reduction of Diphenyl Germanium Dichloride in Ethylamine.—Since the dichloride does not ammonolyze in ethylamine, it was thought that it might be reduced to free diphenyl germanium by means of lithium in ethylamine solution. For this purpose, a weighed quantity of the dichloride was dissolved in ethylamine, cooled in a bath of liquid ammonia, and an equivalent quantity of lithium was added. The metal reacted readily with the dichloride, yielding a pale yellow solution. Only an insignificant quantity of hydrogen was evolved, which showed that the dichloride was not appreciably ammonolyzed. The solvent was evaporated and the two-legged tube was exhausted at a temperature of 100°, dry ether was condensed on the reaction product and the soluble materials were separated from the lithium chloride by decanting the supernatant liquid into the second leg of the reaction tube. After removing the ether, the tube was exhausted at 100° and finally at 200°. The product left in the second leg of the tube was a resinous material which could not be crystallized. Crystals of lithium chloride remained in the first leg.

It was hoped that reaction would occur according to the equation

$$(C_6H_5)_2GeCl_2 + 2Li = (C_6H_5)_2Ge + 2LiCl$$

In spite of the high temperature at which the tube was exhausted, the weight of the reaction tube and its contents indicated the presence of ethylamine. In four experiments the amount of ethylamine retained varied from 0.14 to 0.39 mole of amine per mole of dichloride. Analysis of the resinous product obtained in different reactions gave a germanium content varying from 29.2 to 31.2%. The germanium content of diphenyl germanium is 32.03%. It is evident that the product consisted largely of diphenyl germanium contaminated by some ethylamine and probably some other substances. It has since been found that certain of the metallo-organic free groups are capable of forming stable compounds with ethylamine. Thus Eatough[4] has shown that triphenyl silicon forms a compound $(C_6H_5)_3Si \cdot C_2H_5NH_2$. It is not improbable that ethylamine is retained in combination with the diphenyl germanium group and that the crystalline product cannot be obtained for this reason.

Reduction of Diphenyl Germanium Dichloride in Xylene.—Morgan and Drew[2] reduced triphenyl germanium halides by means of sodium in boiling xylene. It was thought that diphenyl germanium dichloride might be reduced according to the same method. The reduction was carried out in a 100-cc. flask with a long neck which was provided with a condenser jacket. An atmosphere of nitrogen was maintained in the flask throughout the process of reduction. The xylene used was digested with metallic sodium for a considerable period of time and was distilled directly into the reduction

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[4] Eatough, Thesis, Brown University, 1929.

flask under an atmosphere of nitrogen. Three grams of diphenyl germanium dichloride was added to 30 cc. of xylene, followed by thin slices of sodium freshly cut under xylene. The mixture was boiled for six hours and fresh sodium was added from time to time to insure the presence of a fresh metallic surface. As reduction proceeded, the solution took on a red color which gave way to yellow. At the end of the process, only a faint yellow color remained. The solution was rapidly decanted and filtered hot and the brown residue left behind in the flask was washed several times with boiling xylene. On cooling the xylene solution, a small quantity of white crystals separated. These were thrown on a filter, while the filtrate was concentrated. Only a small quantity of crystalline material was obtained on further concentration. When the solvent was completely removed, a viscous yellow liquid remained which, on cooling, solidified to a resinous substance that could be chipped and ground to a powder. Attempts to crystallize this material from benzene, chloroform and xylene yielded only minute quantities of solid. The crystalline product amounted to from 10 to 20% of the theoretical yield. This was analyzed for germanium by the usual methods.

Anal. Subs., 0.1098, 0.0693: GeO_2, 0.0507, 0.0319. Calcd. for $(C_6H_5)_2Ge$: Ge, 32.03. Found: Ge, 32.05, 31.95; mean, 32.00.

The molecular weight of the crystalline product was determined in benzene by the boiling point method, using a modified Cottrell apparatus.

Mol. wt. Solvent, 13.18; solute, 0.5476, 0.7590; Δt 0.123, 0.170°; mol. wt. found, 902, 904; mean, 903.

The molecular weight of diphenyl germanium is 226.7. If four molecules of diphenyl germanium were polymerized, the molecular weight would be 907, which value is in close agreement with that found.

Properties of Diphenyl Germanium.—The crystalline material is readily soluble in benzene so long as the original yellow resin is present but, once separated from this resin, it is only slightly soluble in cold benzene, toluene or chloroform. Its solubility in hot solvents is limited and it is insoluble in petroleum ether. On slow crystallization from benzene, fine white crystals were obtained melting at 294–295° (corr.). These crystals undergo no change on exposure to the atmosphere.

The Resinous Reduction Product.—Analyses of the resinous material varied, depending upon the sample. The germanium content was found to range from 29.6 to 30.4% as against 32.03% for pure diphenyl germanium. The molecular weight of the resinous material, as determined in benzene by the cryoscopic method, was found to be 900 and 930 in two determinations, respectively.

The analyses and the molecular weight determinations indicate that the resin is an impure polymer. In many respects it resembles the product of reduction in ethylamine. No crystals could be obtained from this resinous material although numerous solvents were tried under varying conditions.

Disodium Diphenyl Germanide.—Disodium diphenyl germanide is readily prepared by treating diphenyl germanium with an equivalent quantity of sodium in liquid ammonia. For this purpose a reaction tube is used of the type outlined in the accompanying figure. The diphenyl germanium is introduced into the reaction tube A. The top of this tube is provided with a ground joint B which carries a stirring tube C that reaches to the bottom of the reaction tube. The stirring tube is provided with a stopcock D. The neck of the reaction tube is provided with a second stopcock E. The tubes F and G are connected with the system by means of de Khotinsky cement. The system makes connection with a source of pure ammonia, a manometer, a vacuum pump and with an adjustable mercury trap. The reaction tube is provided with a side arm J which carries a tube K, the end of which projects into the side arm and is fitted to J by means of a ground joint L. The sodium which is to be used in reducing the diphenyl germanium is weighed out under Nujol, washed with petroleum ether and introduced into tube K, which is then inserted into the ground joint. The reaction tube is then evacuated.

The reaction tube A is now surrounded by a bath of boiling ammonia and ammonia vapor is introduced through the stopcock D under a pressure about 20 cm. above that of the atmosphere. This pressure is regulated by the height of mercury in the mercury trap. When a sufficient quantity of ammonia has been condensed in the reaction tube, stopcock E is closed and, by turning the tube K about its axis in the ground joint, sodium is introduced into the reaction tube piece by piece.

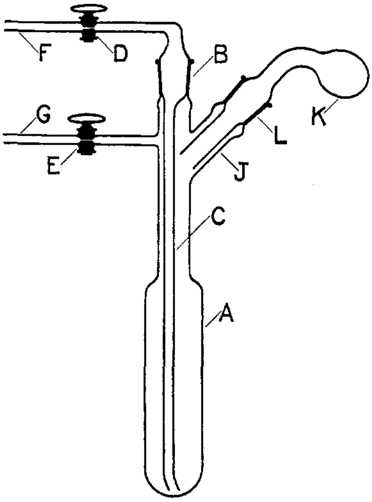

Fig. 1.—Reaction tube.

The sodium goes into a solution and reacts readily with the diphenyl germanium. The blue color, characteristic of the free metal, disappears and a yellow color replaces it. The reaction takes place in two steps, in which respect it resembles the corresponding reaction of dimethyl tin described by Kraus and Greer.[1] On the initial addition of sodium, the solution exhibits a yellow color and, when approximately one-half the equivalent amount of sodium has been added, the diphenyl germanium has been completely dissolved. This stage of the process corresponds to the formation of disodium tetraphenyl germanoethane. On further addition of sodium, the germanium bond is broken and disodium diphenyl germanide is formed. The latter compound is also soluble in liquid ammonia and imparts a deep red color to the solution. At higher concentrations the solutions are almost opaque.

Attempts were made to prepare a diphenyl germane by treating the solution of disodium diphenyl germanide with ammonium bromide. While in certain experiments evidence was found that the dihydride may have been formed initially, the compound could not be isolated. Seemingly, hydrogen is lost and more complex derivatives are formed. The final product was in all cases a viscous liquid.

II. Octaphenyl Germanopropane

Octaphenyl germanopropane could doubtless be prepared by treating disodium diphenyl germanide with triphenyl germanium halide in ammonia or other solvents. However, in view of the difficulty of preparing diphenyl germanium, it seemed preferable to prepare the germanopropane by treating sodium triphenyl germanide with diphenyl germanium dihalide in a suitable solvent. Reaction takes place according to the equation

$$2(C_6H_5)_3GeNa + (C_6H_5)_2GeCl_2 = 2NaCl + (C_6H_5)_8Ge_3$$

Preparation.—Sodium triphenyl germanide was prepared by adding 0.1437 g. (5.876 m. atoms) of sodium to 1.779 g. (2.93 m. moles) of hexaphenyl germano-ethane in liquid ammonia. The ammonia was allowed to evaporate and the tube containing the product was evacuated for twelve hours. The yellow color of the sodium salt gave way to white as the residual ammonia was removed. Dry benzene was then distilled onto the sodium triphenyl germanide, the tube was filled with nitrogen and 0.873 g. (2.93 m. moles) of diphenyl germanium dichloride was added. The reaction mixture was heated with occasional shaking for eight hours. The contents of the tube were then rapidly filtered and most of the solvent was removed by distillation. On cooling, a small crop of crystals appeared. These were separated by filtration and, by their melting point, identified as hexaphenyl germano-ethane. On further concentration of the filtrate, a second crop of crystals was obtained in the form of large flakes. These were removed, washed with cold chloroform and recrystallized from that solvent prior to analysis. On further evaporation of the original solution, a viscous liquid was left behind.

Anal. Subs., 0.1354, 0.2023: GeO_2, 0.0506, 0.0762. Calcd. for $Ge_3(C_6H_5)_8$: Ge, 26.11. Found: Ge, 25.94, 26.14; mean, 26.04.

The molecular weight of the germanopropane was determined in benzene by the boiling point method.

Mol. wt. Solvent, 16.05, 15.67; solute, 0.7071, 0.9811; Δt, 0.135°, 0.195°; mol. wt. found, 871, 875; mean, 864; calcd. for $Ge_3(C_6H_5)_8$: 834.

Properties.—Octaphenyl germanopropane is stable toward air and moisture. On rapid crystallization from chloroform, a fine white crystalline powder is obtained, while on slow crystallization plate-like crystals are formed. The compound is readily soluble in warm benzene and chloroform. It melts at 247–248° (corr.).

Action of Bromine on Octaphenyl Germanopropane.—As a further check on the structure of the germanopropane and in order to test the resistance of the Ge–Ge bond toward bromine, the compound was treated with bromine in carbon tetrachloride. Reaction took place at ordinary temperatures, the intensity of the color due to bromine gradually diminishing until, at the end of eighteen hours, the solution was but faintly yellow. This color disappeared entirely on warming the solution. On evaporation of the solvent, a crystalline mass resulted in which traces of a viscous liquid were present. The reaction product was extracted with petroleum ether and upon evaporation crystals were obtained that melted at 138°. This corresponds to the melting point of triphenyl germanium bromide. A small quantity of a viscous liquid was also obtained and, when this was treated with a drop of water, a white film was formed. This is characteristic of diphenyl germanium dibromide, the white film being due to the oxide formed on hydrolysis. The remainder of the crystalline product was unchanged octaphenyl germanopropane. It is evident that the Ge–Ge bond is less stable toward bromine than is the phenyl germanium bond. On bromination in carbon tetrachloride, the Ge–Ge linkage is broken down.

Summary

Diphenyl germanium dichloride is not ammonolyzed in ethylamine. The reduction of diphenyl germanium dihalide by means of lithium in ethylamine proved unsuccessful. The reduction product was a resinous material whose composition approximated that of diphenyl germanium but which could not be purified.

Diphenyl germanium, in crystalline form, was obtained by the reduction of diphenyl germanium dichloride by means of sodium in xylene. The yields were small, the greater proportion of the product consisting of a resinous material resembling that obtained on reduction in ethylamine.

Disodium diphenyl germanide was prepared by the action of sodium on diphenyl germanium in liquid ammonia.

Octaphenyl germanopropane was prepared by the action of sodium triphenyl germanide on diphenyl germanium dichloride in benzene solution.

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