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CLEAVAGE REACTIONS OF THE LEAD–CARBON BOND
II. THE REACTION OF TETRAORGANOLEAD COMPOUNDS WITH 1-CHLORO-1,2,3-BENZOTRIAZOLE

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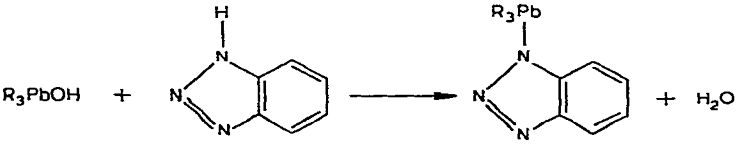
SUMMARY

1-(Triorganoplumbyl)-1,2,3-benzotriazoles were synthesized in excellent yields by the cleavage of an organic group from tetraorganolead derivatives with 1-chloro-1,2,3-benzotriazole in benzene at 50–60°. The order of ease of cleavage of organic groups by 1-chloro-1,2,3-benzotriazole in the case of mixed-tetraorganolead compounds is discussed.

INTRODUCTION

Nitrogen-bonded heterocyclic lead compounds have been known for a number of years[1,2,3]. Willemsens and van der Kerk[4] reported a variety of such compounds obtained in good yield by the reaction of triorganolead hydroxides with five-membered 1,3-diazaheterocycles, *e.g.*:



The observation of a facile and specific cleavage of lead–carbon bonds in tetraorganolead compounds by *N*-bromosuccinimide[5] has led us to explore reactions of other compounds containing nitrogen-bonded "positive" halogen with organolead derivatives as a possible source of organolead compounds containing lead–nitrogen bonds. Such a study, moreover, might contribute to our knowledge of the reactivity of the lead–carbon bond. In the present paper we report the synthesis of 1-(triorganoplumbyl)-1,2,3-benzotriazoles by cleavage of an organic group from tetraorganolead compounds with 1-chloro-1,2,3-benzotriazole.

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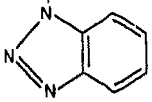
TABLE 1

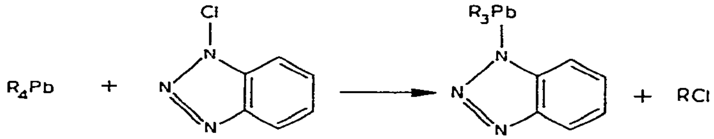
REACTION OF ORGANOLEAD COMPOUNDS WITH 1-CHLORO-1,2,3-BENZOTRIAZOLE

Organolead compound used	Organic chloride formed	1-(Triorganoplumbyl)-1,2,3-benzotriazole obtained X = 	Yield (%)	M.p.[a] (°C)	Analytical data[b], found (calcd.) (%)			
					C	H	N	Pb
$(C_6H_5)_4Pb$	C_6H_5Cl	$(C_6H_5)_3PbX$	88	280	51.95 (51.79)	3.45 (3.42)	7.57 (7.55)	37.22 (37.23)
$(p\text{-}CH_3C_6H_4)_4Pb$	$p\text{-}CH_3C_6H_4Cl$	$(p\text{-}CH_3C_6H_4)_3PbX$	93	235–240	54.09 (54.18)	4.53 (4.18)	7.09 (7.02)	
$(2\text{-}C_4H_3S)_4Pb$	$2\text{-}C_4H_3SCl$	$(2\text{-}C_4H_3S)_3PbX$	80	225	37.91 (37.63)	2.14 (2.26)	7.25 (7.32)	36.24 (36.06)
$(C_6H_5)_3PbCH_2C_6H_5$	C_6H_5Cl	$(C_6H_5)_2PbX$ $\quad\vert$ $CH_2C_6H_5$	80	218	52.74 (52.63)	3.78 (3.68)	7.42 (7.37)	36.97 (36.32)
$(2\text{-}C_4H_3S)_3PbCH_2C_6H_5$	$2\text{-}C_4H_3SCl$	$(2\text{-}C_4H_3S)_2PbX$ $\quad\vert$ $CH_2C_6H_5$	97	150–160	42.81 (43.30)	3.05 (2.89)	7.31 (7.22)	
$(C_6H_5)_3Pb\text{-}i\text{-}C_3H_7$	C_6H_5Cl	$(C_6H_5)_2PbX$ $\quad\vert$ $i\text{-}C_3H_7$	96	195–200	48.29 (48.28)	4.09 (4.02)	8.13 (8.05)	39.53 (39.65)
$(C_6H_5)_3PbCH_2CH{=}CH_2$	$ClCH_2CH{=}CH_2$	$(C_6H_5)_3PbX$	88	280	51.86 (51.79)	3.52 (3.42)	7.58 (7.55)	
$(C_6H_5)_3PbC{\equiv}CC(CH_3)_3$	$ClC{\equiv}CC(CH_3)_3$	$(C_6H_5)_3PbX$	90	280	51.82 (51.79)	3.54 (3.42)	7.59 (7.55)	
$(CH_3)_3PbC_6H_5$	C_6H_5Cl	$(CH_3)_3PbX$	89	175	29.10 (29.19)	3.71 (3.51)	11.40 (11.35)	56.09 (55.94)
$(C_6H_5)_3Pb(C_6H_4CH_3\text{-}p)$	C_6H_5Cl+ $p\text{-}CH_3C_5H_4Cl$	Mixture						

[a] Compounds turned brown or black at this temperature. [b] Analyses were carried out in this Institute by Mr. W. J. Buis.

RESULTS AND DISCUSSION

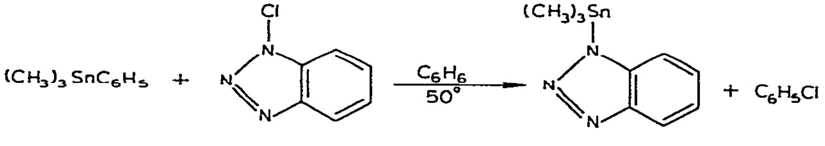
1-Chloro-1,2,3-benzotriazole[6] is a "positive-halogen" compound of the same general type as *N*-bromosuccinimide, and thus it was thought worthwhile to study cleavage reactions of tetraorganolead compounds using this reagent. It was found that 1-chloro-1,2,3-benzotriazole readily reacts with tetraorganolead compounds in benzene solution at 50–60° according to:



The various 1-(triorganoplumbyl)-1,2,3-benzotriazoles obtained in this manner are listed in Table 1.

This type of reaction offers a convenient synthesis of 1-(triorganoplumbyl)-1,2,3-benzotriazoles in excellent yields. No formation of side products is observed. The 1-chloro-1,2,3-benzotriazole starting material which is readily obtained by the reaction of 1,2,3-benzotriazole with sodium hypochlorite in acetic acid[6] is a stable material readily soluble in benzene.

No reaction was found to occur between tetramethyllead and 1-chloro-1,2,3-benzotriazole even in refluxing benzene. Similarly no dephenylation occurred in the case of tetraphenyltin, although the phenyl group was cleaved in trimethylphenyltin yielding 1-(trimethylstannyl)-1,2,3-benzotriazole in quantitative yield:



The relative ease of cleavage of different organic groups attached to the lead atom in mixed-tetraorganolead derivatives with 1-chloro-1,2,3-benzotriazole was also studied. It was found that:

(*i*). In the series $(C_6H_5)_3PbR$ where $R = CH_3$; $i\text{-}C_3H_7$; $C_6H_5CH_2$, the phenyl group was cleaved exclusively.

(*ii*). In the compounds of the type $(C_6H_5)_3PbR$ where $R = -CH_2CH{=}CH_2$; $-C{\equiv}C-C(CH_3)_3$, no phenyl group cleavage was observed and the group R was found to be exclusively cleaved.

(*iii*). In the case of $(C_6H_5)_3Pb(C_6H_4CH_3\text{-}p)$ both the phenyl and *p*-tolyl groups were simultaneously cleaved with approximately the same rate (found by GLC technique).

The results are analogous to those obtained in the cleavage reactions of mixed-tetraorganolead compounds with *N*-bromosuccinimide[5].

The reactions of various other types of organolead compounds in particular those containing lead–hetero atom bonds with 1-chloro-1,2,3-benzotriazole are being investigated.

EXPERIMENTAL

1-Chloro-1,2,3-benzotriazole, prepared as previously described[6], was recrystallized from 1/1 methylene chloride/light petroleum 40–60° (yield 77%; m.p. 106°, lit.[6] 105–106°).

As identical procedures were used for the preparation of 1-(triorganoplumbyl)-1,2,3-benzotriazoles only a few typical examples are described (*cf.* Table 1).

Reaction between tetraphenyllead and 1-*chloro*-1,2,3-*benzotriazole*

To a suspension of tetraphenyllead (5.1 g) in benzene (50 ml) at 50° was added a benzene solution (25 ml) of 1-chloro-1,2,3-benzotriazole (1.5 g) over a period of 15 min. The mixture was stirred at 50–60° for a period of 4 h. The white precipitate was filtered, washed with benzene, and dried. The solid obtained was dissolved in warm dimethylformamide. Pure 1-(triphenylplumbyl)-1,2,3-benzotriazole (4.9 g) was precipitated from this solution with 96% ethanol, filtered and dried at 50°/0.1 mm for 2 h.

Reaction between trimethylphenyllead and 1-*chloro*-1,2,3-*benzotriazole*

A solution of 1-chloro-1,2,3-benzotriazole (0.8 g) in benzene (25 ml) was added to a well-stirred solution of trimethylphenyllead (1.6 g) in benzene (25 ml) at 50–60°. The mixture was stirred at this temperature for 4 h. Removal of benzene and recrystallization of the crude material from boiling acetone containing a small amount of dimethylformamide gave pure 1-(trimethylplumbyl)-1,2,3-benzotriazole (1.6 g).

Reaction between trimethylphenyltin and 1-*chloro*-1,2,3-*benzotriazole*

A benzene solution (25 ml) of trimethylphenyltin (1.5 g) was allowed to react with a solution of 1-chloro-1,2,3-benzotriazole (1.0 g) in benzene (25 ml) at 60° for 3 h. Evaporation of benzene and recrystallization of the residue from boiling acetone containing a small amount of dimethylformamide gave pure 1-(trimethylstannyl)-1,2,3-benzotriazole (1.6 g; 94% yield). M.p. 224–226° (lit. value[7]: 221.5–223°).

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