

hydrogenation of a variety of organic compounds as summarized in the paragraphs in "Other Hydrogenations" and in Table IV.

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## ALIPHATIC GERMANIUM DERIVATIVES. II. DIETHYLDIPHENYLGERMANE, DIETHYLGERMANIUM OXIDE AND DIETHYLGERMANIUM DIBROMIDE

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### I. Introduction

A study of the triphenyl,<sup>1,2</sup> diphenyl<sup>1,3</sup> and triethylgermanium<sup>4</sup> compounds has revealed some interesting contrasts in the chemistries of these little known amphoteric groups. Continuing the study of this class of substances some diethylgermanium derivatives have been isolated and some of their properties determined. It has been found convenient in previous work to use the halide of the group under investigation as the source of subsequent derivatives. Accordingly, the first objective in this research was the preparation and study of diethylgermanium dibromide. The most satisfactory method of preparing this compound involved bromination of triethylgermanium fluoride,<sup>4</sup> hydrolysis of the product and conversion of the resulting diethylgermanium oxide, after purification, into the corresponding bromide.

Diphenylgermanium dibromide can be prepared by the action of bromine on tetraphenylgermane<sup>5</sup> and while it might be expected that diethylgermanium dibromide,  $(C_2H_5)_2GeBr_2$ , could be prepared by the analogous reaction of bromine on tetraethylgermane, this has not been found feasible. All attempts to substitute a second bromine atom for an ethyl group in triethylgermanium bromide by the direct action of bromine gave complex mixtures from which only very low yields of diethylgermanium dibromide could be obtained.

Some preliminary experiments indicated that diethylgermanium dibromide can be prepared by an indirect method starting with diphenylgermanium dibromide. The diphenylgermanium dihalide was treated with ethylmagnesium bromide and the resulting diphenyldiethylgermane on bromination gave impure diethylgermanium dibromide.

<sup>1</sup> Morgan and Drew, *J. Chem. Soc.*, **127**, 1760 (1927).

<sup>2</sup> Kraus and Foster, *THIS JOURNAL*, **49**, 457 (1927).

<sup>3</sup> Kraus and Brown, *ibid.*, **52**, 3690 (1930).

<sup>4</sup> Kraus and Flood, *ibid.*, **54**, 1635 (1932).

<sup>5</sup> Kraus and Brown, *ibid.*, **52**, 3690 (1930).  $(C_6H_5)_2GeBr_2$  was obtained by Morgan and Drew<sup>1</sup> from the reaction of  $GeBr_4$  with  $C_6H_5MgBr$ . Partial ethylation of  $GeBr_4$  by  $C_2H_5MgBr$  yields  $(C_2H_5)_3GeBr$  but little or no  $(C_2H_5)_2GeBr_2$ .<sup>4</sup>

Since diphenyldiethylgermane has hitherto not been described in the literature its preparation and properties will be discussed briefly.

## II. Diphenyldiethylgermane, $(C_6H_5)_2Ge(C_2H_5)_2$

When trimethylphenylstannane is treated with bromine the phenyl group is substituted preferentially.<sup>6</sup> It seemed probable, therefore, that similar preferential substitution would occur in the case of diphenyldiethylgermane, yielding diethylgermanium dibromide and phenyl bromide. Accordingly diphenyldiethylgermane was prepared and brominated. The experimental details appear in the following paragraphs.

**Preparation.**—Diphenyldiethylgermane was prepared by means of the Grignard reaction, using diphenylgermanium dibromide and ethylmagnesium bromide. The yield obtained was about 95% of the theoretical.

A solution of 11.7 g. of diphenylgermanium dibromide in 50 cc. of ether was slowly added to 200 cc. of an ether solution of ethylmagnesium bromide equivalent to 10 g. of ethyl bromide. During the reaction the mixture was cooled by means of an ice-bath and vigorously stirred. The mixture was heated to boiling for a period of three hours, after which the ether was removed by distillation and the residual mass heated to a temperature of 110° for three hours. After cooling the mixture the excess Grignard reagent was hydrolyzed and the product extracted with ether. The extract was dried over calcium chloride, the ether removed and the residual liquid subjected to vacuum distillation; 8.3 g. of a colorless liquid boiling at 316° (uncorr.) under atmospheric pressure was obtained corresponding to a yield of 96%. The product was further purified by slow fractional distillation and the purity of the product which distilled between 315–317° (uncorr.) tested by analysis. Analyses were carried out by a modified Krause method.<sup>4,7</sup>

*Anal.* Subs., 0.3495, 0.2364:  $GeO_2$ , 0.1288, 0.0869. Calcd. for  $(C_6H_5)_2Ge(C_2H_5)_2$ : Ge, 25.50. Found: Ge, 25.58, 25.51, mean, 25.55.

**Properties.**—Diphenyldiethylgermane is a colorless liquid having a rather pleasant odor and boiling at 316° (uncorr.) at atmospheric pressure. It is insoluble in water but miscible with organic solvents. This compound is quite stable toward air and moisture and may be boiled in air without appreciable decomposition; however, it reacts readily with bromine in ethylene dibromide solution.

**Bromination.**—A solution of 1.44 g. of diphenyldiethylgermane in 5 cc. of ethylene dibromide was treated with successive portions of a solution of bromine in ethylene dibromide containing 0.76 g. of bromine per cc. of solution. In all 1.62 g. of bromine was added. The first half of the bromine reacted readily in the cold while the second half was consumed only after heating to 100° for twelve hours. On completion of the reaction, the mixture was fractionally distilled, three distinct fractions being obtained. The first was identified as ethylene dibromide, a small second fraction was found to be largely phenyl bromide and the third, amounting to 1.3 g. which was collected between 199–205° consisted of diethylgermanium dibromide,  $(C_2H_5)_2GeBr_2$  (b. p. 202°).

The chief products of brominating diphenyldiethylgermane were those anticipated, thus indicating a method of preparing diethylgermanium dibromide. However, a more direct method of preparation was developed starting with triethylgermanium derivatives rather than the phenyl compound.

<sup>6</sup> Bullard and Robinson, *THIS JOURNAL*, 49, 1368 (1927).

<sup>7</sup> Krause, *Ber.*, 55, 896 (1922).

The above experiment suggests that the regularities previously observed on the bromination of alkyl-aryl-tin<sup>8</sup> compounds may apply to the corresponding germanium derivatives.

### III. Diethylgermanium Oxide, $(C_2H_5)_2GeO$

An experiment on the relative rates of reaction of bromine with triethylgermanium fluoride, chloride and bromide, showed that reaction occurred about six times more rapidly with the fluoride than with the chloride and with the chloride, in turn, six times more rapidly than with the bromide. Moreover, it was observed that while the reaction of bromine with triethylgermanium bromide yielded considerable quantities of hydrogen bromide, no detectable hydrogen bromide was evolved when the fluoride was brominated under similar conditions. These observations led to a satisfactory method of preparing diethylgermanium derivatives, wherein triethylgermanium fluoride was brominated and the crude diethylgermanium dihalides converted, by hydrolysis, into diethylgermanium oxide. It may be pointed out that a good deal of difficulty was at first encountered in obtaining a pure product because of the proximity of the boiling points of the various ethylgermanium halides and the apparent lack of definite physical properties of diethylgermanium oxide. The peculiar properties of the oxide were found to be due to polymerization and, taking advantage of these properties, a very convenient method of purification was developed.

**Bromination of Triethylgermanium Fluoride,  $(C_2H_5)_3GeF$ .**—Triethylgermanium fluoride was treated first with a concentrated solution of bromine in ethyl bromide and subsequently with two portions of pure bromine, the bromine additions being made after the previously added bromine had been consumed. In all about 5% excess of one mole of bromine per mole of fluoride was used. The bromination was carried out at a temperature of 50° except during the final stage of the reaction, when the mixture was heated to boiling. Carefully dried materials were used and precautions taken to exclude moisture during the reaction, which extended over a period of about three days. When reaction was judged to be complete, the mixture was hydrolyzed by heating with an aqueous solution of sodium hydroxide. The hydrolyzed product was extracted with ether and the ethereal solution dried over anhydrous sodium sulfate.

When the residual aqueous solution was acidified, a relatively small quantity of a white solid was precipitated. Analysis of this substance for germanium indicated impure ethylgermanic acid (calcd. for  $C_2H_5GeOOH$ : Ge, 53.9; found: Ge, 55.6).

Fractional distillation of the ethereal extract yielded a high boiling liquid—collected in three consecutive portions—which distilled in the vicinity of 285° but gave little indication of a definite boiling point. The three samples obtained were liquid and of a bluish "fluorescent" color. After standing for four hours the first solidified to a white mass. The other two samples remained liquid after standing several days; however, when a trace of water was added, they also solidified within a few hours.

The solidified product was found to be insoluble in ether and consequently the three solid samples were combined, pulverized and the soluble impurities extracted with ether in a Soxhlet extractor. Since the product had been extracted previously from the

<sup>8</sup> Bullard, *THIS JOURNAL*, 51, 3065 (1929).

hydrolyzing solution with ether, ether-insoluble impurities were largely absent. The insoluble residue was distilled at a temperature of  $160^{\circ}$  under a pressure of 0.01 mm. A crystalline product was obtained which melted sharply at  $18^{\circ}$ . After standing for twelve hours in a sealed tube the product had changed into a white amorphous solid melting at about  $175^{\circ}$  when heated rapidly, but which liquefied slowly when maintained at a temperature of  $120^{\circ}$ . The liquid yielded crystals melting at  $19^{\circ}$  but solidified again on standing at room temperature.

This material was shown by analysis to be diethylgermanium oxide. The first sample used for analysis was of the liquid form, the second was taken shortly after solidification, the third a solid sample which had been exposed to the air for nine days and the fourth a sample from another preparation which had been exposed for several weeks.

*Anal.* Subs., 0.1809, 0.2471, 0.2383, 0.0921:  $\text{GeO}_2$ , 0.1288, 0.1766, 0.1704, 0.0658. Calcd. for  $(\text{C}_2\text{H}_5)_2\text{GeO}$ : Ge, 49.49. Found: Ge, 49.42, 49.60, 49.63, 49.59.

**Properties of Diethylgermanium Oxide.**—Diethylgermanium oxide exists in two polymeric forms. At room temperature the stable form is a white amorphous solid melting at about  $175^{\circ}$  when heated rapidly. It is insoluble in organic solvents, water and liquid ammonia. The oxide also exists in an unstable liquid form which crystallizes at  $18^{\circ}$  (approx.). In this form diethylgermanium oxide is soluble in organic solvents, but insoluble in water and in liquid ammonia.

That the unstable, soluble form is trimolecular is shown by the following data: mol. wt. (cryoscopic method). Subs., 0.3221, 1.1437;  $\text{C}_6\text{H}_6$ , 16.226, 16.226;  $\Delta t$ , 0.218, 0.758. Calcd. for  $[(\text{C}_2\text{H}_5)_2\text{GeO}]_3$ : mol. wt., 440. Found: mol. wt., 455, 465, mean, 460.

Transformation of the liquid to the solid form at room temperature occurs within a few hours and is accelerated by the presence of a trace of water while transition between the two forms occurs in the vicinity of  $110^{\circ}$ .

When treated with a concentrated aqueous solution of halogen acid, diethylgermanium oxide is converted to the corresponding diethylgermanium dihalide. The oxide reacts readily, with lithium in ethylamine solution but is fairly stable toward oxidation, no sign of decomposition occurring when it is heated to  $290^{\circ}$  in air.

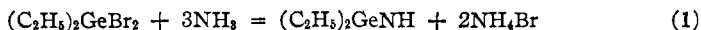
#### IV. Diethylgermanium Dibromide, $(\text{C}_2\text{H}_5)_2\text{GeBr}_2$

**Preparation.**—Diethylgermanium dibromide was prepared by shaking pure diethylgermanium oxide with a concentrated aqueous solution of hydrobromic acid. After allowing the mixture to stand overnight the resulting diethylgermanium dibromide was extracted with petroleum ether, the petrol solution dried over calcium chloride and finally fractionally distilled. The fraction which distilled between the thermometer readings  $201.5$ – $202^{\circ}$  was subjected to vacuum distillation and the final product analyzed for germanium and bromine. The germanium in the compound was determined as germanium oxide by the usual modified Krause method while the bromine was determined by hydrolyzing the sample with an aqueous solution of sodium hydroxide, filtering the mixture and determining the bromine in the aqueous filtrate as silver bromide.

*Anal.* Subs., 0.3168, 0.2342:  $\text{AgBr}$ , 0.4089, 0.3029. Calcd. for  $(\text{C}_2\text{H}_5)_2\text{GeBr}_2$ : Br, 55.02. Found: Br, 54.93, 55.04, mean, 54.99. Subs., 0.2651, 0.2142:  $\text{GeO}_2$ , 0.0954, 0.0770. Calcd.: Ge, 24.99. Found: Ge, 24.98, 24.95, mean, 24.97.

**Properties.**—Diethylgermanium dibromide is a colorless liquid having a sharp odor, suggestive of hydrogen chloride. It boils at  $202^{\circ}$  (uncorr.) under atmospheric pressure but fails to solidify when cooled to  $-33^{\circ}$ . When treated with water or aqueous alkaline solutions the bromide is hydrolyzed, forming diethylgermanium oxide. Similarly, with liquid ammonia ammonolysis occurs, as will be shown below, yielding diethylgermanium imine,  $(\text{C}_2\text{H}_5)_2\text{GeNH}$ .

**Ammonolysis of Diethylgermanium Dibromide.**—Preliminary experiments, in which weighed samples of diethylgermanium dibromide were treated with ammonia, indicated that three molecules of ammonia enter into reaction with one molecule of the dibromide, thus suggesting that ammonolysis occurs according to the equation



The results were confirmed by isolating the amino derivative and determining its composition.

A sample of the dibromide was placed in a special reaction tube, designed to permit adequate stirring of the reaction mixture and equipped also with a side vessel into which the product of the reaction could be distilled and the distillate collected in fragile glass bulbs. Liquid ammonia was condensed into the reaction tube and the mixture stirred vigorously during several hours. On addition of sodium, a vigorous reaction ensued with evolution of hydrogen, indicating the presence of ammonium bromide formed by ammonolysis. Reaction was complete after three days when a permanent blue color, due to excess sodium, was obtained. The excess ammonia was now removed and the product distilled into the collecting chamber containing the fragile bulbs, the distillation being carried out under a pressure of 0.01 mm. The bulbs were filled with the distillate and sealed in an atmosphere of dry nitrogen.

The product was analyzed for nitrogen by breaking a bulb, containing a weighed sample of the amino derivative, under a known volume of dilute standard acid and allowing the well shaken mixture to stand overnight. Titrating the excess acid with standardized sodium hydroxide solution gave indirectly the ammonia formed by hydrolysis of the amino derivative.

*Anal.* Subs., 0.1170, 0.1033: cc. of 0.07044 *N* HCl, 11.12, 9.97. Calcd. for  $(\text{C}_2\text{H}_5)_2\text{GeNH}$ : N, 9.61. Found: N, 9.38, 9.52, mean, 9.45.

Analyses indicate that the product is diethylgermanium imine, thus establishing equation (1).

**Properties of Diethylgermanium Imine**  $(\text{C}_2\text{H}_5)_2\text{GeNH}$ .—Diethylgermanium imine is a colorless liquid which distils when heated to 100° under a pressure of 0.01 mm. It hydrolyzes very easily, being decomposed rapidly on exposure to air, with the liberation of ammonia and the formation of diethylgermanium oxide. A molecular weight determination gave 394, while that calculated for  $(\text{C}_2\text{H}_5)_2\text{GeNH}$  is 146, indicating that the imine is polymerized.

## V. Summary

1. Diphenyldiethylgermane was prepared by means of a Grignard reaction, using diphenylgermanium dibromide and ethylmagnesium bromide.

2. Bromination of diphenyldiethylgermane was shown to yield diethylgermanium dibromide and phenyl bromide.

3. Triethylgermanium fluoride was brominated leading to the preparation of diethylgermanium oxide and diethylgermanium dibromide.

4. Diethylgermanium oxide was found to exist in two polymeric forms.

5. The ammonolysis of diethylgermanium dibromide was studied and diethylgermanium imine isolated.