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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 transmetallation 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 transmetallation 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 $Bu_3PbPbBu_3$ and BuLi [3], produces α-alkoxyalkyltrialkyllead compounds in good to high yields (eqn. (1)) [4]. The synthesis of **1a** is representative in this case. Hexabutyldiplumbum was prepared as described previously [5] and stored in dry ether. Ether was removed under reduced pressure prior to use. To a stirred solution of $Bu_3PbPbBu_3$ (974 mg) in 5 ml of dry THF cooled at 0°C was added 0.7 ml of 1.62 M ^nBuLi 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:Et_3N = 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(Pb–H) = 14.5 Hz), 3.290 (t, 3H, J(Pb–H) = 2.0 Hz), 0.8–1.9 (m, 27H, $PbBu_3$). IR (CCl_4): 2900, 1450, 1075 cm^{-1}. MS: Found, 379 ($M^+ - CH_3OCH_2$) $C_{14}H_{32}OPb$ calcd.: 423.

$$R^1OCHR^2Cl + Bu_3PbLi \xrightarrow[-LiCl]{THF} R^1OCHR^2PbBu_3$$

2a $R^1 = CH_3$, $R^2 = H$
b $R^1 = CH_3$, $R^2 = H$
c $R^1 = CH_2Ph$, $R^2 = H$
d $R^1 = CH_2CH{=}CH_2$, $R^2 = CH_2CH(CH_3)_2$

1a (92%)
b (81%)
c (87%)
d (61%)

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(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(Pb–H) = 14.5 Hz), 4.403 (t, 2H, J(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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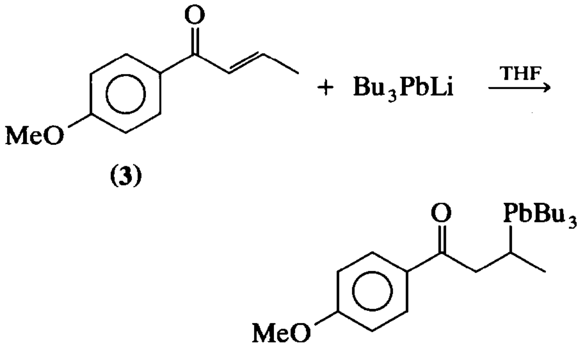
present synthetic method via Bu_3PbLi is, in a certain case, superior to the previous transmetallation procedure, since the preparation of **1d** was not accomplished by the conventional method. Tributyllead lithium is a useful reagent, not only for the synthesis of α-oxygen substituted organoleads but 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.



(2)

(4)

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