[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF BROWN UNIVERSITY]

Preparation of Some Derivatives of Triphenylgermanium by Means of Sodium Triphenylgermanide

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Two general methods are available for coupling organic groups to atoms of amphoteric elements. The first, and most common, is to treat a halogen derivative of the element in question with the Grignard reagent containing the organic group. The second method, which, incidentally, was the method originally employed in the preparation of metallo-organic compounds, is to treat an alkali-metal alloy of the amphoteric element with a halide of the desired organic group. Thus tetraethyllead may conveniently be prepared either by treating lead chloride with ethylmagnesium bromide or by treating a sodium–lead alloy with ethyl bromide. In making organic derivatives of fourth group elements containing a number of different organic groups, two methods are similarly available. Thus, triphenylethylgermanium has been prepared by the action of ethylmagnesium bromide on triphenylgermanium bromide[2] and by the action of ethyl bromide on sodium triphenylgermanide.[3] In both cases the coupling occurs as a result of the splitting off of bromine as bromide. The Grignard reagent is ordinarily the more convenient, but the second method, if it is applicable, generally gives the better yields, in fact it is usually quantitative. In some syntheses the second method is applicable when the first is not. This is particularly true of reactions in which atoms of amphoteric elements are to be coupled to one another. Thus, Kraus and Greer[4] have built up chains containing as many as five tin atoms.

The second method becomes more difficult of application as the atomic number of the amphoteric element diminishes. In the case of silicon, it is not ordinarily possible to prepare the necessary sodium compounds.[5] In the case of the triphenylgermanium group, the salt $NaGe(C_6H_5)_3$ is readily prepared in liquid ammonia solution and reactions with many organic halides take place readily and often quantitatively.[6] We have prepared a number of mono-alkyl triphenylgermanes and have coupled the triphenylgermanium and triethylgermanium groups to form the mixed digermane according to the reaction equation

$$(C_6H_5)_3GeNa + (C_2H_5)_3GeBr = (C_6H_5)_3Ge—Ge(C_2H_5)_3 + NaBr \qquad (1)$$

Experimental

The apparatus and procedure employed is much the same as that of Kraus and Nutting.[6] Triphenylgermanium (hexaphenyldigermane) is treated with an equivalent

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[1] Rice Fellow in Chemistry at Brown University.

[2] Orndorff, Tabern and Dennis, THIS JOURNAL, **49**, 2512 (1927).

[3] Kraus and Nutting, *ibid.*, **54**, 1622 (1932).

[4] Kraus and Greer, *ibid.*, **47**, 2568 (1925).

[5] Walter K. Nelson, Thesis, Brown University, 1930.

[6] Kraus and Nutting, THIS JOURNAL, **54**, 1622 (1932).

amount of sodium in liquid ammonia and the organic halide is added, usually in slight excess. It is necessary to exclude oxygen since sodium triphenylgermanide is readily oxidized. When the reaction is completed, the ammonia is evaporated and the residue is extracted with a suitable solvent.

n-**Propyltriphenylgermanium.**—Approximately 4.5 g. of triphenylgermanium was converted to the sodium salt in liquid ammonia and a slight excess of *n*-propyl bromide was added by means of a stream of ammonia vapor as described by Kraus and Nutting. The end-point of the reaction was indicated by the disappearance of the yellow color characteristic of the sodium salt. After evaporating the ammonia, the contents of the tube were treated with boiling water. The sodium bromide dissolved while the *n*-propyltriphenylgermanium melted and collected as a liquid in the bottom of the tube. The material, when cold, was thrown on a filter and, after drying in air, was extracted with isopropyl alcohol. After concentrating the alcohol solution, needle crystals of *n*-propyltriphenylgermanium were obtained, melting at 85.5–86.5°. A sample of the material, dissolved in chloroform and precipitated by addition of methyl alcohol, melted at 86.0–86.5°. Another sample, sublimed *in vacuo* at 100°, also melted at 86.0–86.5°.

The compound was analyzed for germanium according to the method commonly employed in this Laboratory by oxidizing with fuming sulfuric and nitric acids. The precautions pointed out by Kraus and Flood[7] were found very helpful.

Anal. Subs., 0.2122, 0.2630: GeO_2, 0.0645, 0.0798. Calcd. for $C_3H_7Ge(C_6H_5)_3$: Ge, 20.96. Ge found: Ge, 21.09, 21.06.

n-Propyltriphenylgermanium is very soluble in chloroform, benzene, petroleum ether, and trichloroethylene. It is slightly soluble in isopropyl alcohol and almost insoluble in methyl alcohol. It is insoluble in liquid ammonia and does not react with sodium in that solvent.

n-**Butyltriphenylgermanium.**—Approximately 1.2 g. of triphenylgermanium was reduced to the sodium salt and then treated with *n*-butyl bromide. After evaporating the ammonia, the product was treated with boiling water, the resulting material was filtered and dried in a vacuum desiccator over phosphorus pentoxide. The product was finally extracted with isopropyl alcohol and recrystallized from the same solvent, m. p. 84.5–85.5°.

Anal. Subs., 0.3216, 0.2534: GeO_2, 0.0939, 0.0742. Calcd. for $C_4H_9Ge(C_6H_5)_3$: Ge, 20.15. Ge found: Ge, 20.26, 20.32.

n-Butyltriphenylgermanium is very soluble in petroleum ether, benzene, chloroform, trichloroethylene and ether. It is slightly soluble in isopropyl alcohol and practically insoluble in methyl alcohol. From isopropyl alcohol, it crystallizes in the form of long, colorless needles.

n-**Amyltriphenylgermanium.**—Sodium triphenylgermanide was treated with *n*-amyl bromide as in the previous preparation. After evaporating the ammonia and treating with boiling water, an oily liquid was obtained which solidified only on cooling with a salt–ice mixture. The solution was filtered cold and the mass on the filter paper was dried in a vacuum desiccator over phosphorus pentoxide. It was extracted with isopropyl alcohol. On evaporating the alcohol, an oil separated which crystallized on standing overnight. The material was purified by sublimation at 90°, the condensing surface being cooled by boiling ammonia; m. p. 42–43°.

Anal. Subs., 0.3519, 0.1905: GeO_2, 0.0989, 0.0535. Calcd. for $C_5H_{11}Ge(C_6H_5)_3$: Ge, 19.38. Ge found: Ge, 19.50, 19.49.

n-Amyltriphenylgermanium is exceedingly soluble in benzene, isopropyl alcohol, petroleum ether and trichloroethylene, and fairly soluble in methyl alcohol, from which

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(7) Kraus and Flood, THIS JOURNAL, **54**, 1637 (1932).

solvent it separates in the form of soft, plate-like crystals which are colorless and odorless. It is best recrystallized from that solvent and is most readily purified by sublimation *in vacuo*.

Benzyltriphenylgermanium.—Sodium triphenylgermanide was treated with benzyl chloride, the benzyl chloride being added to the ammonia solution of the salt by means of a special funnel. This procedure was necessary because benzyl chloride ammonolyzes very readily. After evaporating the ammonia, the product was treated with boiling water and the oil which separated was allowed to solidify, after which it was thrown on a filter, dried, and extracted with isopropyl alcohol. It was recrystallized from the same solvent. From a cool solution it slowly crystallized in the form of long, thin, plate-like crystals, m. p. 82.5–83.5°.

Anal. Subs., 0.2103, 0.2185: GeO_2, 0.0558, 0.0580. Calcd. for $C_6H_5CH_2Ge(C_6H_5)_3$: Ge, 18.39. Ge found: Ge, 18.41, 18.42.

Benzyltriphenylgermanium is very soluble in benzene, petroleum ether and chloroform. It is sparingly soluble in isopropyl alcohol and almost insoluble in methyl alcohol. It is best recrystallized from a 50–50 mixture of isopropyl and methyl alcohols.

Triphenylgermanyltriethylgermanium.—This compound was prepared according to reaction (1). This reaction cannot be carried out in liquid ammonia because triethylgermanium bromide is ammonolyzed in that solvent. The reaction may, however, be carried out in a neutral solvent such as benzene in which sodium triphenylgermanide is slightly soluble. The sodium triphenylgermanide is prepared in the usual way in liquid ammonia.

Approximately 1.8 g. of triphenylgermanium was treated with an equivalent quantity of sodium in liquid ammonia. After evaporating the ammonia, the tube was exhausted at room temperature for thirty-six hours, when the pressure had fallen to 0.01 mm. About 20 cc. of dry benzene was distilled into the reaction tube and a slight excess of triethylgermanium bromide was added from a pipet.

The color of the benzene solution, which was originally a deep brown, lightened as reaction proceeded. The tube was allowed to stand for three hours, being shaken at intervals in order to mix the contents. The tube was then heated to the boiling point and the contents thrown on a filter while hot. The benzene solution was concentrated and, upon cooling, fine crystals separated. The last traces of benzene were removed under diminished pressure and the crystals thus obtained were washed with methyl alcohol. The material was then crystallized from absolute ethyl alcohol. From this solvent, fairly large and definite rhombic crystals were obtained which, after several recrystallizations, retained only a trace of brown color. They had the odor characteristic of triethylgermanium compounds.

Anal. Subs., 0.3001, 0.2946: GeO_2, 0.1350, 0.1330. Calcd. for $(C_6H_5)_3Ge\text{-}Ge(C_2H_5)_3$: Ge, 31.34. Found: Ge, 31.22, 31.33.

Triphenylgermanyltriethylgermanium is extremely soluble in benzene and chloroform. It is soluble in trichloroethylene, petroleum ether, ethyl alcohol and isopropyl alcohol and sparingly soluble in methyl alcohol. It is best recrystallized from absolute ethyl alcohol from which it separates in the form of well-defined rhombic crystals. It melts at 89.5–90.5° and is stable in air. On crystallization from benzene, the compound retains benzene of crystallization.

Summary

n-Propyl-, *n*-butyl-, *n*-amyl- and benzyltriphenylgermanium have been prepared by the action of the corresponding alkyl halides on sodium triphenylgermanide in liquid ammonia solution.

Triphenylgermanyltriethylgermanium, $(C_6H_5)_3Ge-Ge(C_2H_5)_3$, has been prepared by the action of triethylgermanium bromide on sodium triphenylgermanide in benzene solution.

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The Reactivity of Atoms and Groups in Organic Compounds. XIV. The Influence of Substituents on the Thermal Stability of Certain Derivatives of Malonic Acid

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It has been shown in this Laboratory[2] that the substitution products of malonic acid begin to lose carbon dioxide at different temperatures and that there is a relationship between these temperatures and the radicals present in the acids. The results indicated the relative effects of the several radicals on the lability toward heat of a carbon to carbon bond in compounds of this type. Other investigations have shown that the rates vary at which these acids decompose in solutions at a fixed temperature and with change of solvent.[3,4,5,6] Hinshelwood[7] has studied the effect of temperature on the rate at which solid malonic acid decomposes.

As it seemed probable that an extension of the work would lead to results of value in interpreting pyrolytic reactions in general, a large number of compounds were studied.

Some time after the appearance of the paper by Norris and Young and when further work was in progress in this Laboratory, Marshall[8] reported a repetition, with slightly modified apparatus, of the published work and the results obtained by him in the study of some additional compounds. With the exception of two acids, which will be considered later in this paper, the temperatures checked within three degrees or less those given in the earlier papers.

The results published from this Laboratory were obtained by heating the acid in a tube connected with a long capillary tube, which contained a bead of mercury. The temperature of the acid was raised at the rate of one degree per minute and the position of the bead and the temperatures noted. The results were plotted and a line drawn through the points. The

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[1] From the thesis of Helen F. Tucker presented in partial fulfilment of the requirements for the degree of Doctor of Philosophy, 1933.

[2] Norris and Young, THIS JOURNAL, **52**, 5066 (1930).

[3] Lindner, *Monatsh.*, **28**, 1041 (1908).

[4] Bernoulli, Wege and Jakubowicz, *Helv. Chim. Acta*, **2**, 511 (1919); **4**, 1018 (1921).

[5] Jakubowicz, *Z. anorg. Chem.*, **121**, 113 (1922).

[6] Burk and Davis, *J. Phys. Chem.*, **35**, 146 (1931).

[7] Hinshelwood, *J. Chem. Soc.*, **17**, 156 (1920).

[8] Marshall, *Rec. trav. chim.*, **51**, 233 (1932).