hydrochloric acid to remove sodium compounds, and then with alcohol. There was obtained 24 g. or 93.7% of the theoretical yield of 1,5-dibenzoyl-2,3,4-triphenyl-3-cyanopentane. After recrystallization from chloroform and benzene there was obtained 9.9 g. of pure substance, m. p. 264.5–265.5° (corr.). The substance agrees in every respect with that obtained by Avery.[8]

Anal. Calcd. for $C_{38}H_{31}O_2N$: C, 85.6; H, 6.1; N, 2.6. Found: C, 85.6; H, 5.9; N, 2.5.

This compound has been prepared by Kohler and Allen,[9] who suggest the same structure but who found a melting point of 257°. Avery has shown that this melting point is probably low, due to impurities, and that the corrected melting point is 264.5–265.5°.

Summary

1. A method for the preparation of pure sodium phenylacetonitrile is described.

2. New evidence for the existence of tautomeric forms of the nitrile and for the imide structure of the salt is presented.

3. It has been shown that the sodium salt enters into condensation reactions of the type produced by sodium methylate and phenylacetonitrile.

LINCOLN, NEBRASKA

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE COLLEGE]

THE PREPARATION OF DIETHYL LEAD DICHLORIDE AND TRIETHYL LEAD CHLORIDE

BY HENRY GILMAN AND JACK D. ROBINSON

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Introduction

Convenient methods have been determined for the ready preparation of diethyl lead dichloride and of triethyl lead chloride in essentially quantitative yields by means of the following reactions carried out in toluene and ether, respectively

$$(C_2H_5)_4Pb + 2HCl \longrightarrow (C_2H_5)_2PbCl_2 \qquad (I)$$

$$(C_2H_5)_4Pb + HCl \longrightarrow (C_2H_5)_3PbCl \qquad (II)$$

The most generally used method for the synthesis of diethyl lead dihalides is that elaborated by Grüttner and Krause,[1] and involves the direct action of halogens on tetraethyl lead at low temperatures. In that method they recommend that the triethyl lead halide be first prepared at −60° and then converted to the dihalide as the solution warms

[8] S. Avery, results soon to be published.

[9] Kohler and Allen, THIS JOURNAL, **46**, 1522 (1924).

[1] (a) Grüttner and Krause, *Ber.*, **49**, 1415 (1916). (b) Other methods, not of preparative value, for the synthesis of diethyl lead dichloride may be found in the following references: Grüttner, *ibid.*, **47**, 3257 (1914); Möller and Pfeiffer, *ibid.*, **49**, 2441 (1916); Goddard and Goddard, *J. Chem. Soc.*, **121**, 256, 482 (1922).

up to −20°. When the reaction with halogens is effected at −20° in large-sized runs, without the preliminary formation of triethyl lead halide, they caution against a vigorous reaction which may be of explosive violence. Incidentally, we have shown in this study that it is possible to prepare diethyl lead dichloride in a 98.6% yield by the direct action of chlorine on 0.05 mole of tetraethyl lead in ether cooled to −10°.

The same authors[1a] object to any method for the preparation of triethyl lead chloride which involves the use of hydrogen chloride or hydrochloric acid, basing such objection on the ground that the yield is lowered when large quantities of materials are used. This objection is not valid at least in a preparation starting with 113 g. (0.35 mole) of tetraethyl lead, inasmuch as our yield by Reaction II of triethyl lead chloride is 96%. Triethyl lead chloride has been prepared by Buckton[2] and Cahours[3] by warming tetraethyl lead with concd. hydrochloric acid, and by Buckton[4] from hydrogen chloride and tetraethyl lead. More recently, Browne and Reid[5] have given splendid directions for the preparation of triethyl lead chloride in 86% yields from tetraethyl lead and concd. hydrochloric acid with a trace of silica gel as a catalyst.

The greater stability of the diethyl and triethyl lead chlorides over the corresponding bromides and iodides, as well as their lesser expensiveness, makes them the most desirable halides. This is particularly the case in our studies of their reactions with other organometallic compounds, in which studies they have been shown to have a very high order of reactivity. When, however, it is desired to use the bromide or iodide, then two general methods are available for the conversion of the chloride to the other halides. One involves the hydrolysis to the corresponding hydroxide and subsequent treatment with the appropriate halogen acid.[6] The other method is based on a double decomposition reaction between an alkyl lead halide and the appropriate halide of sodium or potassium.[7] Both of these methods are applicable to the dialkyl lead dihalides as well as to the trialkyl lead halides.

Although we have not tried our method with halogen acids other than hydrochloric acid, it is probable that they can be extended to some of the other halogen acids. Also, it is altogether reasonable to believe that our methods for the synthesis of diethyl lead dichloride and triethyl lead

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[2] Buckton, *Ann.*, **109**, 218 (1859).

[3] Cahours, *ibid.*, **122**, 48 (1862).

[4] Buckton, *ibid.*, **112**, 220 (1859). See also Pfeiffer and Truskier, *Ber.*, **37**, 1125 (1904), who used the same method and reported a good yield, but gave no details as to solvent, percentages, purity, etc.

[5] Browne and Reid, This Journal, **49**, 830 (1927).

[6] Krause and Pohland, *Ber.*, **55**, 1282 (1922).

[7] Löwig, *J. prakt. Chem.*, **60**, 304 (1853); Klippel, *ibid.*, **81**, 287 (1860); and References 2 and 3 of this paper.

chloride are applicable to tetra-alkyl lead compounds other than tetraethyl lead.

Experimental Part

Diethyl Lead Dichloride, $(C_2H_5)_2PbCl_2$.—After dissolving 107.5 g. (0.3 mole) of tetraethyl lead in 500 cc. of toluene in an open[8] Erlenmeyer flask, and heating the solution to 90°,[9] dry hydrogen chloride is passed into the solution at a moderate rate. Inasmuch as the triethyl lead chloride which first forms is soluble in toluene, no precipitate appears before one-half of the hydrogen chloride has been absorbed. The approximate end of the reaction may be determined by adding hydrogen chloride at the same rate for twice the time necessary to cause the first precipitate of diethyl lead dichloride to form. At this stage the precipitate is removed by filtration and hydrogen chloride is again added in order to precipitate any unreacted triethyl lead chloride. If no precipitate forms on this subsequent addition of hydrogen chloride, the reaction is ended. The yield of 107 g. or 97.5% has been checked many times. The product is free of lead chloride, and if there were any significant quantity of triethyl lead chloride it would probably not contaminate the diethyl lead dichloride because of its high solubility in hot toluene.[10]

In another connection, chlorine was bubbled slowly into a well-stirred solution of 16.5 g. (0.05 mole) of tetraethyl lead dissolved in 150 cc. of dry ether and cooled to −10°. A smooth reaction occurred, and when the chlorine colored the solution, the reaction was considered to be complete. The diethyl lead dichloride was filtered off, and its weight was 16.6 g. which is equivalent to a 98.6% yield. This describes the only experiment we carried out between tetraethyl lead and chlorine.

Triethyl Lead Chloride, $(C_2H_5)_3PbCl$.—Forty-eight and one-half grams (0.15 mole) of tetraethyl lead is dissolved in 400 cc. of absolute ether and saturated with hydrogen chloride at room temperature. This requires about thirty minutes or more, depending on the rate of flow of gas. The rate at which the hydrogen chloride is absorbed appears to reach a maximum and the evolution of ethane is rather constant. Perhaps the best way to determine when the reaction is at an end is to remove the needles of triethyl lead chloride by filtration when the ethane is only slowly evolved, and then to saturate the filtrate again with hydrogen chloride. If no more needles form, the reaction is complete. The yield is 48.6 g. or 98.2%.[11]

In this preparation it is necessary that all moisture be rigorously excluded from the flask and reagents. Triethyl lead chloride is soluble in moist ether but quite insoluble in dry ether which contains moderate amounts of hydrogen chloride. However, triethyl lead chloride appears to be appreciably soluble in dry ether which contains a *large* quantity of hydrogen chloride. This finds support in two observations. First, it has been found that on boiling a solution to remove excess hydrogen chloride, another

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[8] All operations are carried out, of course, with due care because of the toxicity of tetraethyl lead. This involves, primarily, working in a well-ventilated hood. Care should be exercised about long exposure to triethyl lead chloride. The observation of Krause and Pohland, *Ber.*, **55**, 1282 (1922), that compounds of this type cause severe headaches has been confirmed.

[9] The temperature of the solution should be maintained at 90° by the application of heat, although there appears to be no harm with a temperature variation of 10°.

[10] The diethyl lead dichloride is in the reactive form and requires no further treatment prior to use. See Grüttner and Krause, *Ber.*, **49**, 1546 (1916).

[11] The yields may vary between 92 and 98.2% depending on the careful conversion of the last small quantities of tetraethyl lead. The smoothness of these reactions has recommended them for other studies concerned with the lability or polarity of radicals.

crop of crystals frequently appears. Second, the saturation of a suspension of triethyl lead chloride in ether with hydrogen chloride induces some of the triethyl lead chloride to dissolve. This latter phenomenon appears to be unusual with organolead halides.

Summary

Diethyl lead dichloride and triethyl lead chloride can be very conveniently prepared in essentially quantitative yields by the reaction between tetraethyl lead and hydrogen chloride.

AMES, IOWA

[CONTRIBUTION FROM THE LABORATORY OF FOODS AND SANITATION, UNIVERSITY OF WISCONSIN]

SOME PHYSICAL CONSTANTS OF MONACETIN, MONOPROPIN AND MONO-NORMAL-BUTYRIN[1]

BY H. A. SCHUETTE AND JOHN T. HALE

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The discovery of the nature of fatty oils by Chevreul over a century ago gave a marked impetus to the synthesis of simple and mixed glycerides. The monoglyceryl esters of the acids of low molecular weight have not, however, shared the same degree of interest. Published information thereon is apparently non-existent for one of the esters pertinent to this communication; the reported physical constants of another are obviously in need of correction; and such data as are available have been determined at temperatures for which there is no uniformity.

In view of this situation there is an evident need for new data and for a revision of some of that now extant. These ends have been accomplished by the synthesis of the glycerides in question and the determination of their vapor pressures, densities, refractive indices and surface tensions. The method of preparation which was followed led to the formation of racemic compounds which probably possess, as might be expected, different constants than the corresponding naturally occurring glycerides, none of which, however, seems to have been isolated.

Monacetin has been made by Berthelot,[2] who heated a mixture of glycerol and acetic acid under pressure; by Geitel,[3] who isolated it from the reaction product resulting from heating a mixture of glycerol and acetic acid at atmospheric pressure; by Averill, Roche and King,[4] who synthesized α-monoglycerin by a method developed by Fischer[5] and his

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[1] Constructed from a thesis submitted by John T. Hale to the Graduate School of the University of Wisconsin in partial fulfilment of the requirements for the degree of Master of Science, June, 1928.

[2] Berthelot, *Ann. chim. phys.*, [3] **41**, 216 (1854).

[3] Geitel, *J. prakt. Chem.*, **163**, 417 (1897).

[4] Averill, Roche and King, THIS JOURNAL, **51**, 866 (1929).

[5] Fischer, Bergwin and Barwind, *Ber.*, **53**, 1589 (1920).