[CONTRIBUTION FROM THE MALLINCKRODT LABORATORY, HARVARD UNIVERSITY]

Diethylgermanium Compounds

BY EUGENE G. ROCHOW*

The preparation of diethylgermanium halides and oxide has long been a rather difficult matter, requiring either the preparation of the corresponding tetraalkyl of germanium followed by degradative bromination or the addition of alkyl iodide to RGeI reduced from $RGeI_3$ in a sequence of sealed-tube reactions.[1] An extreme example is offered by the preparation of diethylgermanium dibromide (later converted to the oxide, which was used as a foam suppressor in diesel motor oils) by the following sequence of reactions[2]

$$C_6H_5MgBr \xrightarrow{ZnCl_2} (C_6H_5)_2Zn \xrightarrow{GeCl_4} (C_6H_5)_4Ge$$

$$(C_6H_5)_4Ge \xrightarrow{Br_2} (C_6H_5)_2GeBr_2 \xrightarrow{EtMgBr}$$

$$(C_6H_5)_2GeEt_2 \xrightarrow{Br_2} Et_2GeBr_2$$

The direct synthesis of organogermanium compounds from elementary germanium[3] offers a comparatively easy way to prepare diethylgermanium dihalides, once the reaction conditions are worked out. The method has been applied to the preparation of diethylgermanium dichloride, now being used in pharmaceutical studies and for experiments on the polymeric diethylgermanium oxides.

Experimental.—A mixture of 32.7 g. of reduced copper powder and 186 g. of pure metallic germanium (crushed to a powder, the particle size of which ranged from 40-mesh to fine dust) was packed between glass wool plugs in a reaction tube 2 cm. in diameter and 45 cm. long sealed to a water condenser. The portion of the tube containing the charge was heated in a combustion furnace and a slow stream of ethyl chloride was passed through the tube, serving to remove water adsorbed by the powder. When the temperature (indicated by a thermometer with its bulb embedded in the charge) reached 356° a liquid product appeared in the condenser. The rate of flow of ethyl chloride then was adjusted to 150 cc./min. and the temperature to 317°; in forty-eight hours 687 g. of liquid was collected, most of it in the first sixteen hours.[4] The rate of reaction fell off markedly as the smaller particles of germanium were consumed, and finally carbon was deposited on the copper catalyst, rendering it inactive. Residual metallic germanium was recovered by raising the temperature of the tube until a copper–germanium alloy melted and settled out.

The liquid product was distilled in a vacuum-jacketed fractionating column of the Fenske type, 0.9 cm. in internal diameter and 1 m. long, fitted with a total-condensation partial-take off head. Dissolved ethyl chloride distilled out first,[5] and then the boiling point rose rapidly to 137° and leveled off at 140.0° (at 763 mm.) to provide 95 g. of ethylgermanium trichloride. After an intermediate fraction, about 240 g. of pure diethylgermanium dichloride was obtained at 172.8°.[6] The intermediate fractions were combined and fractionated further for $C_2H_5GeCl_3$ and $(C_2H_5)_2GeCl_2$; no $(C_2H_5)_3GeCl$ was found, nor was there any evidence for $GeCl_4$ either in the distillation curve or in the chlorine analysis of the forerun fraction.

Anal. Calcd. for $C_2H_5GeCl_3$: C, 11.5; H, 2.42; Cl, 51.1. Found: C, 11.6; H, 3.00; Cl, 50.6. Calcd. for $(C_2H_5)_2GeCl_2$: C, 23.8; H, 5.01; Cl, 35.2. Found: C, 23.6; H, 4.25; Cl, 35.1.

The yield of distilled material (excepting ethyl chloride) was 446 g. The germanium represented by the separated $C_2H_5GeCl_3$ and $(C_2H_5)_2GeCl_2$, respectively, was 61.5 g. and 91.1 g. Together these constitute 82.0% of the germanium charged into the reaction tube at the start, the balance of the germanium being left in the copper–germanium alloy from which it can be separated by chlorination. An excess of ethyl chloride was employed, and because of the low cost of this reagent compared with the cost of germanium, no attempt was made to determine the yield of ethylgermanium chloride based on the ethyl chloride actually consumed in the reaction.

When 0.1 mole of ethylgermanium trichloride was shaken with 0.3 mole of water, some heat was evolved and a highly acid aqueous layer floated on the surface of a colorless oil. Standing for one month produced no change, but when the organogermanium layer then was separated and shaken with a large excess of distilled water (250 g.) the oil turned cloudy and became a stiff white paste. Further washing with boiling water left a resinous white solid. These observations suggest that stoichiometric proportions of water do not hydrolyze ethylgermanium trichloride completely, but result in an equilibrium similar to that noted for methylgermanium chlorides.[7] Washing out the hydrochloric acid with water eventually produces $C_2H_5Ge(OH)_3$, which condenses to a polymeric $(C_2H_5GeO_{1.5})_x$.

When 0.1 mole of dialkylgermanium dichloride was shaken with 0.2 mole of water and allowed to stand a month, a colorless oil remained beneath the layer of aqueous acid. Prolonged shaking with fresh water left the $(C_2H_5)_2GeO$ as a colorless oil, probably a mixture of polymers. The oil had an appreciable solubility in water, but less than that of the dimethyl compound.[7] Films deposited on glass by hydrolysis of diethylgermanium dichloride or mixtures of ethylgermanium chlorides were water-soluble, not water-repellent as are the corresponding silicone films.[8] The various diethylgermanium halides and the oxide may be derived from each other, by methods previously worked out by Flood[9] and by Horvitz and Flood.[1]

Summary

Ethylgermanium trichloride and diethylgermanium dichloride have been prepared from metallic germanium by a method much simpler and easier than those employed in the past.

CAMBRIDGE, MASS. RECEIVED SEPTEMBER 2, 1949

---

[*] Harvard University Faculty, 1948–.

[1] Horvitz and Flood, THIS JOURNAL, **55**, 5055 (1933).

[2] Trautman and Ambrose, U. S. Patent 2,416,360, Feb. 25, 1947.

[3] Rochow, THIS JOURNAL, **69**, 1729 (1947).

[4] Most of this collected in the receiver for the water condenser, but some liquid product was swept over by excess ethyl chloride into the cold trap which followed the condenser. The ethylgermanium chlorides are recovered from the trap by allowing the ethyl chloride to distil off slowly.

[5] The crude reaction product was known to contain considerable ethyl chloride, for if its average composition were represented by $(C_2H_5)_2GeCl_2$ it would represent 30% more germanium than was employed at the start.

[6] The boiling points previously given for $C_2H_5GeCl_3$ and $(C_2H_5)_2GeCl_2$ were 144° and 175°, respectively,[1] which are 4.0° and 2.8° higher than those obtained here. The present investigation may have provided a better opportunity to observe the true boiling points because much larger amounts of material were being fractionated and the synthesis allowed of no halogen interchange or mixture.

[7] Rochow, THIS JOURNAL, **70**, 1801 (1948).

[8] Pathode, U. S. Patent 2,306,222, Dec. 22, 1942.

[9] Flood, THIS JOURNAL, **54**, 1663 (1932).