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Preliminary Communication

Synthesis of α -alkoxyalkyltributyllead compounds *via* the reaction of tributylplumbyllithium with α -chloroethers, and the conjugate addition of tributylplumbyllithium to enones

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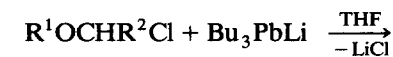
Abstract

α -Alkoxyalkyltributylleads **1** were prepared from the reaction of tributylplumbyllithium with α -chloroethers **2**. This procedure is more convenient than the conventional method which involves transmetalation from the corresponding α -alkoxyalkyltrialkyltin. Tributylplumbyllithium was also used for the synthesis of β -oxo-organolead **4**.

Previously we reported the diastereodivergent and asymmetric synthesis of 1,2-diol derivatives *via* the reaction of α -alkoxytrialkylleads with aldehydes [1]. More recently we demonstrated a new approach to the construction of β -alkoxy-substituted cyclic ethers *via* the intramolecular cyclization of ω -trialkyllead ether acetals [2]. In these syntheses α -alkoxyorganoleads act as important organometallic reagents, but their synthesis is difficult. A conventional procedure involves transmetalation from α -alkoxytins to α -alkoxyleads [1,2], which is not convenient and sometimes results in low yields.

We report a new synthetic method for α -alkoxyorganolead compounds (**1**); the reaction of α -chloroether compounds **2** with tributylplumbyllithium, that is prepared from $\text{Bu}_3\text{PbPbBu}_3$ and BuLi [3], produces α -alkoxyalkyltrialkyllead compounds in good to high

yields (eqn. (1)) [4]. The synthesis of **1a** is representative in this case. Hexabutylidiplumbum was prepared as



2a $\text{R}^1 = \text{CH}_3, \text{R}^2 = \text{H}$

b $\text{R}^1 = \text{CH}_3, \text{R}^2 = \text{H}$

c $\text{R}^1 = \text{CH}_2\text{Ph}, \text{R}^2 = \text{H}$

d $\text{R}^1 = \text{CH}_2\text{CH}=\text{CH}_2,$
 $\text{R}^2 = \text{CH}_2\text{CH}(\text{CH}_3)_2$

$\text{R}^1\text{OCHR}^2\text{PbBu}_3$

1a (92%)

b (81%)

c (87%)

d (61%)

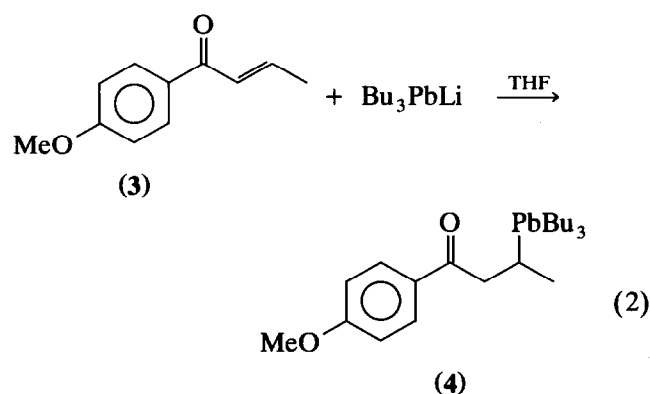
described previously [5] and stored in dry ether. Ether was removed under reduced pressure prior to use. To a stirred solution of $\text{Bu}_3\text{PbPbBu}_3$ (974 mg) in 5 ml of dry THF cooled at 0°C was added 0.7 ml of 1.62 M $n\text{-BuLi}$ in hexane. After 30 min, the resulting solution was cooled to -78°C and 70 μl of MOMCl (0.92 mmol) was added via a microsyringe. Stirring was continued for an additional 30 min and the mixture was allowed to warm to room temperature. The reaction was quenched by adding 0.1 ml of water. A small amount of K_2CO_3 was added to remove water. Filtration, concentration, and purification by column chromatography (10 g Merck SiO_2 , n-hexane:AcOEt:Et₃N = 100:3:1) gave 360 mg of **1a** (92% yield) as a colorless oil. ^1H NMR (270 MHz, CDCl_3): δ 4.375 (t, 2H, $J(\text{Pb-H}) = 14.5$ Hz), 3.290 (t, 3H, $J(\text{Pb-H}) = 2.0$ Hz), 0.8–1.9 (m, 27H, PbBu_3). IR (CCl_4): 2900, 1450, 1075 cm^{-1} . MS: Found, 379 ($\text{M}^+ - \text{CH}_3\text{OCH}_2$) $\text{C}_{14}\text{H}_{32}\text{OPb}$ calcd.: 423.

A similar procedure as above was used for the preparation of **1b–d**. **1b** (81% yield). ^1H NMR (CDCl_3): δ 4.455 (t, 2H, $J(\text{Pb-H}) = 15.5$ Hz), 3.5–3.56 (m, 2H), 3.4–3.5 (m, 2H), 3.376 (s, 3H), 0.8–1.8 (m, 27H). **1c** (87% yield). ^1H NMR (CDCl_3): δ 7.25–7.38 (m, 5H), 4.425 (t, 2H, $J(\text{Pb-H}) = 14.5$ Hz), 4.403 (t, 2H, $J(\text{Pb-H}) = 2.1$ Hz), 0.8–1.8 (m, 27H). **1d** (61% yield). ^1H NMR (CDCl_3): δ 5.97–5.82 and 5.28–5.10 (allylic protons, 3H), 3.98–3.77 (m, 3H), 0.8–1.0 (bs, 15H), 1.1–1.8 (m, 21H).

The α -alkoxyorganoleads thus prepared can be used for the synthesis of 1,2-diols [1]. It is evident that the

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present synthetic method via Bu_3PbLi is, in a certain case, superior to the previous transmetallation procedure, since the preparation of **1d** was not accomplished by the conventional method. Tributyllead lithium is a useful reagent, not only for the synthesis of α -oxygen substituted organoleads but also for the preparation of β -oxygen substituted organolead compounds. For example, the conjugate addition of Bu_3PbLi to the enone **3** proceeded smoothly to give **4** in 70% yield (eqn. (2)). To a THF solution of Bu_3PbLi , prepared from 1.0 g of Bu_6Pb_2 , was added a THF solution (4 ml) of **3** (138 mg) at -78°C . The mixture was stirred at -78°C for 30 min, and the reaction was quenched with a solution of HOAc (60 μl) dissolved in THF (2 ml). The mixture



was allowed to warm to room temperature, diluted with Et_2O , washed with sat. aqueous NaHCO_3 . The organic layer was separated, dried over anhyd K_2CO_3 , and concentrated under reduced pressure. Purification by column chromatography (10 g Merck SiO_2 , n-hexane: Et_3N = 100:1) gave 300 mg of **4** (70%) as a colorless oil. ^1H NMR (CDCl_3): δ 7.90–8.00 (m, 2H), 6.90–7.00 (m, 2H), 3.87 (s, 3H), 3.38 (dd, 1H, J = 7.1 and 16.1 Hz), 3.26 (dd, 1H, J = 7.7 and 16.1 Hz), 2.34 (qdd, 1H, J = 7.7, 7.1, and 7.9 Hz), 1.48 (d, 3H, J = 7.9 Hz), 0.8–1.8 (m, 27H). β -Oxo-alkylorganolead compounds such as **4** are a new class of homoenolates, whose reactivity is now under investigation.

References

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