Neither sodium acetate nor sodium bicarbonate can be successfully substituted for the sodium carbonate in this test.

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DEPARTMENT OF CHEMISTRY
UNIVERSITY OF GEORGIA
ATHENS, GEORGIA

ALFRED W. SCOTT

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE COLLEGE OF LIBERAL ARTS, NORTHWESTERN UNIVERSITY]

THE MERCURATION OF HEMIMELLITIC ACID

BY FRANK C. WHITMORE AND R. P. PERKINS

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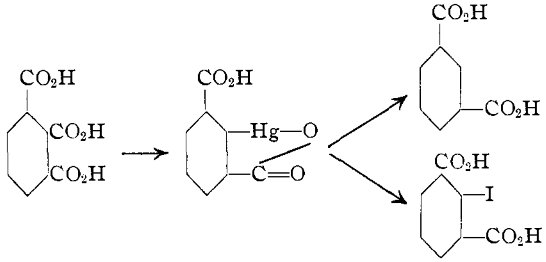
Since the treatment of 3-nitrophthalic acid with mercuric acetate[1] gives over 90% of the calculated amount of the product in which the 2-carboxyl group is replaced by mercury, it seemed desirable to study the effect of other groups on the replacement of one of two ortho carboxyl groups. The simplest case of this kind is presented by hemimellitic acid (benzene-1,2,3-tricarboxylic acid). It was found that the 2-carboxyl is replaced by mercury. No evidence of any replacement of the 1- or 3-carboxyl was found. The structure of the mercury compound was determined by replacing the mercury by hydrogen to give isophthalic acid and by iodine to give 2-iodo-isophthalic acid.



The best method of obtaining the 2-halogen isophthalic acids is undoubtedly by this procedure, starting with hemimellitic acid prepared from acenaphthene.

Experimental

Hemimellitic acid was prepared by a modification of the method of Graebe and Leonhardt.[2] From 100 g. of naphthalic anhydride was obtained 46 g. of hemimellitic acid (44% yield), m. p. 201–203° with decomposition to form the anhydride.

A method is being developed in this Laboratory for the preparation of hemimellitic acid by the direct oxidation of acenaphthene.

A solution of 40 g. (0.2 mole) of hemimellitic anhydride in 110 cc. of 6 *N* sodium

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[1] Whitmore and Culhane, THIS JOURNAL, **51**, 602 (1929).

[2] Graebe and Leonhardt, *Ann.*, **290**, 218 (1896).

hydroxide and 170 cc. of water was treated with a solution of 43.3 g. (0.2 mole) of mercuric oxide in 40 cc. of glacial acetic acid and 70 cc. of water and refluxed for sixteen hours. At the end of that time no more carbon dioxide was evolved and the precipitate which had formed was soluble in sodium hydroxide. The product was separated by filtration, washed and dried to constant weight at 105°; weight, 70.2 g. of anhydro-2-hydroxymercuri-isophthalic acid (96% yield).

Anal. Calcd. for $C_8H_4O_4Hg$: Hg, 55.0. Found: 55.0.

Ten grams of the mercury compound was dissolved in dilute sodium hydroxide, filtered from a slight residue and refluxed for two hours with enough excess hydrochloric acid to make the solution about 6 *N* in hydrochloric acid. The isophthalic acid obtained weighed 3.6 g. (79% yield). It sublimed without melting or decomposing. The dimethyl ester prepared by means of thionyl chloride and methanol melted at 67–68°.

Ten grams of the mercury compound was powdered and dissolved in 75 cc. of 20% potassium iodide solution. To this was added 7.5 g. of iodine. After standing for one hour, the small excess of iodine was removed by concentrated sodium thiosulfate solution. The mixture was acidified and cooled. Highly twined colorless needles separated almost immediately; weight of 2-iodo-isophthalic acid, 5.9 g. (73% yield), m. p. 241.5–243°. Crystallization from water raised the melting point to 243–244°.[3] Treatment of the acid with thionyl chloride and methanol gave the dimethyl ester, m. p. 49.5–50.50°.[4]

Summary

1. Hemimellitic acid reacts with mercuric acetate with the replacement of the 2-carboxyl by mercury.

2. Treatment of this mercury compound with halogens gives the best method of preparing 2-halogenated isophthalic acids.

EVANSTON, ILLINOIS

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

THE PYROLYSIS OF HYDROCARBONS: NORMAL-BUTANE AND ISOBUTANE[1]

BY CHARLES D. HURD[2] AND L. U. SPENCE[3]

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The present investigation with *n*- and *iso*butane inaugurates a series of studies dealing with the behavior of individual hydrocarbons at high

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[3] The melting point of this substance is given as 236–238° by James, Kenner and Stubbings, *J. Chem. Soc.*, **117**, 774 (1920).

[4] *Cf.* Mayer, *Ber.*, **44**, 2301 (1911).

[1] This paper contains results obtained in an investigation on "The Non-Catalytic Thermal Decomposition of Pure Hydrocarbons and Related Compounds," listed as Project No. 18 of American Petroleum Institute Research. Financial assistance in this work has been received from a research fund of the American Petroleum Institute donated by the Universal Oil Products Company. This fund is being administered by the Institute with the coöperation of the Central Petroleum Committee of the National Research Council.

[2] Director, Project No. 18.

[3] American Petroleum Institute Junior Research Fellow.