

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

STUDIES OF ORGANIC LEAD COMPOUNDS. III. THE REACTION OF ORGANIC LEAD SALTS ON MERCURY AND LEAD ARYLS

BY PAUL R. AUSTIN¹

RECEIVED MARCH 7, 1932

PUBLISHED AUGUST 5, 1932

Various metallic and organo-metallic halides have been arylated by means of mercury derivatives² and it was thought that this reaction might be utilized in the synthesis of organic lead compounds as follows



Diphenyllead dichloride and diphenylmercury heated in pyridine gave a 21% yield of triphenyllead chloride. Phenylmercuric chloride was easier to isolate and a 57% yield was obtained. When the following reaction $(o-C_7H_7)_2PbCl_2 + (C_6H_5)_2Hg \longrightarrow (o-C_7H_7)_2(C_6H_5)PbCl + (C_6H_5)HgCl$, was carried out in an attempt to obtain mixed compounds, phenylmercuric chloride was obtained in a 38% yield, but the expected phenyldi-*o*-tolyllead chloride could not be isolated from the mixture of reaction products. A small amount of diphenyllead dichloride which was isolated indicated that a further reaction had taken place.

Triphenyllead chloride when refluxed with diphenyl- or dibenzylmercury in a variety of solvents did not react. A small amount of tetraphenyllead was formed in every case, but a study of the decomposition of trialkyl and triaryl lead halides on heating showed that the tetraphenyllead resulted from disproportionation according to the equation



a type of reaction which has been previously observed in the pyrolysis of triethyllead bromide³ and triphenyltin hydroxide.⁴ Triphenyllead chloride heated in butyl alcohol yielded about 10% of the expected compounds. Similar results were obtained when triethyllead chloride was heated in toluene or benzene. These yields suggested that the reaction might be reversible when carried out in organic solvents. This was found to be the case and tetraphenyllead and diphenyllead dichloride heated in butyl alcohol gave an 86% yield of triphenyllead chloride. Tetraethyllead and diethyllead dichloride heated in benzene gave a 39% yield of triethyllead chloride. Tetraphenyllead and di-*o*-tolyllead dihalides heated in benzene or toluene in an attempt to form a mixed aryl lead halide did not react.

¹ National Research Fellow in Chemistry.

² Aronheim, *Ann.*, **194**, 145 (1878); Hasenbaumer, *Ber.*, **31**, 2911 (1898); Goddard, *J. Chem. Soc.*, **121**, 40, 1161 (1922); Leicester and Bergstrom, *THIS JOURNAL*, **53**, 4428 (1931).

³ Calingaert, *Chem. Reviews*, **2**, 73 (1925).

⁴ Chambers and Scherer, *THIS JOURNAL*, **48**, 1056 (1926).

Experimental Part

Diphenyllead Dichloride and Diphenylmercury.—Four and five-tenths grams of diphenyllead dichloride and 3.5 g. of diphenylmercury in 75 cc. of pyridine were refluxed for ten hours. After cooling and filtering, the pyridine mother liquor was concentrated by distillation and then water was added to throw out the product. This was almost completely soluble in hot alcohol and on cooling gave 1.8 g. of crude phenylmercuric chloride which on recrystallization from alcohol melted at 250–252°. The product obtained on concentration of the alcohol mother liquor above was fractionated from alcohol or petroleum ether. One gram of triphenyllead chloride was obtained which after recrystallization from alcohol melted at 204–205°.

Di-*o*-tolyllead Dichloride and Diphenylmercury.—Di-*o*-tolyllead dichloride and diphenylmercury (4.6 g. and 3.5 g., respectively), in 200 cc. of alcohol were refluxed for six hours. The solution was concentrated and the reaction products separated by fractional crystallization first from alcohol and then from petroleum ether. There was obtained 1.2 g. of phenylmercuric chloride, m. p. 251–252°, and 0.5 g. of what was shown to be diphenyllead dichloride by halogen analysis and solubility behavior. Exhaustive fractionation of the remainder of the material failed to yield any other product which could be identified. The expected reaction product, phenyldi-*o*-tolyllead chloride, was prepared by a separate synthesis and its solubility and behavior on heating studied in order that it might not be overlooked.

Phenyldi-*o*-tolyllead Chloride.—This compound was prepared in a 70% yield from the bromide using the general procedure described for triphenyllead acetate.⁵ It was recrystallized from ligroin or aqueous alcohol and melted at 113–114°.

Anal. Calcd. for $C_6H_5(C_7H_7)_2PbCl$: Pb, 41.29; Cl, 7.07. Found: Pb, 41.54; Cl, 6.77.

A small amount of the compound was refluxed in benzene and in alcohol for six hours and in each case it was recovered unchanged.

Disproportionation of Triphenyllead Chloride.—Five grams of triphenyllead chloride in 100 cc. of butyl alcohol was refluxed for six hours. Filtration gave 0.2 g. of an organic material which was undoubtedly diphenyllead dichloride. The solution on cooling gave 4 g. of product. Extraction with three 50-cc. portions of alcohol left 0.3 g. of tetraphenyllead which after recrystallization from benzene melted at 222–223°.

Disproportionation of Triethyllead Chloride.—Thirty-three grams of triethyllead chloride in 100 cc. of toluene was refluxed for five hours. Filtration gave 3 g. of insoluble material which was shown by analysis to be largely lead chloride. Most of the toluene was distilled and was replaced by petroleum ether. From this there was recovered 21.8 g. of triethyllead chloride and concentration of the filtrate gave 3.5 g. of an oil which was undoubtedly tetraethyllead. It was distilled under diminished pressure in an atmosphere of carbon dioxide and the index of refraction and density corresponded closely to the known values.

Tetraphenyllead and Diphenyllead Dichloride.—Five and one-tenth grams of tetraphenyllead and 4.3 g. of diphenyllead dichloride were dissolved and suspended in 250 cc. of butyl alcohol. The mixture was refluxed for eighteen hours and then filtered. The crude product obtained from the filtrate was recrystallized from alcohol and gave 8.1 g. of triphenyllead chloride, m. p. 202°.

Tetraethyllead and Diethyllead Dichloride.—Sixteen grams of tetraethyllead and 17 g. of diethyllead dichloride were dissolved and suspended in 100 cc. of benzene and refluxed for five hours. The mixture was filtered and most of the benzene was removed from the filtrate by distillation and was then replaced by petroleum ether.

⁵ Austin, *THIS JOURNAL*, **53**, 3517 (1931).

The hot solution was clear and on cooling gave 13 g. of what was shown by halogen analysis and melting point to be triethyllead chloride.

The author is indebted to Professor C. S. Marvel for many helpful suggestions.

Summary

Diaryl lead dichlorides react in some cases with mercury diaryls to form the aryl mercuric chloride and a triaryl lead chloride.

Triaryl or alkyl lead halides disproportionate on heating to form a tetra-substituted lead derivative and a disubstituted lead dihalide. Diaryl or alkyl lead dihalides react with their corresponding tetraaryl or alkyl derivatives to form trisubstituted lead halides in good yields.

URBANA, ILLINOIS

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

SUBSTITUTION PRODUCTS OF ALPHA-NAPHTHOYL-ORTHO-BENZOIC ACID

BY E. H. JOHNSON,¹ V. WEINMAYR² AND ROGER ADAMS

RECEIVED MARCH 18, 1932

PUBLISHED AUGUST 5, 1932

The formation of anthraquinone and its substitution products through the condensation of phthalic anhydride with benzene and its derivatives has found wide commercial application. Among the variations of this general procedure certain substituted anthraquinones, otherwise difficult to obtain, can be prepared by substituting the intermediate benzoyl-*o*-benzoic acids and subsequently closing the ring to the anthraquinone.

Benzanthraquinones have likewise been prepared from phthalic anhydride or substituted phthalic anhydrides with naphthalene or substituted naphthalenes,³ though more difficulties are encountered so far as isomers are concerned than appear in the benzene series. The substitution of the intermediate α -naphthoyl-*o*-benzoic acids with subsequent conversion to the benzanthraquinones, however, has not been previously described. A number of such reactions are reported in this communication.

¹ This communication is an abstract of a thesis submitted by E. H. Johnson in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Chemistry at the University of Illinois.

² Dr. V. Weinmayr, in the Laboratories of the Organic Chemicals Department, Dyestuffs Division of the du Pont Company, carried out the experiments on the chlorine derivatives.

³ Ador and Crafts, *Bull. soc. chim.*, **34**, 531 (1880); Elbs, *Ber.*, **19**, 2209 (1886); Gabriel, *ibid.*, **33**, 446 (1900); Scholl, *ibid.*, **44**, 2992 (1911); *ibid.*, **44**, 2370 (1911); *Monatsh.*, **32**, 997 (1911); **33**, 507 (1913); **41**, 583 (1920); Graebe, *Ann.*, **340**, 249 (1905); **340**, 259 (1905); Heller, *Ber.*, **41**, 3672 (1908); **45**, 665 (1912); Groggins, *Ind. Eng. Chem.*, **22**, 157 (1930); U. S. Patent 941,320 (1910); German Patent 234,917 (1911); Waldmann, *J. prakt. chem.*, **127**, 185 (1930); **127**, 201 (1930); Dziewonski, *Bull. Int. Acad. Pol.*, **3A**, 181 (1927); U. S. Patent 968,533.