Journal of Organometallic Chemistry
Elsevier Publishing Company Amsterdam
Printed in The Netherlands

NEW REACTIONS OF ORGANOLEAD COMPOUNDS NOT INVOLVING LEAD–CARBON BOND CLEAVAGE

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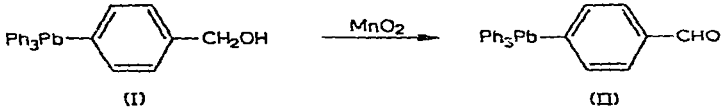
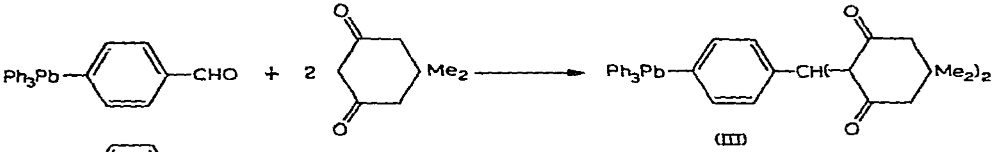
(Received March 31st, 1966)

Few reactions of organolead compounds not involving cleavage of the lead–carbon bond are known and most of these involve unsymmetrical compounds. Two examples of the reaction of symmetrical compounds are the reaction of tetrakis-[*p*-(dimethylamino)phenyl]lead with dimethyl sulphate to form a quaternary ammonium salt[1], and the recently described unusual addition compounds formed by the action of dinitrogen tetra-oxide on certain tetraalkylleads[2]. Examples of the reactions of unsymmetrical compounds mostly involve oxidation of unsaturated carbon linkages[3] or primary alcoholic groups attached to the benzene ring[4]. Cleavage frequently accompanies the oxidation[3,4]. The coupling of several unsymmetrical hydroxy- and aminoaryllead compounds with diazonium salts has been described[5].



(I) (II)



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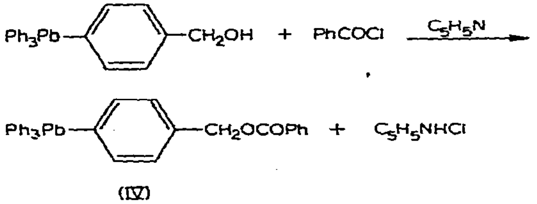

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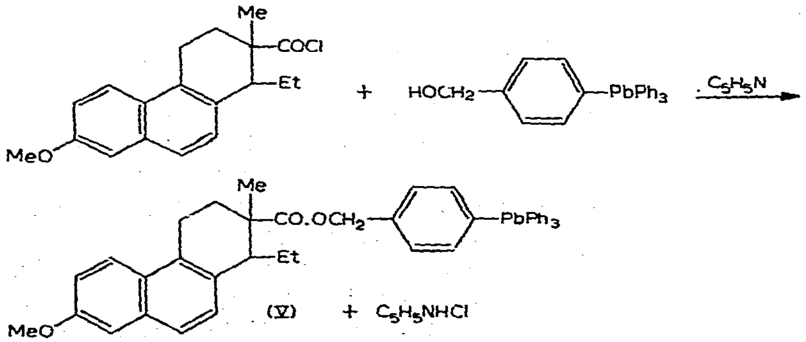

(V)

Some reactions of [*p*-(hydroxymethyl)phenyl]triphenyllead (I) are summarised as follows: oxidation to the corresponding aldehyde can be followed by reaction with 5,5-dimethyl-1,3-cyclohexanedione. Esterification of the alcohol (I) with benzoyl chloride and (±)-*cis*-7-methylbisdehydrodoisynolyl chloride was carried out. The benzoate is dimorphic and crystallizes from alcohol as a mixture of prisms (m.p. 102–103°) and needles (m.p. 86–87°).

An attempt to oxidize the aldehyde with silver oxide failed and the aldehyde was recovered.

Thin-layer chromatography was used to aid evaluation of the reaction mixtures and determine the purity and probable identity of some of the products. For example, the $Ph_3PbC_6H_4R$-*p* compounds where R = CH_2OH, CHO or CH_2OCOPh showed increasing R_f value in the given order as would be expected. Tetraphenyllead, the benzoate and the steroid ester referred to all had high R_f values relative to the aldehyde and alcohol, as would be expected. Actual R_f values are not quoted as these were not sufficiently reproducible under the conditions used. 250 μ Silica gel G layers were used throughout. Ethanol/benzene 1:99 proved to be a suitable solvent and iodine vapour was in most cases used as the chromogenic reagent.

TABLE 1

CHARACTERISTIC GROUP FREQUENCIES OF $Ph_3PbC_6H_4R$ IN cm^{-1}

R	*OH*	*C=O*	*C(O)-H*	*CH_2*
$-CH_2OH$	3295s			2840–2960w
-CHO		1705s	(2740m) (2840m)	
$-CH_2OCOPh$		1730s		(2860m) (2940m)

The alcohol, aldehyde and benzoate have been examined spectroscopically using IR and NMR techniques. The IR spectra (Table 1) were recorded using hexachlorobutadiene and Nujol mulls. The appearance in (II) of two bands at 833 cm^{-1} and 812 cm^{-1} confirms the presence of the *p*-benzaldehyde ring, the latter band being characteristic of *p*-substituted benzaldehydes[6]. The aldehyde derivative (III) showed loss of the C=O band at 1705 cm^{-1} and appearance of new characteristic bands. The benzoate of the alcohol (IV) showed loss of the OH band and appearance of the C=O band and other strong bands characteristic of benzoates[7] at 1269 cm^{-1} and 1107 cm^{-1}. The NMR spectra were run in carbon tetrachloride 15% w/v with tetramethylsilane as an internal standard, a Perkin Elmer 60 Mc instrument being used. The alcohol showed a singlet at 7.80 τ which can be assigned to the hydrogen atom of the OH group, and a single peak at 5.57 τ attributed to the methylene resonance. The broad OH proton resonance ($\omega_{0.5}$ 6 c/s), and the absence of splitting may have been due to a trace of hydrogen chloride in the solvent. The aromatic proton resonance showed complex splitting centred at 2.6 τ. Integration of the peak areas showed a ratio of 1:2:19 respectively (theoretically 1:2:19). The aldehyde showed a single peak to low field at 0.12 τ attributed to the aldehydic proton resonance, and complex splitting of the aromatic proton resonance centred at 2.6 τ including a strong sharp peak at 2.23 τ. Average integration of peak areas gave a ratio of 1:4:17 for CHO proton:

peak at 2.23 τ: remaining aromatic resonance. If the peak at 2.23 τ was due in some complex way to the protons on the aldehydric ring, the theoretical figure would be 1 : 4 : 15, but further investigation is necessary for detailed interpretation. The benzoate showed a single peak at 4.68 τ attributed to the methylene resonance and complex splitting of the aromatic resonance centred at 2.55 τ. Integration gave a ratio of 24 : 2 (theoretically 24 : 2).

EXPERIMENTAL

Starting materials

p-Bromobenzyl alcohol was prepared in a similar way to that used by Field and Grundy[8] for the *o*- and *m*-isomers. A stirred suspension of *p*-bromobenzoyl chloride (52.2 g, 1 mol.) in ether (220 ml) at −20 to −30° was reduced by adding a suspension of lithium aluminium hydride (17.9 g, 2 mol.) in ether (250 ml) in portions down the condenser. The mixture was heated under reflux on a water bath for 2 h, cooled to about −20°, and decomposed with water and dilute sulphuric acid in the usual manner. Further ether was added to replace that lost in the reaction, and the ethereal extract was washed with bicarbonate solution and water and dried over magnesium sulphate. Ether was removed on a water bath and finally at 20°/16 mm to leave an off-white crystalline solid (41.5 g, 93%), m.p. 76.8–78°. The crude product (40.5 g) was recrystallized from petroleum (b.p. 60–80°) yielding *p*-bromobenzyl alcohol (39.0 g) m.p. 76.7–77.7°, lit. m.p. 76–77°, 77–78°.

[*p*-(Hydroxymethyl)phenyl]triphenyllead was prepared in 60% yield by the method of Gilman and Melstrom[4] from triphenyllead chloride (27.9 g, 1 mol.), and the dilithium compound formed from *p*-bromobenzyl alcohol (14.3 g, 1.3 mol.) in ether (40 ml) and n-butyllithium (9.8 g, 2.6 mol.) in ether (200 ml), in a nitrogen atmosphere. Purification was effected by recrystallization from ethanol/water and petroleum (b.p. 60–80°) containing a little chloroform. Contrary to Gilman and Melstrom's findings, the crude material was completely soluble in hot ethanol and hence no tetraphenyllead was isolated at this stage.

*p-(Triphenylplumbyl)benzaldehyde**

A solution of [*p*-(hydroxymethyl)phenyl]triphenyllead (1.6 g, 1 mol.) in dry ether (19 ml) was shaken mechanically with a suspension of Hopkins and Williams "precipitated" manganese dioxide** (4.8 g) for 21.5 h. The solution was filtered and the residue washed with chloroform, the washings being added to the filtrate. Most of the solvent was removed on the steam bath and finally at 20°/16 mm to leave a white crystalline solid, which was recrystallized from absolute ethanol to give *p*-(triphenylplumbyl)benzaldehyde (0.80 g, 50%) as white crystals m.p. 110.5–112° (*uncorr.*). (Found: C, 55.1; H, 3.6. $C_{25}H_{20}OPb$ calcd.: C, 55.25; H, 3.7%.) The mother liquors yielded further crude product (0.35 g), but neither the alcohol nor any aldehyde was obtained by Soxhlet extraction of the residue with alcohol.

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* Procedure based on the method of Harfenist, Bavley and Lazier[9].

** The type of manganese dioxide used has a marked effect on the reaction[9].

5,5 Dimethyl-1,3-cyclohexanedione (dimedone) derivative of p-(triphenylplumbyl)-benzaldehyde

The aldehyde (0.10 g, 1 mol.) was added to a solution of dimedone (0.06 g, 2.4 mol.) in absolute ethanol (2.5 ml). The mixture was warmed until a clear pale yellow solution was obtained. After 2.5 h at 23° and 1.75 h at 35°, the crystalline material (0.073 g) which had formed was removed by centrifuging. After addition of water (0.8 ml) to the mother liquor, warming, cooling, scratching and standing for 72 h a solid (0.060 g) was formed, and on isolation by centrifuging this was combined with the crystals obtained previously. Recrystallization of the crude solid (0.133 g, 90%) from 95% ethanol yielded {*p*-[bis(4,4-dimethyl-2,6-cyclohexanedionyl)methyl]-phenyl}triphenyllead as white crystals m.p. 161.5–163° with some decomposition. (Found: C, 61.2; H, 5.3. $C_{41}H_{42}O_4Pb$ calcd.: C, 61.1; H, 5.2%.)

Attempted oxidation of p-(triphenylplumbyl)benzaldehyde with silver oxide

To 0.1 *N* silver nitrate (1.6 ml) 2 *N* sodium hydroxide (2 drops) was added. Ammonium hydroxide (2 *N*) was then added dropwise until the precipitate just dissolved. This solution was added to the aldehyde (0.050 g, 1 mol.) and the mixture heated on the steam bath. After 3 h, the black precipitate was filtered off and washed with 3 × 0.5 ml hot ethanol the washings being added to the filtrate. The filtrate was then made just acid to litmus with dilute nitric acid. The precipitate was removed by centrifuging, washed once with water, and recrystallized from ethanol/water to give white crystals of the aldehyde as shown by thin layer chromatography (TLC) (solvent: chloroform/ethanol 99 : 1, iodine vapour for visualization).

Esterification of [p-(hydroxymethyl)phenyl] triphenyllead

(a) With benzoyl chloride. The hydroxy compound (4.0 g, 1 mol.) was dissolved in pyridine (16 ml), and benzoyl chloride (0.93 ml, 1.1 g, 1.1 mol.) was added. After 1 h, further benzoyl chloride (0.1 ml) was added, whereupon there was a pink colouration turning pale yellow after a short time. After a further 2 h, the white precipitate was filtered off, washed with ether and dried at 20°/14 mm to give mainly pyridine hydrochloride (0.71 g, 0.84 mol.). The filtrate was poured into an ice/water mixture containing acetic acid (15 g). The oil was extracted with ether, washed with 10% acetic acid, water, saturated bicarbonate solution and finally again with water, and dried over magnesium sulphate. The ethereal solution was filtered and the ether removed on the steam bath and finally at 20°/10 mm to leave an oil which became a white solid (3.73 g) by recrystallization from absolute ethanol. The solid was dissolved in ethanol at 70° to yield on cooling very slowly a mixture of two crystalline types: needles (0.2 g), m.p. 86–87°, and prisms (2.0 g), m.p. 102–103°, which were separated by hand picking. The prism material was recrystallized from hot alcohol to yield mainly the needle form, and some prism form. All of the material was dissolved in the hot mother liquor and seeded with pure prism material to yield the prism form (1.76 g) only. Some of this material (0.90 g) was dissolved in about half the hot mother liquor and seeded with pure needle material to yield only the needle form (0.93 g). Thin layer chromatography showed the two crystalline forms to have the same R_f value. Infra-red spectra (using a Nujol mull) showed small differences. These might be attributable to the different crystalline structure, but no evidence for this was obtained. Analytical data

were indentical. (Needle form found: C, 59.3; H, 4.1; Pb, 31.8. Prism form found: C, 59.2; H, 4.1; Pb, 31.7. $C_{32}H_{26}O_2Pb$ calcd.: C, 59.1; H, 4.0; Pb, 31.9%.)

(b) With (±)-cis-7-methylbisdehydrodoisynolic acid. The acid chloride of the steroid was prepared[10] in 82% yield from the steroid (1.00 g, 1 mol.) and oxalyl chloride (2.5 g, 6 mol.) in benzene (20 ml). After 3 days the mixture was warmed to 30° for 3 h. Volatile matter was removed at 20°/12 mm. The crude solid was recrystallized from benzene/petroleum to give pale yellow crystals (0.87 g), m.p. 143–147° with decomposition (reported[10] m.p. 143–145° with decomposition).

[*p*-(Hydroxymethyl)phenyl]triphenyllead (1.40 g, 1 mol.) was dissolved in pyridine (4 ml) and the solution cooled in ice. The acid chloride (0.87 g, 1.1 mol.) in pyridine/benzene (3 ml/11 ml) was added. The mixture was kept overnight at room temperature, and then poured into an ice/water mixture containing acetic acid (10 ml). An ethereal extract was washed with bicarbonate solution, water, and dried over magnesium sulphate. Solvent was removed at 19°/13 mm leaving an oil. Most of the unreacted alcohol and acid were removed by treating with hot ethanol (50 ml) and subsequent cooling and filtration. The residue was treated with ethanol/chloroform, and during several days yielded crystalline material together with a little amorphous solid. The desired crystals (0.22 g) m.p. 152.5–153.5° were picked out by hand. (Found: C, 64.6; H, 5.1. $C_{44}H_{42}O_3Pb$ calcd.: C, 64.7; H, 5.2%.) TLC of this material showed a trace of impurity of slightly lower R_f value. Solvent was removed under reduced pressure from the mother-liquors and the residue was added to the amorphous solid. Several recrystallizations from chloroform/absolute ethanol yielded the rather impure ester (0.14 g), containing a larger proportion of the same impurity as the crystalline material. The crude ester (69 mg) was eluted from an alumina column with chloroform/benzene 5:95. The eluate was tested for organolead content by spotting 20–30 μ l onto a piece of unhandled Whatmans No. 1 filter paper. Presence of an organolead compound was indicated by the appearance of a permanent yellow spot after exposure to iodine vapour for 1–2 min. [*p*-(hydroxymethyl)phenyl]-triphenyllead (5 μg) is easily detected and 2 μg can be detected satisfactorily.

All eluates showing positive lead content were examined by TLC using 20–30 μl of eluate. On removal of solvent from the appropriate fractions, a pale yellow solid (29 mg) was obtained. This was recrystallized from ethanol containing a little chloroform to give pure white crystals (11 mg). 24 μg of this on a thin layer plate indicated the presence of only one component.

ACKNOWLEDGEMENTS

The authors thank the CB Research Fund for sponsoring this research. The collaboration of Dr. R. REES and Mr. D. RACKHAM with NMR, and of Dr. M. GOLDSTEIN with IR spectra is gratefully acknowledged.

SUMMARY

The oxidation of [*p*-(hydroxymethyl)phenyl]triphenyllead (I) to the corresponding aldehyde, and the formation of a derivative of the aldehyde with 5,5-dimethyl-1,3-cyclohexanedione are described. Esterifications of the alcohol (I) with benzoyl chloride, and with a steroid acid chloride are described. NMR and IR data for (I), the corresponding aldehyde, and the benzoate of (I) are briefly discussed.

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