PREPARATION OF CONJUGATED BUTADIENYLLEAD AND -TIN COMPOUNDS

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(Received August 11th, 1969; in revised form November 26th, 1969)

SUMMARY

The preparation of a new class of compounds containing organolead substituents located at the 1 and 2 positions of butadiene is described: triethyl(1,3-butadien-2-yl)lead, triphenyl(1,3-butadien-2-yl)lead, triphenyl(1,3-butadien-1-yl)lead. The new technique developed for the preparation of these compounds from 1-chloro-1,3-butadiene was also effective in the preparation of the corresponding butadienyltin compounds.

INTRODUCTION

As part of our effort to prepare various types of organolead-substituted hydrocarbons, organolead compounds containing small rings (with lead attached[1], incorporated[2], or spiro[3] relative to the ring) and vinyl groups[4] have been synthesized. A new class of organolead compounds containing butadienyl groups with the organolead substituents attached at the 1 and 2 positions is now described.
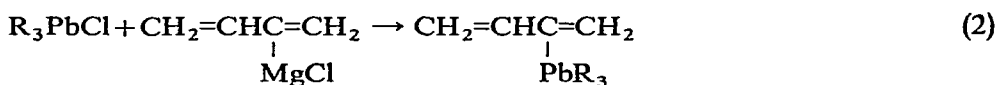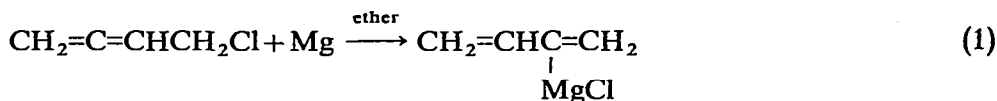
The synthesis of butadienyllead compounds presents a novel synthetic problem. The more traditional means of synthesizing 1,3-butadienyl functional compounds are unacceptable because of the ease of cleavage of unsaturated groups from lead, the low reactivity of the butadienyl halides, and the ease of polymerization of butadienes, particularly in the presence of active metal catalysts. The only previously reported butadienyl–heavy metal derivative of a Group IV element is tri-n-butyl(1,3-butadien-2-yl)tin[5]. We have prepared triethyl(1,3-butadien-2-yl)lead, triphenyl(1,3-butadien-2-yl)lead, triphenyl(1,3-butadien-1-yl)lead by methods generally applicable to other Group IV metals as illustrated by the preparation of tri-n-propyl(1,3-butadien-1-yl)tin.

RESULTS AND DISCUSSION

Triethyl(1,3-butadien-2-yl)lead and triphenyl(1,3-butadien-2-yl)lead were prepared by a method analogous to that used by Aufdermarsh in the preparation of tri-n-butyl(1,3-butadien-2-yl)tin[5], *i.e.*, the reaction of (1,3-butadien-2-yl)magnesium chloride with the corresponding trialkyl- or triarylmetal chloride.

TABLE 1

Compound	Appearance and b.p. [°C(mm)] or m.p. (°C)	Analysis found (calcd.) (%) C	H	Major IR peaks					Treatment with alcoholic $AgNO_3$
$Et_3PbC=CH_2$ $-CH=CH_2$	Pale yellow liquid 44–50(1–2)	34.76 (34.58)	6.04 (5.80)	1850	1160	1380	1640	1590	Green $\longrightarrow$ black
$Ph_3PbC=CH_2$ $-CH=CH_2$	White solid 54–56	54.12 (53.75)	4.11 (4.11)	1850			1640	1590	Yellow $\overset{slow}{\longrightarrow}$ black
$Ph_3PbCH=CHCH=CH_2$	White solid 160	53.26 (53.75)	4.72 (4.11)	1820				1590	Green $\longrightarrow$ black
$Pr_3SnCH=CHCH=CH_2$	Colorless liquid 80–90(1–2)	51.77 (51.88)	8.56 (8.64)	1820		1380		1590	Green $\overset{blue}{\longrightarrow}$ black
$Et_3PbCH=CHCH=CH_2$	Pale yellow liquid 45–50(0.5)			1850	1160	1380		1590	Brown $\longrightarrow$ black

$$CH_2=C=CHCH_2Cl + Mg \xrightarrow{\text{ether}} CH_2=CHC=CH_2 \atop \qquad\qquad\qquad\qquad\qquad\quad MgCl \tag{1}$$

$$R_3PbCl + CH_2=CHC=CH_2 \rightarrow CH_2=CHC=CH_2 \tag{2} \atop \qquad\qquad\qquad MgCl \qquad\qquad\qquad PbR_3$$

Triphenyl(1,3-butadien-1-yl)lead, triethyl(1,3-butadien-1-yl)lead and tri-n-propyl(1,3-butadien-1-yl)tin were prepared in $\sim 20\%$ yield by a new procedure: the reactions of triphenylplumbyllithium, triethylplumbyllithium, and tripropylstannyllithium with 1-chloro-1,3-butadiene.

$$R_3MLi + ClCH=CHCH=CH_2 \rightarrow R_3MCH=CHCH=CH_2 \tag{3} \atop \textit{trans (cis)}$$
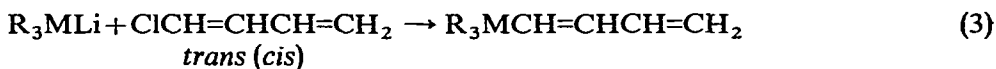
Efforts to extend the Grignard method of synthesis to 1,3-butadien-1-yl systems have all failed because of the lack of reactivity of 1-chloro-1,3-butadiene toward the formation of the Grignard reagent, (1,3-butadien-1-yl)magnesium chloride. This Grignard reagent failed to form in ether, tetrahydrofuran, or diglyme as solvents, and iodine or ethylmagnesium bromide as catalysts. The reaction illustrated in eqn. (3) seems to reflect an unusual reactivity toward substitution for such an unsaturated halide. A marked increase in the ease of substitution of *trans*-1-chloro-1,3-butadiene over *cis*-1-chloro-1,3-butadiene was noted. The analyses, IR data, and other pertinent physical data are given in Table 1. It is interesting to note that while tri-n-propylstannyllithium and *cis*-1-chloro-1,3-butadiene reacted to yield tri-n-propyl(1,3-butadien-1-yl)tin, reactions more subject to steric hindrance, namely, the preparation of butadienyllead compounds from triethylplumbyllithium or triphenylplumbyllithium and *cis*-1-chloro-1,3-butadiene, failed.

Heasley and Lais[6] and Viehe[7], in studies relating *cis* and *trans*-1-chloro-1,3-butadiene postulate a degree of bonding between the chlorine atom and the vinylic 3-hydrogen atom in *cis*-1-chloro-1,3-butadiene that is absent in the *trans* isomer. This could be accounted for by the fact that the *trans* isomer may be more reactive toward
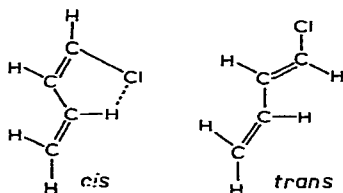
substitution than the *cis* isomer. Thus, whereas Newman's rule of 6 applies to saturated compounds, a rule of 5 would apply to conjugated dienes accounting for the bonding shown in the *cis* compound with resultant inhibition toward reaction. Our work supports this postulate in that the reaction of *cis*-1-chloro-1,3-butadiene with triorganoplumbyllithium failed to yield butadienyllead compounds, while the reaction of triphenyl- or triethylplumbyllithium and *trans*-1-chloro-1,3-butadiene yielded 20% of the substitution products, triphenyl(1,3-butadien-1-yl)lead and triethyl(1,3-butadien-1-yl)lead, respectively. In the case of the more stable triorganostannyllithium compounds, the difference in the reactivity of the *cis*- and *trans*-chloro-

butadiene was not studied.

Gas chromatography was used for separation of the liquid products, with exception of triethyl(1,3-butadien-1-yl)lead, which underwent decomposition. The latter compound was identified by cleavage by acetic acid which gave butadiene (93 %) and triethyllead acetate. Examination by thin layer chromatography indicated that separation by solution chromatographic techniques was not promising.

The comparative IR data reported in Table 1 were obtained using a Perkin Elmer Model 137 spectrophotometer. All of these unsaturated compounds showed a peak at 1850–1820 cm^{-1} ascribed to the unsaturated carbon–to–carbon bond over-tone. Strong, sharp absorption also was found in the 1640–1560 cm^{-1} area ascribed to carbon–to–carbon double bond stretching vibration. The 2-substituted conjugated butadienes showed doublets in this region. Absence of absorption at 1380 cm^{-1} in the spectrum of triphenyl(1,3-butadien-2-yl)lead and triphenyl(1,3-butadien-1-yl)lead was ascribed to absence of the symmetrical vibration of the CH_3–C group in this compound, as distinguished from the other compounds in the group. Only triethyl(1,3-butadien-2-yl)lead and triethyl(1,3-butadien-1-yl)lead showed a peak at 1160 cm^{-1} which has been associated with the ethyl-to-lead group absorption[4].

A study of the polymerization of these butadienyllead compounds and other related compounds is presently underway.

EXPERIMENTAL

Starting materials

trans-1,4-Dichloro-2-butene was obtained from Matheson Company, Inc., and used as received. *cis*-1-Chloro-1,3-butadiene was prepared by the procedure of Muskat and Northrup[8], and was subsequently rearranged to *trans*-1-chloro-1,3-butadiene by the procedure described by Onishchanko[9]. 4-Chloro-1,2-butadiene was prepared by the procedure of Carothers, Berchet, and Collins[10]. Tetraethyllead was obtained from the Ethyl Corporation and used as received. Tri-n-propyltin chloride was obtained from Alpha Inorganics, Inc., and was used as received. Triethyllead chloride[11] and triphenyllead chloride[12] were synthesized by the established procedures of Gilman and Robinson. Powdered lithium was purchased from Fine Inorganic Chemical, Inc., and stored under argon. Tetrahydrofuran was purified by distillation from lithium aluminum hydride. Tripropylstannyllithium[13], triphenylplumbyl-lithium[14], and triethylplumbyllithium[14] were prepared by established procedures.

Gas chromatography

The analytical samples of triethyl(1,3-butadien-2-yl)lead and tri-n-propyl(1,3-butadien-1-yl)tin were obtained by gas–liquid chromatography (GLC). Triethyl(1,3-butadien-1-yl)lead was shown to undergo decomposition during chromatography. The chromatography used was an Aerograph Manual Temperature Programmer gas chromatograph, model A-90-P, the column, a 3′ × ¼″ piece of aluminum tubing packed with 10 % diisodecyl phthalate on 45/60 mesh chromosorb P. The injector temperature was 125°, the oven temperature was 110°, and the detector temperature was 145°. The flow rate was 35 ml per min.

Preparation of triethyl(1,3-butadien-2-yl)lead

These reactions generally were carried out in a 500 ml, three-necked flask,

fitted with a ground glass sleeved, motor driven stirrer, a pressure equalizing dropping funnel, and a West reflux condenser, topped with a nitrogen inlet tube. The entire system was flushed with nitrogen and kept under a slight positive pressure of nitrogen throughout the preparation.

The Grignard reagent, (1,3-butadien-2-yl)magnesium chloride, was prepared according to the published procedure[5] from 13 g (0.15 mole) of 4-chloro-1,2-butadiene and 3.65 g (0.15 g-atom) of magnesium turnings in 75 ml of diethyl ether. The Grignard solution was refluxed for 2 h after spontaneous reflux had stopped, cooled with an ice bath and then 200 ml of dry benzene was added. To this solution was added, in small amounts, 50 g (0.15 mole) of triethyllead chloride. The resulting reaction mixture was refluxed for 8 h and subsequently cooled to 0° and carefully hydrolyzed with water. The benzene layer was separated, dried over calcium sulfate and decanted. Hydroquinone was added as an inhibitor, and the mixture of solvents removed using a rotary evaporator. The residual high boiling liquid was distilled under vacuum, and the distillate obtained was fractionally distilled under vacuum to give 18–20 g (40%) of triethyl(1,3-butadien-2-yl)lead, b.p. 44–50°/1–2 mm. The analytical sample was isolated by GLC.

Triethyl(1,3-butadien-2-yl)lead reacted with alcoholic silver nitrate in a very distinctive manner. While most lead alkyls give an immediate black precipitate of silver upon reaction with alcoholic silver nitrate, this butadienyllead compound reacts with alcoholic silver nitrate to give a brilliant yellowish-green solution which subsequently turns black.

Preparation of triphenyl(1,3-butadien-2-yl)lead

Triphenyl(1,3-butadien-2-yl)lead was prepared in the same manner on a 0.034 mole scale, using triphenyllead chloride. Upon completion of the reaction, the solvents were removed by rotary evaporation and the remaining residue was distilled (Hickman Still) to give 5–6 g (35%) of triphenyl(1,3-butadien-2-yl)lead, m.p. 54–56°.

The analytical sample was isolated by distillation (Hickman Still) and subsequent recrystallization from ligroin, b.p. 60–90°. Triphenyl(1,3-butadien-2-yl)lead gave very distinctive canary yellow color on treatment with alcoholic silver nitrate.

Preparation of tri-n-propyl(1,3-butadien-1-yl)tin

Tripropylstannyllithium was prepared under argon from 2.1 g (0.3 g-atom) of lithium and 17 g (0.6 mole) of tri-n-propyltin chloride according to the procedure of Gilman *et al.*[11], and filtered in an inert atmosphere. *cis*-1-Chloro-1,3-butadiene, 8.8 g (0.10 mole), in 10 ml of tetrahydrofuran was added dropwise with stirring to the filtered solution. A slight exothermic reaction occurred, after which the solution was refluxed for 4 h. The solvents were removed under vacuum, and the residue was fractionally distilled under vacuum, yielding approximately 5 g (20% estimated by GLC analysis) of tri-n-propyl(1,3-butadien-1-yl)tin, b.p. 80–90°/1–2 mm. The analytical sample was isolated by GLC.

Upon treatment with alcoholic silver nitrate, tri-n-propyl(1,3-butadien-1-yl)tin gave a green color which subsequently changed to black and then to blue.

Preparation of triphenyl(1,3-butadien-1-yl)lead

Triphenylplumbyllithium was prepared from 9.47 g (0.02 mole) of triphenyllead chloride[12] and 0.169 g (0.10 g-atom) of lithium in 40 ml of tetrahydrofuran

according to the procedure of Tamborski[14]. The solution was filtered under argon through glass wool. trans-1-Chloro-1,3-butadiene[7], 4.4 g (0.05 mole) in 10 ml of tetrahydrofuran, was then added to the filtered solution, and the mixture was stirred for 15 h. Hydrolysis with water followed. The reaction mixture was extracted with three 75 ml portions of diethyl ether. The combined ether extracts were dried over anhydrous calcium sulfate and concentrated under reduced pressure to yield 4.4 g of crude yellow-white solid which was dissolved in a mixture of absolute ethanol/ dioxane (in which tetraphenyllead shows only slight solubility), treated with charcoal, filtered, and cooled. The yellow-white solid which precipitated was removed by filtration. This material (0.62 g) melted at 210–225°, and its IR spectrum was identical to that of tetraphenyllead (lit. m.p. 225°)[10].

The filtrate from above was concentrated, and water was added until cloudiness appeared and precipitation of the product occurred. The mixture was filtered, and the product was collected on a fritted disk to yield 40% (3.78 g) of white product, m.p. 160°. Upon treatment with alcoholic silver nitrate, triphenyl(1,3-butadien-1-yl)- lead gave a green color which subsequently changed to black.

Preparation and selective cleavage of triethyl(1,3-butadien-1-yl)lead

Triethylplumbyllithium was prepared from 1.38 g (0.20 g-atom) of powdered lithium and 32.9 g (0.10 mole) of triethyllead chloride in 120 ml anhydrous tetrahydro- furan according to the procedure of Tamborski[14]. The yellow-green solution was filtered through glass wool. It is extremely important that air be excluded during this part of the experiment to prevent decomposition resulting in deposition of metallic lead. In runs where this occurred, no product was obtained. To the filtered solution was added dropwise 13.2 g (0.15 mole) of trans-1-chloro-1,3-butadiene in 50 ml tetrahydrofuran during 1 h. The mixture was stirred for an additional hour and then was hydrolyzed with 200–300 ml of water whereupon the dark green solution turned to reddish-brown. The product was extracted with three 100 ml portions of diethyl ether. The combined ether extracts were dried over anhydrous calcium sulfate, and the solvents were removed under reduced pressure to yield 17 g of crude yellow solution. This crude material was distilled (Hickman Still) under vacuum. The result- ing distillate was fractionally distilled to yield 14 g (40%) of a pale yellow liquid (b.p. 45–50°/0.5 mm). Purification by GLC failed due to decomposition of the plumbane. A sample of the crude distillate was analyzed, but the sample obviously was impure. (Found: C, 37.62; H, 6.55. $C_{10}H_{20}Pb$ calcd.: C, 34.58; H, 5.80%.) The IR spectrum of the crude triethyl(1,3-butadien-1-yl)lead showed a prominent sharp peak at 1560 cm^{-1} attributed to carbon-to-carbon double bond stretch vibration and strong, sharp peaks at 970 and 920 cm^{-1} attributed to a terminal vinyl group. Upon treat- ment with alcoholic silver nitrate, the triethyl(1,3-butadien-1-yl)lead gave a brown color which then turned to black.

The substance was further characterized by cleavage with glacial acetic acid (3% excess) in tetrahydrofuran with silica gel as a catalyst. Within a few minutes, gas began to evolve. The temperature was raised to 50° to speed evolution and within an hour the cleavage produced 93% butadiene and triethyllead acetate. The gas was identified as butadiene by IR which also indicated absence of any appreciable amount of ethane. The crystals of triethyllead acetate after recrystallization from hexane melted at 160°.

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