

NOTE**Reactions of Hexaphenyldilead with β -Diketones and β -Ketoesters**

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The reactions of hexaphenyldilead with β -diketones and β -ketoesters in the molar ratio of 1:2 were studied in anhydrous benzene. Complexes of the type R_3Pb-L (where $R = -C_6H_5$ and $L = \beta$ -diketones or β -ketoesters) have been synthesized. All the reactions were found to be quite facile. It was observed that lead-lead bond was cleaved. The resulting derivatives of organolead(IV) were obtained in the form of yellow solids. They are quite stable to atmospheric moisture and are insoluble in common organic solvents. The lead atom is probably penta-coordinated and structure is trigonal bipyramidal.

Key Words: Hexaphenyldilead, β -Diketones, β -Ketoesters.

A survey of literature reveals that scanty reports are available on the β -diketone derivatives of lead(IV) compounds. Tanaka and co-workers¹ reported the study of infrared spectra of dimethyltin *bis*(acetylacetonate) and diethyllead *bis*(acetylacetonate). The asymmetric stretch of Sn-C and Pb-C bonds appear at 556 and 541 cm^{-1} , respectively. Tanaka and co-workers² also reported the infrared spectra of a series of acetylacetonates, $XX'Sn(acac)_2$ ($X, X' =$ alkyl or aryl and/or halogen), $CH_3Pb(acac)_2$, $Cl_2Ti(acac)_2$, $Cl_2Ge(acac)_2$ and $Cl_4Sb(acac)_2$ in the region of 4000-400 cm^{-1} . Huber and co-workers³ reported diphenyllead dibenzoyl-acetonate ($PbC_{32}H_{28}O_4$). Kawasaki and co-workers^{1,2} studied the PMR and infrared spectra of some dimethyllead(IV) complexes. Das *et al.*⁴ synthesized stable complexes of trimethyl lead chloride with triphenylphosphine oxide, pyridine N-oxide and triphenylarsine. Triphenyllead(IV) and 8-hydroxyquinoline are reported to coordinate in benzene solution⁵.

Hills and Henry⁶ synthesized some stable complexes of phenyllead halides and reported the formation of 5 and 6-coordinate adducts. A survey of literature revealed that there is hardly any report on the studies of the reactivity of lead-lead bond with β -diketones or β -ketoesters. In the present investigations, β -diketones and β -ketoesters have been used as ligands.

Reaction of hexaphenyldilead with acetylacetone in 1:2 molar ratio:

Hexaphenyl-dilead (0.87 g) was dissolved in benzene (25 mL) and acetylacetone (0.20 g) was added. The reaction mixture was refluxed for 5.5 h. An excess of solvent was pumped out and petroleum ether (60-80 °C) was added. Some insoluble portion was precipitated which was filtered. The filtrate was concentrated and petro-

leum ether (60-80 °C) added. On cooling, light yellow crystalline compound was obtained. It melted at 258-260 °C.

Reaction of hexaphenyldilead with benzoylacetone in 1:2 molar ratio:

Hexaphenyldilead (0.87 g) was dissolved in anhydrous benzene (25 mL) and benzoylacetone (0.32 g) was added. The contents were refluxed for 7 h. An excess of solvent was distilled out and petroleum ether (60-80 °C) was added to the reaction mixture. An insoluble part settled down which was removed by filtration. The filtrate was cooled in ice. A yellow crystalline compound was obtained. It decomposed at 213-215 °C on heating.

Reaction of hexaphenyldilead with dibenzoylmethane in 1:2 molar ratio:

Hexaphenyldilead (0.87 g) was dissolved in benzene (20 mL) and dibenzoylmethane (0.45 g) was added. The contents were refluxed for 8 h. The reaction mixture was left over night at room temperature. Yellow shining crystals settled down in the bottom. They were separated out and dried under reduced pressure. The melting point was found to be 233-235 °C.

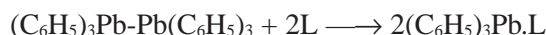
Reaction of hexaphenyldilead with ethylacetoacetate in 1:2 molar ratio:

To hexaphenyldilead (0.87 g) in benzene (25mL) ethylacetoacetate (0.26 g) was added. The reaction mixture was refluxed for 7 h. An excess of solvent was distilled out. Petroleum ether (60-80 °C) and chloroform were added. On cooling, a light yellow crystalline solid was obtained. It decomposed at 192-194 °C on heating.

Reaction of hexaphenyldilead with ethylbenzoylacetate in 1:2 molar ratio:

Hexaphenyldilead (0.87 g) was dissolved in benzene (30 mL) and ethylbenzoylacetate (0.38 g) was added. The contents were refluxed for 8 h. An excess of solvent was distilled off. Petroleum ether (60-80 °C) was added to this compound. On cooling, light yellow shining crystalline compound was obtained. It decomposed at 185-187 °C on heating.

The reactions between hexaphenyldilead with β -diketones or β -ketoesters were carried out in the molar ratio of 1:2 and represented by the following general equation:



(where L = β -diketones or β -ketoesters)

The resulting triphenyllead(IV) complexes of either β -diketones or β -ketoesters are yellow crystalline solids. They appear to be quite stable in air and are insoluble in common organic solvents. The insolubility of these complexes in organic solvents did not permit the determination of the molecular weights. The physical properties of these complexes have been recorded in Table-1.

In these complexes, the central lead atom probably acquires coordination number of 5 and can be structurally represented as shown below:

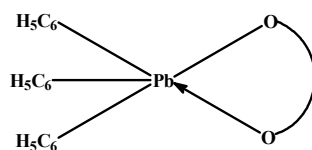


TABLE-1
PHYSICAL PROPERTIES OF LEAD(IV) DERIVATIVES OF
 β -DIKETONES AND β - KETOESTERS

Compound/m.f.	Colour/State	m.p. (°C)	Yield (%)	ν_{\max} , cm^{-1} (Pb-O)	
				asym.	sym.
$(\text{C}_6\text{H}_5)_3\text{Pb}/(\text{C}_5\text{H}_7\text{O}_2)$	Light yellow/Solid	258-260	82	560 s	470 m
$(\text{C}_6\text{H}_5)_3\text{Pb}/(\text{C}_{10}\text{H}_9\text{O}_2)$	Yellow/Solid	213-215, decomp.	81	555 s	475 m
$(\text{C}_6\text{H}_5)_3\text{Pb}/(\text{C}_{15}\text{H}_{11}\text{O}_2)$	Shining yellow/Solid	233-235	79	545 s	485 s
$(\text{C}_6\text{H}_5)_3\text{Pb}/(\text{C}_6\text{H}_9\text{O}_2)$	Light yellow/Solid	192-199, decomp.	84	555 m	475 m
$(\text{C}_6\text{H}_5)_3\text{Pb}/(\text{C}_{11}\text{H}_{11}\text{O}_2)$	Light yellow/Solid	185-187, decomp.	86	550 m	470 m

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