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The Preparation and Reactions of Triphenyllead- and Triphenylgermanium Pentachlorophenoxides

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The preparation of triphenyllead- and triphenylgermanium pentachlorophenoxides $(C_6H_5)_3PbOC_6Cl_5$ and $(C_6H_5)_3GeOC_6Cl_5$ are given along with their reactions with unsaturated substrates ($C_6H_5N{=}C{=}O$, $S{=}C{=}S$, $O{=}S{=}O$) which add across the M–O (M=Pb, Ge) bond of the alkoxides. The products have been identified and details of reactions discussed.

INTRODUCTION

The synthetic methods for obtaining the compounds of $R_3MOC_6X_5$ (where $R{=}CH_3$, C_6H_5, M=Pb, Ge and X=Br and F) are reported[1,2]. Though the details of the preparations or characteristic properties were not mentioned, the corresponding perchloro derivatives have been used for its biocidal activity[2]. Similarly the preparation and reactions of aryltin pentachlorophenoxides have also been reported with unsaturated substrates[3] ($C_6H_5N{=}C{=}O$, $S{=}C{=}S$, $O{=}S{=}O$). We now wish to report the synthesis of thriphenyllead- and triphenylgermanium pentachlorophenoxides and the insertion reactions of the Pb–O and Ge–O bonds of these phenoxides. The M–O (M=Pb, Ge) bond of organolead- and organogermanium phenoxides add to multiply bonded groups of acceptor molecules[1,4].

$$>\!M{-}O + A{=}B \rightarrow\ >\!M{-}A{-}B{-}O \qquad (1)$$

(where M=Pb, Ge, (A=B)=PhNCO, CS_2, SO_2 etc.).

EXPERIMENTAL

Triphenyllead pentachlorophenoxide

To a well stirred solution of triphenyllead chloride (9.47 g, 0.02 mole) in 50 ml of dry acetone was added sodium pentachlorophenoxide (5.77 g, 0.02 mole) dissolved in 50 ml of dry acetone. The sodium chloride was precipitated immediately. After 1 hr. it was filtered off and on removal of solvent triphenyllead pentachlorophenoxide was obtained, which was purified by sublimation; yield (11.25 g, 80%), m.pt. 123–5°. [Found: C, 40.55; H, 2.00; Calc. for $C_{24}H_{15}Cl_5OPb$: C, 41.88; H, 2.10%.]

TABLE 1
TRIPHENYLGERMANIUM- AND TRIPHENYLLEAD PENTACHLOROPHENOXIDE

Compounds	M. pt. °C	Yield %	Analysis (%)			
			Found		Calc.	
			C	H	C	H
$(C_6H_5)_3GeOC_6Cl_5$	88–90	83.5	50.96	2.62	52.07	2.71
$(C_6H_5)_3PbOC_6Cl_5$	123–125	80	40.55	2.00	41.88	2.10

Addition Reaction

Experimental procedure of a representative reaction is described below. Further details of similar reactions are given in Table 2.

TABLE 2
PRODUCTS OF THE REACTION OF VARIOUS ACCEPTOR MOLECULES WITH TRIPHENYLGERMANIUM AND TRIPHENYLLEAD PENTACHLOROPHENOXIDE

S. No.	Acceptor	Compound	Products	Yield (%)	M.pt. (°C)
1.	PhNCO	$Ph_3GeOC_6Cl_5$	$Ph_3Ge{\cdot}N(Ph){\cdot}CO{\cdot}OC_6Cl_5$	85	132–135
2.	CS_2	$Ph_3GeOC_6Cl_5$	$Ph_3Ge{\cdot}S{\cdot}CS{\cdot}OC_6Cl_5$	75	165–168
3.	SO	$Ph_3GeOC_6Cl_5$	$Ph_3Ge{\cdot}O{\cdot}SO{\cdot}OC_6Cl_5$	79	230 dec.
4.	PhNCO	$Ph_3PbOC_6Cl_5$	$Ph_3Pb{\cdot}N(Ph){\cdot}CO{\cdot}OC_6Cl_5$	95	102–105
5.	CS_2	$Ph_3PbOC_6Cl_5$	$Ph_3Pb{\cdot}S{\cdot}SC{\cdot}OC_6Cl_5$	89	95–98
6.	SO_2	$Ph_3PbOC_6Cl_5$	$Ph_3Pb{\cdot}O{\cdot}SO{\cdot}OC_6Cl_5$	84	195 dec.

The addition of triphenyllead pentachlorophenoxide to acceptor molecules.

A. Addition of phenyl isocyanate:

To a solution of triphenyllead pentachlorophenoxide (7.0 g, 0.01 mole) in dry benzene (200 ml) phenyl isocyanate (1.19 g, 0.01 mole) was added during 10 min. at refluxing. After complete addition it was further refluxed for 3 hrs. The reaction was freed from solvent under reduced pressure to yield (pentachlorophenyl) triphenyllead-N-phenylcarbamate $(C_6H_5)_3PbN(C_6H_5).COOC_6Cl_5$ as a white solid which was recrystallized from pet. ether; yield (7.78 g, 95%), m.pt. 102–5°C. [Found: C, 44.95; H, 2.20; N, 1.55; Calc. for $C_{31}H_{20}Cl_5NO_2Pb$: C, 45.22; H, 2.43; N, 1.70%.]

B. Addition of carbon disulphide

Carbon disulphide (0.76 g, 0.01 mole) was added to a solution of triphenyllead pentachlorophenoxide (7 g, 0.01 mole) in acetone during 10 min. After the complete addition the solution was further stirred for 30 min. to ensure the completion of the reaction. It was freed from solvent at reduced pressure to yield S-triphenyllead-O-pentachlorophenyldithiocarbonate $(C_6H_5)_3Pb.S.CS.OC_6Cl_5$ as a white solid, m.pt. 95–8°C (6.86 g, 89%). [Found: C, 39.00; H, 1.81; S, 7.95; Calc. for $C_{25}H_{15}Cl_5OS_2Pb$: C, 39.76; H, 1.92; S, 8.19%.]

C. Addition of sulphur dioxide

Sulphur dioxide was passed through a solution of triphenyllead pentachlorophenoxide (7 g, 0.01 mole) in light petroleum ether at room temperature. After 50 min. the solvent was removed by filtration to yield (pentachlorophenyl) triphenyllead sulphite $[(C_6H_5)_3Pb.OSO.OC_6Cl_5]$ as a white solid which was recrystallised from carbon tetrachloride (6.41 g, 84%), m.pt. 195 dec. [Found: C, 36.85; H, 1.75; S, 3.90; Calc. for $C_{24}H_{15}Cl_5O_3SPb$: C, 37.41; H, 1.94; S, 4.16%.]

TABLE 3
ANALYTICAL DATA

Products	Found (%)				Calc. (%)			
	C	H	N	S	C	H	N	S
$(C_6H_5)_3Ge{\cdot}N(C_6H_5){\cdot}CO{\cdot}OC_6Cl_5$	55.15	2.80	1.95	—	54.86	2.94	2.06	—
$(C_6H_5)_3Ge{\cdot}S{\cdot}CS{\cdot}OC_6Cl_5$	45.20	2.11	—	9.71	46.51	2.32	—	9.92
$(C_6H_5)_3Ge{\cdot}O{\cdot}SO{\cdot}OC_6Cl_5$	45.00	2.21	—	4.85	45.49	2.52	—	5.05
$(C_6H_5)_3Pb{\cdot}N(C_6H_5){\cdot}CO{\cdot}OC_6Cl_5$	44.95	2.20	1.55	—	45.22	2.43	1.70	—
$(C_6H_5)_3Pb{\cdot}S{\cdot}CS{\cdot}OC_6Cl_5$	39.00	1.81	—	7.95	39.76	1.92	—	8.18
$(C_6H_5)_3Pb{\cdot}O{\cdot}SO{\cdot}OC_6Cl_5$	36.85	1.75	—	3.90	37.41	1.94	—	4.16

RESULTS AND DISCUSSION

Phenylisocyanate reacted with triphenyllead pentachlorophenoxide after 2 hrs on refluxing in benzene and the product isolated was pentachlorophenyltriphenylplumbyl-N-phenyl carbamate. The sample after a few days turned black.

$$Ph_3PbOC_6Cl_5 + PhNCO \xrightarrow{2\ hrs.} Ph_3Pb.N(Ph)CO.OC_6Cl_5 \tag{2}$$

Davies[5] reported that both tributyl- and triphenyl-plumbylcarbamates were approximately monomolecular in dilute solution in benzene. The tributylplumbyl compound was less hydrolytically and thermally stable, and a sample in a sealed tube turned brown after few days. Triphenylgermanium pentachlorophenoxide reacted with phenylisocyanate after 4 hrs on refluxing in benzene and the product isolated was pentachlorophenyltriphenyl germanyl-N-phenylcarbamate.

$$Ph_3GeOC_6Cl_5 + PhNCO \xrightarrow{4\ hrs} Ph_3Ge{\cdot}N(Ph)CO{\cdot}OC_6Cl_5 \tag{3}$$

Both compounds showed characteristic C=O stretching in the I.R. absorption at 1640 ± 10 cm^{-1}.

Carbon disulphide reacted with triphenyllead pentachlorophenoxide at room temperature to give S-triphenyllead-O-pentachlorophenyldithiocarbonate.

$$Ph_3PbOC_6Cl_5 + CS_2 \rightarrow Ph_3Pb{\cdot}S{\cdot}CS{\cdot}OC_6Cl_5 \qquad (4)$$

CS_2 also reacted with triphenylgermanium pentachlorophenoxide to give S-triphenylgermanium-O-pentachlorophenyldithiocarbonate.

$$Ph_3GeOC_6Cl_5 + CS_2 \rightarrow Ph_3Ge{\cdot}S{\cdot}CS{\cdot}OC_6Cl_5 \qquad (5)$$

Triphenyllead pentachlorophenoxide reacted readily with sulphur dioxide to give pentachlorophenyl triphenyllead sulphate.

$$Ph_3PbOC_6Cl_5 + SO_2 \rightarrow Ph_3Pb{\cdot}O{\cdot}SO{\cdot}OC_6Cl_5 \qquad (6)$$

Sulphur dioxide also reacted readily with triphenylgermanium pentachlorophenoxide to yield pentachlorophenyltriphenylgermanium sulphite.

$$Ph_3GeOC_6Cl_5 + SO_2 \rightarrow Ph_3Ge{\cdot}O{\cdot}SO{\cdot}OC_6Cl_5 \qquad (7)$$

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