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Secondary and Tertiary Phosphine Adducts of Germanium(II) Iodide

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Germanium(II) iodide reacts with various alkyl and aryl phosphine derivatives in hydrocarbon solvents at 130° to form adducts of the general formula $R_3P{\cdot}GeI_2$. These compounds, formally analogous to the phosphinedihalomethylenes, form yellow air-sensitive solids soluble in certain organic solvents.

Recently triphenylphosphinedihalomethylene derivatives have been reported.[1,2] The characteristic feature of phosphinedihalomethylene and other phosphinemethylene derivatives is the presence of a carbon–phosphorus double bond. The interesting chemistry of these phosphinemethylene derivatives makes of special significance analogous compounds with similar double bonding between phosphorus and silicon, germanium, tin, or lead. In this paper the synthesis of several germanium compounds of the general formula $R_3P{\cdot}GeI_2$ which are at least formally analogous to the phosphinedihalomethylenes is described.

Experimental

Germanium(II) iodide was obtained from germanium(IV) oxide by the procedure described in *Inorganic Syntheses*.[3] Triphenylphosphine was purchased from Metal and Thermit, New York 17, New York. The remaining phosphines were generously supplied by Dr. Roy Hayter of this Institute.

General Procedure for the Preparation of the Secondary and Tertiary Phosphine Adducts of Germanium(II) Iodide.—A mixture of 3.26 g. (10 mmoles) of germanium(II) iodide, 10 mmoles of the secondary or tertiary phosphine, 20 ml. of ethylcyclohexane, and 5 to 10 ml. of xylene was heated at the boiling point 1.5 to 7 hr. under nitrogen with magnetic stirring. The resulting yellow reaction mixture was filtered at the boiling point with rigorous exclusion of air. Upon cooling the filtrate the product separated either as yellow crystals or as a yellow viscous liquid. The crystalline products were washed under nitrogen with two to four 20-ml. portions of pentane and sucked dry. The liquid products were washed by decantation with one to three 20-ml. portions of pentane and dried at ~1 mm. Analytical and yield data are given in Table I.

Attempts to prepare analogous germanium(II) iodide adducts of triphenylarsine and of triphenylphosphite using these reaction conditions led only to the recovery of unchanged germanium(II) iodide.

General Properties of the $R_3P{\cdot}GeI_2$ Adducts.—The germanium(II) iodide adduct of tri-*n*-butylphosphine is a yellow extremely viscous liquid. All of the other germanium(II) iodide adducts listed in Table I are yellow crystalline solids. A characteristic property of these componds is the tendency to turn red on exposure to air. Among the compounds of general formula $(C_6H_5)_2PR{\cdot}GeI_2$ the derivatives where R is an alkyl group (methyl, ethyl, isopropyl, and *n*-butyl) become red more slowly in air than the derivatives where R is a phenyl group or hydrogen. The latter compounds turn red in a few seconds on exposure to air.

Pyrolysis of $(C_6H_5)_2PC_2H_5{\cdot}GeI_2$.—A sublimation apparatus was charged with 0.50 g. (0.92 mmole) of $(C_6H_5)_2PC_2H_5{\cdot}GeI_2$. It was heated gradually at ~0.1 mm. At ~100° the germanium complex began to melt. The temperature was kept at 140–160° until the molten complex resolidified to form the characteristic yellow leaflets of germanium(II) iodide. These were washed with three 10-ml. portions of benzene to give 0.28 g. (93% yield) of germanium(II) iodide identified by comparison of its X-ray powder pattern with that of authentic germanium(II) iodide.

TABLE I

ANALYTICAL DATA ON THE PHOSPHINE ADDUCTS OF GERMANIUM(II) IODIDE[a]

Compound	Yield[b]		C	H	P	I
$(C_6H_5)_3P{\cdot}GeI_2$[c]	34%	Calcd.	36.7	2.6	5.3	43.2
		Found	36.2	2.9		
			35.1	2.8	5.8	42.9
$(C_6H_5)_2PCH_3{\cdot}GeI_2$	34%	Calcd.	29.7	2.5	5.9	48.2
		Found	30.8	2.6	6.2	46.8
$(C_6H_5)_2PC_2H_5{\cdot}GeI_2$	52%	Calcd.	31.0	2.8	5.7	47.0
		Found	30.8	2.9	6.1	47.0
$(C_6H_5)_2PCH(CH_3)_2{\cdot}GeI_2$	47%	Calcd.	32.4	3.1	5.6	45.8
		Found	32.2	3.1	5.9	45.6
$(C_6H_5)_2P(n\text{-}C_4H_9){\cdot}GeI_2$	21%	Calcd.	33.8	3.3	5.5	44.7
		Found	34.3	3.3	5.9	44.5
$(C_6H_5)_2PH{\cdot}GeI_2$	23%	Calcd.	28.1	2.2	6.1	49.6
		Found	28.2	2.2	6.5	49.2
$(n\text{-}C_4H_9)_3P{\cdot}GeI_2$	13%	Calcd.	27.2	5.1	5.9	48.0
		Found	27.0	5.2	6.3	47.6
$(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2{\cdot}2GeI_2$	Low	Calcd.	29.6	2.3		
		Found	29.2	2.2		

[a] Carbon, hydrogen, phosphorus, and iodine analyses were performed by Dr. A. Bernhardt, Mikroanalytisches Laboratorium, Max-Planck-Institut für Kohlenforschung, Mülheim (Ruhr), Germany. [b] The yields reported in this paper represent pure material. No efforts were made to optimize the yields or to obtain additional product from the residues or the mother liquors. [c] Germanium: calcd., 12.3; found, 11.5 (ignition to GeO_2).

A similar pyrolysis of 0.50 g. (0.90 mmole) of $(C_6H_5)_2PCH(CH_3)_2{\cdot}GeI_2$ gave 0.18 g. (61% yield) of germanium(II) iodide.

Infrared Spectra (KBr Pellets), Perkin-Elmer Model 21 Machine, 2000–685 cm.$^{-1}$.—(1) $(C_6H_5)_3P{\cdot}GeI_2$: 1632 (w), 1623 (w), 1612 (w), 1605 (w), 1580 (w), 1478 (m), 1435 (s), 1329 (w), 1307 (vw), 1182 (w), 1176 (w), 1155 (w), 1115 (m), 1093 (m), 1066 (w), 1023 (w), 996 (w), 872 (m, br), 741 (s), 720 (m), and 686 (s) cm.$^{-1}$.

(2) $(C_6H_5)_2PCH_3{\cdot}GeI_2$: 1480 (vw), 1435 (w), 1122 (w), 884 (w), 870 (w), 737 (m), and 686 (m) cm.$^{-1}$.

(3) $(C_6H_5)_2PC_2H_5{\cdot}GeI_2$: 1480 (vw), 1430 (w), 1120 (w, br), 1095 (w), 995 (w), 738 (m), and 686 (m) cm.$^{-1}$.

(4) $(C_6H_5)_2PH{\cdot}GeI_2$: 1580 (w), 1480 (vw), 1435 (m), 1125 (m), 1030 (w, br), 1005 (w, br), 980 (w), 745 (sh, br), 730 (br, m), and 684 (m) cm.$^{-1}$.

(5) $(C_6H_5)_2PCH(CH_3)_2{\cdot}GeI_2$: 1475 (vw), 1455 (vw), 1435 (m), 1115 (w), 1095 (w, br), 1029 (vw, sh), 1025 (vw), 995 (vw), 875 (vw), 735 (m), 720 (vw), 709 (w), and 690 (w) cm.$^{-1}$.

(6) $(C_6H_5)_2PC_4H_9{\cdot}GeI_2$: 1570 (vw), 1480 (vw), 1460 (vw), 1435 (m), 1118 (m), 1092 (w), 1065 (vw), 1020 (vw), 995 (w), 740 (m), 722 (m), and 688 (m) cm.$^{-1}$.

Molecular Weight Determinations (Mechrolab Vapor Pressure

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(1) A. J. Speziale and K. W. Ratts, *J. Am. Chem. Soc.*, **84**, 854 (1962).

(2) F. Ramirez, N. B. Desai, and N. McKelvie, *ibid.*, **84**, 1745 (1962).

(3) L. S. Foster and A. F. Williston, *Inorg. Syn.*, **2**, 112 (1946); L. S. Foster, *ibid.*, **3**, 63 (1950).

Osmometer in Benzene Solution under Nitrogen).—(1) $(C_6H_5)_3P \cdot GeI_2$: calcd., 588; found, 466. (2) $(C_6H_5)_2PC_2H_5 \cdot GeI_2$: calcd., 541; found, 420. (3) $(C_6H_5)_2PCH(CH_3)_2 \cdot GeI_2$: calcd., 555; found, 458.

Discussion

The reactions of secondary and tertiary phosphines with germanium(II) iodide to give compounds of the general formula $R_3P \cdot GeI_2$ are analogous to the reaction between triphenylphosphine and dichlorocarbene (carbon(II) chloride) to give triphenylphosphinedichloromethylene.[1] This suggests possible carbenoid behavior for germanium(II) iodide at least at elevated temperatures. Such carbenoid behavior of germanium(II) iodide has been observed previously by Vol'pin, *et al.*,[4] in the reactions between germanium(II) iodide and various acetylene derivatives to give the corresponding germirene (3-germacyclopropene) derivatives.

Although these new germanium compounds are formally analogous to the phosphinedihalomethylenes, some differences in chemistry might be expected because of the great differences between the chemistry of germanium and carbon. Due to the relative stability of divalent germanium as compared with divalent carbon it is of interest that pyrolyses of $(C_6H_5)_2PC_2H_5 \cdot GeI_2$ and of $(C_6H_5)_2PCH(CH_3)_2 \cdot GeI_2$ at 150° (0.1 mm.) give germanium(II) iodide in good yield. In connection with this apparent tendency for these germanium(II) iodide complexes to be converted to germanium(II) iodide on pyrolysis with loss of the ligand, it is also of interest that molecular weight determinations were consistently only about 80% of the calculated value for $R_3P \cdot GeI_2$ in benzene solution, suggesting that a certain amount of dissociation also occurs under these conditions. Moreover, like the free phosphines these germanium(II) iodide adducts are decomposed by carbon disulfide giving red solutions. All of these observations suggest that although the stoichiometry of these phosphine adducts of germanium(II) iodide corresponds to that of the phosphinedihalomethylenes, the chemical properties of these germanium complexes correspond more to those of a typical phosphine addition compound. However, the phosphorus–germanium bond in these $R_3P \cdot GeI_2$ compounds may be similar to the phosphorus–carbon multiple bond in the phosphinemethylenes, possibly stabilized by overlap of the filled 3d orbitals of the germanium atom with the empty 3d orbitals of the phosphorus atom. The differences in the chemical properties of the $R_3P \cdot GeI_2$ compounds and the phosphinemethylenes then would be due to the greater stability of divalent germanium as compared with divalent carbon.

The reaction between germanium(II) iodide and the chelating diphosphine $(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2$ in a 2:1 mole ratio was investigated and found to yield a compound of stoichiometry $(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2 \cdot 2GeI_2$. This adduct was more air-sensitive than even $(C_6H_5)_3P \cdot GeI_2$, turning red almost instantly on exposure to air. Because of its lower solubility in organic solvents its preparation was carried out in xylene without any added ethylcyclohexane in order to permit isolation in the same manner as the other germanium derivatives; however, even in pure xylene most of the product precipitated at the boiling point and only small quantities were isolated on cooling the filtered reaction mixture.

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[4] M. E. Vol'pin, U. D. Koreshkov, V. G. Dulova, and D. N. Kursanov, *Tetrahedron*, **18**, 107 (1962).