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HYDRIDE HYDROGEN-EXCHANGE BETWEEN ORGANOTIN AND -LEAD COMPOUNDS: FORMATION OF ORGANOLEAD HYDRIDE ADDUCTS

by

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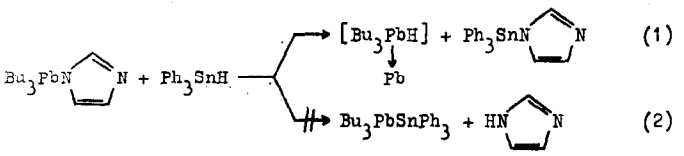
As part of our studies on hydrogenolytic reactions of organotin hydrides[1-3] the reaction of organolead compounds containing a lead--hetero bond with organotin hydrides was investigated. From the reaction of the pentacoordinated tributyllead imidazole[4] and triphenyltin hydride in tetrahydrofuran at room temperature triphenyltin imidazole[5] was isolated in high yield. Metallic lead rather than a well-defined organolead compound was formed as well. Apparently an exchange reaction (1) (cf. also ref. 6) rather than a hydrogenolysis reaction (2) has taken place, the organolead hydride being unstable un under the conditions applied:



Under appropriate conditions exchange reactions of type (3) offer a route for generating organolead hydrides which may be reacted

in situ with suitable reactants.

$$R_3PbX + R'_3SnH \rightleftharpoons R_3PbH + R'_3SnX \qquad (3)$$

Alkyllead hydrides have been previously prepared by $LiAlH_4$-reduction of alkyllead halides[7,8] in ether solvents at -60°C.

Reactions of type (3) are fast equilibrium reactions*. As appears from low-temperature NMR studies the equilibrium lies on the left side if X stands for chlorine, bromine, alkoxide[9] or thioalkyl and -aryl[4]. For organolead acetates, which because of their ready availability have mostly been used in our work, the equilibrium lies essentially on the right. Of course, by selectively removing the more readily reacting organolead hydride or the R'_3SnX compound formed, reaction (3) may be forced to completion.

Organolead hydride adducts have been prepared either by mixing the organolead derivative and the organotin hydride in T.H.F. at -80° followed by adding the unsaturated compound (method A), or by mixing the organolead derivative and the unsaturated component in T.H.F., followed by adding the organotin hydride at -20°C. (method B):

$$Bu_3PbOAc + Ph_3SnH \xrightarrow[H\text{-}C\equiv C\text{-}CN]{T.H.F.} \underset{Bu_3Pb}{\overset{H}{\diagdown}}C{=}C\overset{H}{\diagup}_{C\equiv N} + \underset{H}{\overset{H}{\diagdown}}C{=}C\overset{PbBu_3}{\diagup}_{C\equiv N} + Ph_3SnOAc \qquad (A)$$

$$Bu_3PbOAc + H\text{-}C\equiv C\text{-}COOMe \xrightarrow[Et_3SnH]{T.H.F.} \underset{Bu_3Pb}{\overset{H}{\diagdown}}C{=}C\overset{H}{\diagup}_{COOMe} + Et_3SnOAc \qquad (B)$$

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* Similarly, upon reacting triphenyltin hydride with compounds containing a tin-sulphur bond an exchange reaction[6] occurs exclusively. However, reactions with organotin alkoxides[6], diphenylphosphides[10] and -arsides[10] hydrogenolysis and exchange reactions take place simultaneously.

NMR spectroscopy of the reaction-mixture after removal of the organotin acetates or imidazoles by fractional crystallization revealed the formation of organolead adducts in 60-90% yield. In reactions with cyanoacetylene both the cis-β and the α-adduct were found to be present (cf. ref. 11). Methods (A) and (B) give approximately the same yield**.

TABLE I

Organolead adducts obtained via exchange reactions

Pb compound	Sn compound	Unsaturated comp.	cis β	α	yield
Bu_3Pb imidazole	Ph_3SnH	H-C≡C-CN	23%	77%	75%[a]
idem	Et_3SnH	idem	80	20	d
Et_3Pb imidazole	Ph_3SnH	idem	46	54	80
idem	Et_3SnH	idem	82[b]	18[b]	d
Bu_3Pb imidazole	Ph_3SnH	H-C≡C-COOMe	100	-	d
Bu_3PbOAc	Ph_3SnH	H-C≡C-CN	71	29	d
idem	Et_3SnH	H-C≡C-COOMe	100	-	70
idem	idem	H-C≡C-CN	25	75	60
Et_3PbOAc	Ph_3SnH	idem	16	84	94
idem	Et_3SnH	idem	3	70	62[c]

a) bp. 110-111°/0.2 mm; n_D^{20} = 1.5174 (mixture of isomers)

b) bp. 71-72°/0.1-0.2 mm; n_D^{20} = 1.5337 (idem)

c) a small amount of organotin adduct is formed as well.

d) not determined.

** Adding an ether suspension of $LiAlH_4$ to organolead halides in the presence of unsaturated reactants under similar conditions afforded organolead adducts in very poor yields.

Under the present conditions organolead hydrides are sufficiently more reactive towards the acetylenic compounds used than organotin hydrides to prevent the occurrence of competitive reactions of the latter. If these reactions are carried out at room temperature 10-20% of the corresponding organotin adducts[12] are found as well. In Table I the results of some experiments are summarized.

Starting from dibutyllead diacetate and triethyltin hydride similar adducts derived from dibutyllead dihydride have been obtained. Further work on the scope and preparative usefulness of this reaction is in progress.

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