[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

Magnetic Measurements on Trimethyltin and Tricyclohexyllead[1]

BY HUMBERT MORRIS AND P. W. SELWOOD

Previous measurements on triphenylgermanium[2] and on triphenyllead[3] have shown that even at great dilution these compounds exist in the diamagnetic or dimeric state. No molecular weight measurements on triphenylgermanium have been published, but the magnetic results on triphenyllead are inconsistent with the low molecular weight reported by others.[4,5]

Under these circumstances it seemed desirable to make magnetic measurements on other so-called "organo-metallic free radicals." Among the better known examples of such compounds are trimethyltin,[6] tricyclohexyllead,[7] and triethyllead ("diplumbic hexaethyl").[8] The first two of these were chosen for the present investigation.[9]

Experimental Part

Magnetic Measurements.—The magnetic susceptibilities were measured by means of the Gouy balance previously described.[2,3] Measurements were made at the temperatures 40 and 90°, benzene being used as the solvent. Employment of a temperature somewhat above the boiling point of benzene emphasizes the versatility of the magnetic method. A field strength of 13,100 oersteds was used throughout.

Preparation of Materials.—Trimethyltin was prepared according to the method of Kraus and Sessions.[6] It was a colorless, foul-smelling substance, melting at 23°. Solutions were prepared by weighing out small samples of the trimethyltin and dissolving them in highly purified benzene. The solutions were then sealed into the magnetic susceptibility tube, under high vacuum.

Tricyclohexyllead was prepared according to the procedure of Krause.[7] Although Krause reports that the substance is yellow, it was found that rapid recrystallization from hot benzene yielded a product that was almost white. Heat or light soon turned it yellow again. The solutions in benzene were, as reported by Krause, particularly sensitive to light. Exposure of a dilute solution to sunlight for a few minutes resulted in darkening of the solution and formation of a precipitate. This parallels observations made on triphenyllead.[3] Solutions of tricyclohexyllead were prepared the same way as those of trimethyltin.

(1) Presented at the Atlantic City meeting of the American Chemical Society, September 8–12, 1941.

(2) Selwood, THIS JOURNAL, **61**, 3168 (1939).

(3) Preckel and Selwood, ibid., **62**, 2765 (1940).

(4) Krause and Reissaus, Ber., **55**, 894 (1922).

(5) Foster, Dix and Gruntfest, THIS JOURNAL, **61**, 1685 (1939).

(6) Kraus and Sessions, ibid., **47**, 2361 (1925).

(7) Krause, Ber., **54B**, 2060 (1921).

(8) Midgley, Hochwalt and Calingaert, THIS JOURNAL, **45**, 1821 (1923).

(9) See, also, "Twelfth Catalysis Report" (National Research Council), John Wiley and Sons, Inc., New York, N. Y., 1940, p. 25.

Results

In the following tables the susceptibilities of the solutions are calculated for zero dissociation and for complete dissociation to the monomer. These data are compared with the observed susceptibilities. Methods of calculation are given elsewhere.[3]

TABLE I

Temp., °C.	Calcd. for zero diss. $\chi \cdot 10^6$	Calcd. for complete diss. $\chi \cdot 10^6$	Observed $\chi \cdot 10^6$
Susceptibility of a 0.0041 m solution of trimethyltin in benzene			
40	−0.704	−0.700	−0.704 ± 0.001
90	−0.717	−0.713	−0.717
Susceptibility of a 0.047 m solution of trimethyltin in benzene			
40	−0.702	−0.650	−0.703
90	−0.715	−0.668	−0.716
Susceptibility of a 0.011 m solution of tricyclohexyllead in benzene			
40	−0.703	−0.691	−0.703
90	−0.716	−0.705	−0.716

Kraus and Sessions claim approximately complete dissociation of trimethyltin into the monomer, on the basis of boiling point measurements made on benzene solutions at a concentration of 0.0072 m. In the present experiments 50% dissociation could have been detected at 0.0041 m. They also observed an apparent molecular weight of 246 (corresponding to 53% dissociation) at a concentration of 0.0587 m. But the present experiments show that if dissociation exists at 0.047 m it cannot exceed about 2%. It must also be borne in mind that at 90° the degree of dissociation is expected to be greater than at the boiling point of benzene.

Krause gives the molecular weight of tricyclohexyllead in freezing benzene at 0.0124 m as 697 (corresponding to 47% dissociation). But in the present experiments as little as 10% dissociation could have been detected at 0.011 m, and the temperatures employed were much higher. It should perhaps be pointed out that the solutions of tricyclohexyllead showed no sign of decomposition after being heated to 90°, provided they were kept from the light.

Discussion of Results

In view of these measurements, and of those previously reported for triphenylgermanium and triphenyllead, it may be concluded that no long-life organo-metallic free radical has yet been prepared. There remain, of course, the results of Midgley, Hochwalt and Calingaert on triethyllead. But the writers have no doubt that this compound too will prove to be diamagnetic, even in very dilute solution, and there seems little use in bothering to make measurements on it.

This work raises two questions. First, how can the low molecular weights of Krause, Kraus, Foster, Midgley, *et al.*, be explained? And, second, why do these compounds not exist in the free radical form, at least in the case of the triphenyl series, when the Ge–Ge, Sn–Sn, and Pb–Pb bond-energies are probably considerably less than the corresponding C–C bonds, as in hexaphenylethane?

A clue to the first problem may possibly be found in the reactions undergone by hexaaryl-ethanes. Although no evidence is at hand on this point, yet it seems not improbable that a compound such as hexaphenyldiplumbane might slowly decompose to several fragments of relatively low molecular weight, especially at moderately elevated temperatures.

As regards the second problem: why are free radicals not found? the writers suggest that the explanation is to be found in the much greater atomic radius of the metal atoms as compared with that of carbon. The covalent radius of lead is at least twice that of carbon,[10] hence the effect of three phenyl groups is more that of three protuberances on the surface of the lead, rather than of a tightly-fitting envelope, as in the case of carbon. Consequently the effective collision frequency leading to formation of the dimer must be far greater in the case of the metal radicals than of the carbon radicals. It is suggested that failure to observe an organo-metallic radical is principally a result of steric effects brought about by the large size of the metal atom. Failure to obtain trimethyltin as a monomer is then in no way surprising. In the failure to find tricyclohexyllead, the present work destroys a possible objection to the resonance theory of free radical stability. The probabilities are that if organo-metallic radicals are to be found they will be compounds such as tri-*o*-tolyltin or better tri-*o*-xenyltin, in which both steric and resonance effects are strong. Experiments in this direction are being undertaken.

Summary

Trimethyltin and tricyclohexyllead, in dilute benzene solution, do not exist as the monomer. It is suggested that the relatively large size of the tin and lead atoms greatly reduces the stability of organo-metallic free radicals as compared with carbon free radicals.

(10) Skinner and Sutton, *Trans. Faraday Soc.*, **36**, 1209 (1940).

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Ketene in the Friedel-Crafts Reaction.   II.[1]   The Use of Mixed Acetic Anhydrides[2]

BY JONATHAN W. WILLIAMS, YANCEY J. DICKERT[3] AND JOHN A. KRYNITSKY

A mixed acetic anhydride, the product of the reaction of ketene and a carboxylic acid,[4] may be used in the synthesis of a higher alkyl phenyl ketone in either of two ways. It may be used directly in a Friedel–Crafts reaction with an aromatic hydrocarbon, or it may be decomposed by heating or standing into acetic anhydride and a higher anhydride,[4,5] from which a ketone may easily be prepared.[6] The first of these two methods is described in this paper.

A study of the reactions of some unsymmetrical aromatic anhydrides with benzene in the presence of aluminum chloride has been made by Zeavin and Fisher.[7] They found that the ketone of lower molecular weight is obtained in the greater quan-

(1) For the first paper in this series, see Williams and Osborn, THIS JOURNAL, **61**, 3438 (1939).

(2) Presented before the Organic Division of the American Chemical Society at the St. Louis meeting, April, 1941.

(3) Taken in part from the M.A. Thesis of Yancey J. Dickert.

(4) Hurd and Dull, THIS JOURNAL, **54**, 3427 (1932).

(5) Williams and Krynitsky, "Organic Syntheses," Vol. XXI, p. 13.

(6) Noller and Adams, THIS JOURNAL, **46**, 1889 (1924).

(7) Zeavin and Fisher, *ibid.*, **54**, 3738 (1932).