Summary

Some physical properties of the pairs of isomers, 3- and 4-heptanol, 3- and 4-chloroheptane and 3- and 4-bromoheptane have been determined. The boiling points and refractive indices of any pair are very similar, while of only one substance, 4-heptanol, could a freezing point be obtained. The reaction of ethyl formate with butyl magnesium bromide and ethylmagnesium bromide gave 2-pentanol and 4-nonanol but no 3-heptanol.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE COLLEGE]

A METHOD FOR THE QUANTITATIVE ANALYSIS OF LEAD IN ORGANIC COMPOUNDS

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RECEIVED FEBRUARY 20, 1928 PUBLISHED JUNE 5, 1928

In connection with studies on organolead compounds a need was felt for a convenient method for the quantitative estimation of total lead in compounds having an aryl group attached directly to lead. None of the present methods was found satisfactory for our purposes. The method described here consists essentially in the decomposition of the sample by sulfuric and nitric acids, and estimation as lead sulfate. It has been used successfully by different workers in this Laboratory for the analysis of various aryl and aryl-alkyl lead compounds.

Polis[1] analyzed his organolead compounds, as lead sulfate, after decomposition by concentrated sulfuric acid and oxidation by potassium permanganate. Grüttner and Krause[2] decomposed their compounds with a 30% solution of bromine in carbon tetrachloride, and estimated the lead as lead bromide. They also used the Carius method of decomposition for volatile compounds. Calingaert[3] modified the method of decomposition by bromine, and obtained highly satisfactory results with *alkyl* lead compounds. This method, with our compounds, has not given acceptable analyses, very probably because of the greater firmness of attachment of *aryl* groups to lead.[4] Treadwell and Hall[5] recommend decomposition in a crucible by concentrated sulfuric acid and weighing as lead sulfate. We have not obtained consistent results by this method,

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[1] Polis, *Ber.*, **19**, 1024 (1886); **20**, 718 (1887).

[2] Grüttner and Krause, *Ber.*, **49**, 1125 (1916).

[3] Calingaert, *Chem. Reviews*, **2**, 43 (1925).

[4] Dr. Calingaert has found that the aryl lead compounds submitted by us to him for a comparative rating of their antiknock effectiveness can be analyzed satisfactorily by heating with concentrated nitric acid subsequent to treatment with bromine in carbon tetrachloride.

[5] Treadwell and Hall, "Analytical Chemistry" (5th English edition), John Wiley and Sons, Inc., New York, 1919, Vol. II, p. 175.

probably because of loss due to spattering. The procedure adopted by us is a slight modification of the general treatment suggested by Noyes and Bray[6] for the decomposition of organic matter in a sample to be prepared for qualitative analysis.

The analysis described here has not been used with volatile organolead compounds having only alkyl groups attached to lead. Such compounds are readily analyzed by the bromine method[2,3] and it is quite likely that a special technique would be needed with the nitric and sulfuric acid treatment to avoid loss by spattering.

Method of Analysis

About 0.5 g. of sample is placed in a 400-cc. Pyrex beaker (or casserole of about the same size) and to this is added 7.5 cc. of concentrated sulfuric acid. The beaker is covered with a watch glass and very gently warmed over a small flame. A too vigorous reaction can be avoided by removing the beaker and agitating by a rotatory motion when the first indication of reaction appears (about 50–90°). The process of mild warming, removal from flame and gentle stirring is repeated until the white precipitate of lead sulfate settles out and none of the sample remains suspended in the sulfuric acid. The contents are then gradually heated until white fumes are copiously evolved.

After cooling to about 80°, 1–1$^1/_2$ cc. of concentrated nitric acid (sp. gr., 1.42) is added; heat is again applied, gently at first; and, when any vigorous evolution of nitrogen oxides has ceased, the watch glass is removed and the beaker heated until copious white fumes are evolved. One cc. of concentrated nitric acid is added, after cooling the beaker and contents, and the heating is then repeated to the evolution of white fumes. By these operations, the organic matter is totally oxidized when the acids have been sufficiently heated; and the lead sulfate is dissolved completely in the hot concentrated sulfuric acid.

The solution is cooled to about 30° and any material adhering to the sides of the beaker is washed down with 5–10 cc. of distilled water. After slight agitation to mix the water and acids, the mixture is again heated to the evolution of white fumes. The evaporation may cause bumping if done over a flame, but this may be avoided by heating on the ordinary 220-volt electric hot-plate, with the heat on "low." The beaker is then heated strongly to remove all nitric acid, after which it is cooled, more water is added and the operations through strong heating are repeated.

To the cooled beaker there is then added 150 cc. of water and 100 cc. of 95% alcohol. After standing for one hour, the precipitate is filtered through a Gooch crucible, washed with 10% sulfuric acid and then with 95% alcohol to remove all of the sulfuric acid. The crucible and contents

[6] Noyes and Bray, THIS JOURNAL, **29**, 144 (1907).

are then dried, in the customary manner, by heating for one hour at 110°, and weighed as lead sulfate.

The results of a few representative analyses follow.

TABLE I

RESULTS OF ANALYSES

Compound	% Pb Calcd.	% Pb Found	
Tetraphenyl lead	40.18	39.83	40.03
Tetra-*p*-bromophenyl lead	24.91	24.68	24.38
Diphenyl-di-*p*-bromophenyl lead	30.76	30.65	30.80
Triphenyl-*n*-butyl lead	41.82	41.52	41.46
Diphenyl-di-*iso*butyl lead	43.58	43.08	43.53

The authors wish to acknowledge helpful suggestions from Dr. J. A. Wilkinson.

Summary

A method is described for the quantitative estimation of total lead in non-volatile organolead compounds by decomposition with concentrated sulfuric and nitric acids.

AMES, IOWA

[CONTRIBUTION FROM THE KENT CHEMICAL LABORATORY OF THE UNIVERSITY OF CHICAGO]

THE THERMAL DECOMPOSITION OF NITRITES. THE NITRITES OF TRIPHENYLETHYLAMINE AND DIPHENYLETHYLAMINE[1]

BY LESLIE HELLERMAN, MAURICE LEON COHN AND REU EVERETT HOEN

RECEIVED FEBRUARY 23, 1928 PUBLISHED JUNE 5, 1928

That the action of nitrous acid upon a primary aliphatic amine does *not* in general produce *exclusively* the alcohol of corresponding structure, has been pointed out by a number of investigators; an impression to the contrary regarding this fundamental class of organic reactions appears, nevertheless, to be held by many. In view of this and of the experimental results to be reported in this paper, it will not be out of place to include a few references[2] to researches which may in themselves be held to have demonstrated strikingly that *if conversion of an amine to an alcohol of corresponding structure be considered the "normal" course of the action, then*

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[1] This paper is based in part upon dissertations submitted to the University of Chicago by Maurice Leon Cohn and Reu Everett Hoen, in partial fulfilment of the requirements for the degree of Master of Science. An account of some of the work herein reported was presented before the Seventh Midwest Regional Meeting of the American Chemical Society at Chicago, May, 1927.

[2] (a) Meyer and Forster, *Ber.*, **9**, 535 (1876); (b) Demjanow, *Ber.*, **40**, 4393 (1907); (c) Wallach, *Ann.*, **353**, 318 (1907); **359**, 312 (1908); (d) Henry, *Compt. rend.*, **145**, 899 (1907); (e) Jeffreys, *Am. Chem. J.*, **22**, 36 (1899).