Journal of Organometallic Chemistry
Elsevier Sequoia S.A., Lausanne
Printed in The Netherlands

NOTE

A SYNTHESIS OF UNSYMMETRICAL ORGANOLEAD COMPOUNDS

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(Received June 6th, 1969)

One unsymmetrical organolead compound, benzyltriphenyllead, has been made in high yield from triphenylplumbylmagnesium chloride and benzyl chloride in tetrahydrofuran (THF). The lead-containing Grignard reagent was made from phenylmagnesium bromide and either lead(II) chloride or diphenyllead[1,2]. Low yields of tetraphenyllead and tetramethyllead, accompanied by much free lead, were obtained in a one-step reaction from lead(II) chloride, Grignard reagent and appropriate aryl of alkyl iodide in diethyl ether[3]. The yields of R_4Pb compounds by this one-step reaction were improved markedly by using an alkyllithium compound instead of a Grignard reagent[4,5].

We wish to report a convenient one-step method for the synthesis of unsymmetrical alkyl lead or alkyl vinyl lead compounds from a Grignard reagent, lead(II) chloride and an alkyl chloride. Yields of R_3PbR' compounds were high, product

$$3\,RMgX + PbCl_2 + R'Cl \rightarrow R_3PbR' + 3\,MgXCl$$

selectively was good, and little or no free lead was produced as a co-product. Moreover, the method is readily applicable to unsymmetrical alkyl aryllead compounds as well as symmetrical tetraalkyllead compounds. Some compounds made in high yields by this one-step procedure include methyltrivinyllead, allyltrimethyllead, methyltriphenyllead and tetramethyllead.

Effects of reaction variables on yield and purity of methyltrivinyllead were studied in depth. Optimum yield of the unsymmetrical compound was obtained when lead(II) chloride was added to a mixture of vinylmagnesium chloride and methyl chloride in THF at 0–5°. Yields were consistently around 95–100% (based on $PbCl_2$) and product purity was 98–99%; small amounts (1–2%) of dimethyldivinyllead always accompanied the main product. Addition of methyl chloride to Grignard reagent plus lead(II) chloride or addition of the Grignard reagent to lead(II) chloride plus methyl chloride resulted in yields of only 60–65% of total organolead compounds. Decreased yields were the result of increased formation of lead metal, up to 40%. Concomitant with low yields was a significant drop in reaction selectively; methyltrivinyllead represented only 50–55% of the product, the remainder of the product being tetravinyllead and dimethyldivinyllead.

The yield of methyltrivinyllead was not especially sensitive to temperature. Generally, the temperature was kept somewhere in the range of 5–25°. The molar ratio of $RMgX/PbCl_2/RCl$ was at least 3/1/1 and generally was about 3/1/3. Ratios of RMgX to $PbCl_2$ as high as 4/1 did not adversely affect either the yield of R_3PbR' or the selectivity of the reaction.

The relative reactivities of methyl- and vinylmagnesium chloride were briefly investigated. When lead(II) chloride was added to equivalent amounts of the two Grignard reagents and methyl chloride, mixed methyl vinyl lead compounds containing 15% vinyl groups were formed. Thus, methylmagnesium chloride reacted significantly faster than vinylmagnesium chloride.

With a reactive chloride like allyl chloride, a much lower reaction temperature was employed and the mode of addition was modified. Lead(II) chloride was added to the Grignard at −55°; then the allyl chloride was added and the mixture was permitted to warm to ambient temperature. The yield of mainly allyltrimethyllead was 75%.

The previous formation of triphenylplumbylmagnesium bromide[1,2] from lead(II) chloride, diphenyllead and phenylmagnesium bromide, suggests that, in the one-step reaction, $R_3PbMgCl$ complexes are formed also as intermediates in THF and that the lead-containing Grignards then react with the alkyl chloride. This reaction path is consistent with the need to add lead(II) chloride to the Grignard reagent at a low temperature or in the presence of the alkyl chloride to obtain high yields of R_4Pb or R_3PbR' compounds. Further studies on the mechanism of the reaction of alkyl Grignard reagents with lead(II) chloride will be reported by another investigator.

EXPERIMENTAL

General comments

All reactions with Grignard reagents were run under a nitrogen atmosphere. Methyl- and vinylmagnesium chloride were prepared in THF at 55° from the organic chloride. A temperature of 63–65° was employed for phenylmagnesium chloride. All Grignard reactions were initiated with a small amount of 1,2-dibromoethane. Tetrahydrofuran was dried by $NaAlH_4$ and stored in a nitrogen box after distillation.

Total organic lead (upon which yields were based) was determined by the dithizone method[6]. Lead alkyl compositions were determined by gas–liquid chromatography (GLC) at 80° on a 4-foot, 1/4 inch column of tricresyl phosphate on Chromosorb W. Whenever possible Grignard concentrations were determined by gas evolution, otherwise, the single acid titration method was used.

Satisfactory lead analyses were obtained for the new compounds methyltrivinyllead and allyltrimethyllead. Methyltriphenyllead was characterized by a mixture melting point with an authentic sample[7].

Methyltrivinyllead

To 0.200 mole of vinylmagnesium chloride and 7.8 g (0.155 mole) of methyl chloride in THF at 5° were added 13.9 g (0.05 mole) of lead(II) chloride in small portions during 14 minutes and with rapid stirring. The lead(II) chloride was fed from a small flask connected to the main reactor by large rubber tubing. The mixture was allowed to warm to 25° and was stirred at this temperature for 15 min. The reaction mixture was hydrolyzed at 10° with aqueous ammonium chloride and the hydrolyzed mixture was steam-distilled. The distillate was flooded with water. The lower organic lead layer was separated and combined with a hexane extract of the aqueous layer.

Total organic lead was 11.1 g (96% based on $PbCl_2$); GLC analysis indicated 98.2 wt. % methyltrivinyllead and 1.8 wt. % dimethyldivinyllead, b.p. 84° (85 mm).

Methyltriphenyllead

Lead(II) chloride, 11.1 g (0.04 mole), was added to 0.132 mole of phenylmagnesium chloride and 7.7 g (0.152 mole) of methyl chloride in 100 ml of THF at 25°. The mixture was hydrolyzed and the product extracted with n-hexane. Lead analysis of the extract indicated 18.8 g (96% based on $PbCl_2$) of methyltriphenyllead. Solvent was evaporated to leave a white solid, m.p. 60–62° C.

Allyltrimethyllead

Lead chloride, 16.7 g (0.06 mole), was added to 0.2 mole of CH_3MgCl in THF at −55° during 8 min. Then 5.4 g (0.07 mole) of allyl chloride was added and the mixture was allowed to warm to ambient temperature during 25 min. Following hydrolysis and steam distillation 9.3 g (75%) of allyltrimethyllead containing little tetramethyllead was obtained. The allyl derivative was distilled, b.p. 27–30° (0.1 mm), before analysis. Even after distillation the product contained a small amount of tetramethyllead.

Tetramethyllead

To 0.16 mole of methylmagnesium chloride and excess methyl chloride was added 13.9 g (0.05 mole) of lead(II) chloride in 150 ml of THF at 5° during 30 min. Work-up, as for methyltrivinyllead, afforded 12.3 g (93%) of tetramethyllead.

Reaction of lead(II) chloride and methyl chloride with mixed methyl- and vinylmagnesium chlorides

Lead(II) chloride, 8.35 g (0.03 mole), was added during 12 min to 0.095 mole of methylmagnesium chloride, 0.095 mole of vinylmagnesium chloride and 7.8 g (0.15 mole) of methyl chloride at 5°. The mixture was stirred at 5° for 15 min and then at 25° for 15 min before hydrolysis with aqueous ammonium chloride. Work-up as described in the preceding experiment afforded 5.9 g (94%) of organic lead. Composition of the product was: tetramethyllead, 48.6 wt. %; trimethylvinyllead, 41.3 wt. % and dimethyldivinyllead, 10.1 wt. %. Total vinyl content was 15%.

ACKNOWLEDGEMENT

Analytical assistance from S. R. Henderson and experimental help from Dr. K. C. Williams are greatly appreciated.

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