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PROPYLCHLOROGERMANES AND PROPYLGERMANES[1]

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PART I. PROPYLTRICHLOROGERMANE

The alkyl- and aryl-trihalogermanes are of theoretical interest since the hydrolysis of these compounds is as yet the only known procedure that might yield organogermanoic acids of the type RGeOOH (1–3).

Methods successfully used for the preparation of organotrihalogermane are heating diarylmercury (4, 5) or tetraarylgermanes (6) with germanium tetrachloride in a sealed tube; direct combination of ethyl iodide with germanium (II) iodide (2), also in a sealed tube; and the reaction between an alkyl or aryl halide and cesium trichlorogermane (7). More recently Rochow (8) has reported the successful formation of propyltrichlorogermane by his direct synthesis method. In this paper the results from the preparation of propyltrichlorogermane by the germanium tetrachloride propyllithium reaction are reported.

EXPERIMENTAL

Preparation of n-propyltrichlorogermane. Petroleum ether, b.p. 35–40° (300 ml.) and 23.8 g. (0.11 mole) of germanium tetrachloride were placed in a one-liter three-necked flask fitted with a stirrer, reflux condenser, and separatory-funnel and the flask was placed in a cooling bath of solid carbon dioxide in equal volumes of chloroform and carbon tetrachloride. A quantity of a petroleum ether (35–40°) solution containing 0.1 mole of *n*-propyllithium was then added dropwise to the vigorously stirred germanium tetrachloride solution. When all of the *n*-propyllithium solution had been added, the cooling bath was removed and the stirring continued for 30 minutes while the flask attained room temperature.

The resultant lithium chloride was removed from the reaction mixture and the residue was washed with three 50-ml. portions of petroleum ether. The filtrate was then distilled on a glycol bath maintained slightly below 75°.

Distillation of the residual liquid at 380 mm. removed most of the unreacted germanium tetrachloride at 60–65°. Reduction of the pressure to 20 mm. gave *n*-propyltrichlorogermane at a vapor temperature of 45–53° while at 5 mm. a mixture of dipropyldichlorogermane and tripropylchlorogermane at 60–70° was obtained.

Redistillation of the 45–53° fraction gave a liquid with a boiling point range of 48–50° at 20 mm. which proved to be propyltrichlorogermane; yield, 3.7 g. (16% on basis of propyllithium).

Anal. Calc'd for $C_3H_7Cl_3Ge$: C, 16.23; H, 3.18; Ge, 32.69.

Found: C, 16.5, 16.3; H, 3.37, 3.2; Ge, 32.0, 32.5.

The fraction collected at 60–70°/5 mm. was combined with the residue from the redistillation of the 45–53°/20 mm. fraction and refractionated at 5 mm. into two fractions. One fraction, b.p. 60–63°, was identified as dipropyldichlorogermane; yield, 4.6 g. (20% on basis of propyllithium).

Anal. Calc'd for $C_6H_{14}Cl_2Ge$: C, 31.4; H, 6.14; Ge, 31.6.

Found: C, 30.9; H, 6.02; Ge, 30.7.

The other fraction, b.p. 65–70° while not positively identified, appeared to be a mixture of approximately one-half dipropyldichlorogermane and one-half tripropylchlorogermane; yield, 3.2 g. No tetrapropylgermane was obtained.

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Anal. Found: C, 37.3; H, 7.38; Ge, 30.9.

The amount of unreacted germanium tetrachloride was determined by hydrolysis with sodium hydroxide solution. Weight of GeO_2 = 4.8 g., equiv. to 10 g. of $GeCl_4$ (42% of orig. $GeCl_4$).

Using twice the equivalent quantity of germanium tetrachloride yielded 31.6% of propyltrichlorogermane and 54% of dipropyldichlorogermane on the basis of the propyllithium or about the same as that with equimolar ratios on the basis of the germanium tetrachloride. No tripropylchlorogermane was found when this ratio of reactants was used.

Separation of the reaction products by hydrolysis: A preparation made by using a 1:2 ratio of propyllithium (0.05 mole) to germanium tetrachloride (0.1 mole) was filtered and the filtrate was reduced to about 100 ml. by distillation, mixed with 25 ml. of water and carefully neutralized with dilute sodium hydroxide. After 24 hours the mixture was filtered and the precipitate was washed twice with petroleum ether and twice with water. The following reaction had taken place during hydrolysis and neutralization.

$$GeCl_4 + 4NaOH \rightarrow GeO_2 + 4NaCl + 2H_2O$$
$$2C_3H_7GeCl_3 + 6NaOH \rightarrow (C_3H_7GeO)_2O + 6NaCl + 3H_2O$$
$$(C_3H_7)_2GeCl_2 + 2NaOH \rightarrow (C_3H_7)_2GeO + 2NaCl + H_2O$$

Dipropyl germanium oxide is soluble in petroleum ether and on slow evaporation of the ether layer on a steam-bath the oxide remained as an oily liquid which was dried overnight by contact with calcium oxide. Molecular weight determinations by the freezing point depression method in benzene indicated that the dipropyl germanium oxide was a tetramer. This conclusion is in accord with molecular weight determinations on diethyl germanium oxide (9, 10) and diphenyl germanium oxide (1).

The aqueous layer was evaporated and the residue was combined with the dried precipitate obtained from the original hydrolysis. This material, which consisted mainly of germanium dioxide, propylgermanoic acid anhydride, and sodium chloride, was treated with an excess of concentrated hydrochloric acid and allowed to stand for a week in an ice-bath during which time it was saturated with dry hydrogen chloride each day. Distillation of the liquid layer which formed at the bottom of the flask gave *n*-propyltrichlorogermane in nearly quantitative yield.

Influence of temperature on the reaction: At temperatures above 85–90° changes occurred in the solution resulting in the formation of a translucent gel-like solid. Small quantities of this solid always appeared in every reaction but if the reaction or the fractionation of the product was carried out at about 90° the liquid changed rapidly to the gel and the yield of propyltrichloro- and dipropyldichloro-germane became very small. Distillation of the petroleum ether extract of the translucent solid always yielded a small amount of a high-boiling viscous liquid. Distillation of the viscous liquid at 4 mm. into a solid carbon dioxide-cooled receiver yielded a colorless liquid. This liquid was not identified but analysis agreed closely with that of the polymeric compound with the formula $(C_3H_7Ge)_x$: C, 45.38; H, 8.89; Ge, 45.7. The liquid was insoluble in water and showed no reaction with water, dilute alkalies, or dilute acids, but was decomposed by boiling with 10 *N* NaOH and fuming nitric acid.

Properties of n-propyltrichlorogermane. n-Propyltrichlorogermane is a colorless liquid fuming strongly in moist air with the formation of hydrogen chloride. Its density is 1.51 g./ml. at 25°. It boils at 47–50° at 20 mm. When the compound was heated above 150° at atmospheric pressure, rapid decomposition took place. Rochow, Didtschenko, and West (8) have reported b.p. 167° at 763 mm. for this compound.

At the temperature of Dry Ice *n*-propyltrichlorogermane becomes very viscous. When cooled in liquid nitrogen it forms a glassy solid showing no tendency to crystallize at the end of two days.

Hydrolysis of n-propyltrichlorogermane. When this compound is added to an excess of water a white oily film forms on the surface of the water. The film disappears on standing for several hours leaving a clear, acid solution. Evaporation at room temperature to about one-eighth of the original volume causes a "cellophane-like" film to form on the surface similar to the one described by Flood (2) for ethyltrichlorogermane. Further evaporation yields a fluffy amorphous precipitate.

Anal. Calc'd for $(C_3H_7Ge)_2O$: Ge, 51.98. Found: Ge, 51.5.

Properties of n-propylgermanoic anhydride. This anhydride decomposes when heated at atmospheric pressure to 285–290°. A similar result was obtained when sublimation at 4 mm. was attempted. The compound is moderately soluble in water giving a neutral, odorless solution. The anhydride is readily soluble in 4 *N* sodium hydroxide. Hot, 10 *N* sodium hydroxide destroys the compound with the formation of a thin film of oily material on the surface. Neutralization of the strongly alkaline solution causees precipitation of germanium dioxide.

n-Propylgermanoic anhydride reacts with hydrochloric acid to yield *n*-propyltrichlorogermane.

$$(C_3H_7GeO)_2O + 6HCl \rightarrow 2C_3H_7GeCl_3 + 3H_2O$$

The reaction appears to be reversible, a liquid layer of *n*-propyltrichlorogermane forming on the bottom when the hydrochloric acid is concentrated and gradually disappearing when the concentration of hydrogen chloride is allowed to decrease by evaporation. This result is in agreement with Laubengayer and Allen's (11) observations on methyltrichlorogermane.

PART II. PROPYL-SUBSTITUTED GERMANES

Only a limited number of compounds of the general formulas R_3GeH, R_2GeH_2, and $RGeH_3$ have been prepared. Teal and Kraus (12) prepared methyl-, ethyl, and propyl-germane by the action of germylsodium, H_3GeNa, on the appropriate alkyl halide in liquid ammonia. Triethylgermane has been prepared by the reaction of triethylgermyllithium with liquid ammonia (13).

$$(C_2H_5)_3GeLi + NH_3 \rightarrow (C_2H_5)_3GeH + LiNH_2$$

and triphenylgermane by the action of triphenylgermylsodium on ammonium bromide dissolved in liquid ammonia (14).

The recently developed reduction techniques using lithium aluminum hydride have been used for the preparation of tricyclohexylgermane (15) and diphenylgermane (16). Since this latter reaction had not been used for the reduction of any trichlorogermane it was decided to apply it to reduction of propyltrichlorogermane and also to tripropylchlorogermane.

EXPERIMENTAL

Teal and Kraus (12) reported the boiling point of propylgermane to be "slightly above room temperature". Isopropyl ether was therefore selected as a solvent with a boiling point sufficiently different from that of the expected product so that it would not interfere with the final fractionation.

A mixture of 3.8 g. (0.1 mole) of lithium aluminum hydride in 200 ml. of isopropyl ether was refluxed with stirring for 3 to 4 hours to dissolve the hydride. A second condenser was then connected to the top of the reflux condenser by means of a conventional angle still head. The reflux condenser was cooled by water from a water bath maintained at 35–40° and the conventional condenser was cooled by water flowing through an ice-bath. This arrangement permitted the removal of the *n*-propylgermane as soon as it was formed without too great a change in the concentration of the reaction mixture through loss of the high-boiling constituents. The receiver was immersed in an ice-bath and a Dry-Ice cooled trap connected to the outlet of the receiver. Through the dropping-funnel 11.0 g. (0.05 mole) of *n*-propyltrichlorogermane, dissolved in 100 ml. of isopropyl ether was added dropwise to the refluxing solution of lithium aluminum hydride. The thermometer at the top of the reflux condenser indicated a vapor temperature of 31° as long as any *n*-propylgermane distilled over. Redistillation of the condensate under anhydrous conditions gave *n*-propylgermane, b.p. 30°; yield, 5 g. (85%).

Reduction of n-propyltrichlorogermane at 100°. The above experiment was repeated using purified dioxane as a solvent and the reaction was carried out at the reflux temperature. At this higher temperature the germanium-carbon bond was attacked as well as the germanium-chlorine bond resulting in the deposition of germanium metal in the bottom of the flask and the formation of germane, GeH_4. The germane was not condensed at the Dry Ice temperature maintained in the traps and so quantitative yields were not taken. The presence of germane was ascertained by its reaction with silver nitrate solution to give a brownish-black precipitate (17).

In the case of arylgermanes, Johnson and Harris (16) observed that the diphenylgermane and the triphenylgermane obtained by a general reduction of the mixture resulting from the bromination of tetraphenylgermane, could be separated readily by distillation. This technique was applied directly to the mixture resulting from the reaction between 0.11 mole of germanium tetrachloride and 0.1 mole of propyllithium. The resulting precipitate was removed and the petroleum ether and excess germanium tetrachloride were removed by distillation at 60°/380 mm. The concentrated residue of propylchlorogermanes was diluted to 100 ml. with isopropyl ether and added dropwise to a mixture of 9.5 g. (0.24 mole) of lithium aluminum hydride dissolved in 600 ml. of redistilled anhydrous isopropyl ether. The monopropylgermane, $C_3H_7GeH_3$, passed out of the mixture as soon as it was formed and was collected in an ice-packed receiver. The vapor temperature at the still head rose from 27 to 31°; yield, 2.3 g. (19%).

The isopropyl ether was replaced by purified petroleum ether, b.p. 90–92°. This change of solvent was necessary to precipitate the lithium aluminum hydride which was then removed on a fritted glass filter under anhydrous conditions.

The petroleum ether was then removed by distillation and the small residual volume of tripropylgermane was transferred to a small distilling flask and redistilled. Yield, 0.3 g., b.p. 65°/20 mm., 183°/742 mm.

Anal. Cal'd for $C_9H_{22}Ge$: C, 53.3; H, 10.93; Ge, 35.78.
Found: C, 53.7; H, 11.21, 10.9; Ge, 35.4, 35.5.

Tripropylgermane is a colorless liquid distilling without decomposition at atmospheric pressure. No change was noted after storage in a stoppered vial for three months.

No *dipropylgermane*, $(C_3H_7)_2GeH_2$, could be detected in the reaction products. This result is so radically different from results previously obtained on the reduction of analogous phenylbromogermanes (16) that the reaction is being investigated further.

Bromination of propylgermane: In the usual apparatus was placed 5 g. of propylgermane diluted with 50 ml. of redistilled ethylene bromide. Then bromine was added dropwise with stirring until the color was no longer destroyed on continued stirring. The solution was transferred to a 100-ml. distilling flask and the ethylene bromide was distilled off at 57/60 mm. The pressure was then reduced and the *n*-propyltribromogermane was distilled at 50–55°/5 mm.

Anal. Calc'd for $C_3H_7Br_3Ge$: C, 10.14; H, 1.97; Ge, 20.43.
Found: C, 10.56; H, 1.66; Ge, 20.3.

SUMMARY

1. The preparation of propyltrichlorogermane by the germanium tetrachloride-propyllithium reaction has been investigated and the hydrolysis products of propyltrichloro- and dipropyldichloro-germane have been studied.

2. The reduction of propyltrichlorogermane and of mixtures of propylchlorogermanes by lithium aluminum hydride is reported.

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