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MERCURATED TEREPHTHALIC ACID

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The mercuration of aromatic acids converts them to amphoteric substances of weakly acid properties. The sodium salts and the chlorides are readily hydrolyzed to give the insoluble anhydro-hydroxymercuri aromatic acids. It was thought that a second carboxyl group in the molecule would give stronger acidic properties. Consequently, mercurated terephthalic acid was prepared and studied. The difference between it and mercurated benzoic acid in forming stable salts is very slight. Both are precipitated from sodium carbonate solution by carbon dioxide. In the case of mercurated terephthalic acid, however, a very careful adjustment of concentration is necessary to obtain complete precipitation. No such precaution is mentioned by the workers with mercurated benzoic acid.[1]

Anhydro-hydroxymercuriterephthalic acid seems to be more soluble in sodium acetate solution than does the corresponding anhydro-hydroxymercuribenzoic acid, although no quantitative study has been made.

The most interesting comparison of the two acids is between their *n*-butyl esters as regards their stability in hot 95% alcohol. Di-*n*-butyl chloromercuriterephthalate can be crystallized satisfactorily from hot alcohol. *n*-Butyl chloromercuribenzoate is hydrolyzed to anhydro-hydroxymercuribenzoic acid by boiling with 90% alcohol.

Of many methods attempted for mercurating terephthalic acid only two were successful. One was to reflux an aqueous mixture of terephthalic acid, mercuric acetate, acetic acid and sodium acetate. The other was to fuse diethyl terephthalate with mercuric acetate and a trace of acetic acid at 117°. The use of higher temperatures gave large amounts of an unmanageable dimercurated product.

A method of purification applicable to other mercurated aromatic acids was developed. The mercurated acid was converted to the acid chloride and then to the *n*-butyl ester.[2] The ester of mercurated terephthalic acid was readily crystallized from hot ethyl or *n*-butyl alcohol. Since the *n*-butyl ester of the original acid is a liquid and that of the di-mercurated acid is very insoluble, this method of purification was very successful.

The esters of chloromercuribenzoic acid are more easily hydrolyzed and so must be crystallized from absolute alcohol.

The structure of the mercurated terephthalic acid was determined by conversion to the following mercurated derivatives, the anhydro com-

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[1] Pesci, *Atti Accad. Lincei*, [5] **9**, I, 255 (1899); Dimroth, *Ber.*, **31**, 2154 (1898); **32**, 758 (1899); **35**, 2032, 2853 (1902).

[2] Whitmore and Middleton, THIS JOURNAL, **44**, 1546 (1922).

pound, the di-*n*-butyl ester, the amide and the anilide, and by replacing the mercury by bromine to form 2-bromoterephthalic acid.

The positions of the mercury atoms in the di-mercurated terephthalic acid have not been determined.

Experimental Part

Preparation of Terephthalic Acid. 1. From Commercial Xylene.—Xylene was oxidized by alkaline potassium permanganate. Isophthalic and terephthalic acids were precipitated. They were then dissolved in ammonium hydroxide and the very insoluble barium terephthalate was precipitated and then converted to the free acid; yield, 150 cc. of acid from 600 cc. of crude xylene.

2. From Commercial Cymene.—The oxidation was carried out with dilute nitric acid to give *p*-toluic acid, which was converted to terephthalic acid by alkaline permanganate.

Mercuration of Terephthalic Acid.—A solution of 34 g. (0.2 mole) of terephthalic acid in a slight excess of sodium hydroxide was mixed with a solution of 44.7 g. (0.2 mole) of mercuric oxide in a slight excess of acetic acid and 10 g. of sodium acetate and refluxed for 240 hours. At that time the mixture gave no test for inorganic mercury and was completely soluble in sodium hydroxide solution. The precipitated material was filtered off, washed and dried; wt., 102 g. The filtrate on acidification gave 10 g. of unchanged terephthalic acid. The mercurated product was digested for one hour with 1 liter of concentrated ammonium hydroxide solution and 500 cc. of water. The insoluble material was filtered off and extracted again in a similar way. The two extracts were barely acidified with acetic acid. The white precipitate was collected on a filter, transferred to a large beaker and dissolved in a very slight excess of hot saturated sodium carbonate solution. The solution was filtered from a small amount of insoluble material, cooled and treated with carbon dioxide to precipitate a mixture of the mono-mercurated acid and a little of the di-mercurated product. The mixture was digested for about one hour with 500 cc. of saturated (20°) sodium acetate solution and 1 liter of water. This treatment dissolved the mono-mercury compound. The filtrate was acidified with 40 cc. of glacial acetic acid, filtered, washed with water and alcohol and dried *in vacuo* over phosphorus pentoxide; yield of pure anhydro-2-hydroxymercuriterephthalate, 18 g. More of the product was obtained from the various residues and mother liquors.

Anal. Calcd. for $C_8H_4O_4Hg$: Hg, 55.0. Found: Hg, 54.5.

Mercuration of Diethyl Terephthalate.—A mixture of 40 g. (0.18 mole) of diethyl terephthalate, 57.5 g. (0.18 mole) of mercuric acetate and 2 cc. of glacial acetic acid was heated for seventy hours at 117° (bath of boiling *n*-butyl alcohol). No test for inorganic mercury was then given. The pasty mass was then steam distilled for twenty-four hours. The residue was digested with ammonium hydroxide solution, filtered and acidified. The mercurated terephthalic acid was purified as before.

Di-*n*-butyl 2-Chloromercuriterephthalate.—A suspension of 5 g. of the anhydro compound in 200 cc. of chloroform was treated with 20 g. of phosphorus pentachloride. Some heat was evolved. After refluxing for half an hour solution was almost complete. A slight residue was removed by filtration and the filtrate was evaporated on a water-bath to 50 cc. *in vacuo*. It was cooled in ice. The acid chloride separated in crystalline form but it was not possible to prepare it in definite purity for analysis. In its crude state it was heated with 25 cc. of anhydrous *n*-butyl alcohol. On cooling, fine white crystals of the ester separated. It was crystallized from 15 cc. of hot 95% alcohol and dried *in vacuo* over phosphorus pentoxide; m. p. 82–85°; yield, 70%.

Anal. Calcd. for $C_{16}H_{21}O_4ClHg$: Hg, 39.1. Found: Hg, 39.7.

2-Chloromercuriterephthalamide.—A solution of 2 g. of the ester in 300 cc. of 95% alcohol was treated with dry ammonia gas and allowed to stand for two days. The white precipitate was collected and dried at 100°; wt., 1 g. It did not melt at 300°. Analyses of several samples gave consistently 48.0 ±0.2 for the mercury content instead of the calculated 50.1. This mercury content corresponds to a monohydrate but no water was given off even at 200°.

The amide was prepared from the crude acid chloride and dry ammonia in chloroform. It was dried *in vacuo* at 140°; yield, 90%.

Anal. Calcd. for $C_8H_7O_2N_2ClHg$: Hg, 50.1. Found: Hg, 49.5.

Anilide of 2-Chloromercuriterephthalic Acid.—The crude acid chloride from 10 g. of the anhydro compound was heated with 50 cc. of aniline. The extract was evaporated *in vacuo* to 5 cc. and treated with 10 cc. of alcohol and 400 cc. of water. The anilide was a brown, amorphous product, somewhat soluble in hot water and readily soluble in hot alcohol. It did not melt at 300°.

Anal. Calcd. for $C_{20}H_{15}O_2N_2ClHg$: Hg, 36.4. Found: Hg, 36.3.

Treatment of the Mercurated Terephthalic Acid with Bromine.—A suspension of 10 g. of the anhydro compound was treated with a solution containing 10 g. of sodium bromide and 1.5 cc. of bromine. The bromine was decolorized at once. The mixture was acidified with hydrochloric acid and the resulting precipitate crystallized from hot alcohol. It showed the properties of 2-bromoterephthalic acid and melted at 299°. Its molecular weight in alcohol as determined by the McCoy method was 269 (calcd. 245).

Purification of Anhydro-2-hydroxymercuribenzoic Acid.—A sample of the crude product containing 62.5% of mercury was converted to the acid chloride and then to the *n*-butyl ester. This was crystallized from absolute alcohol. It was then hydrolyzed by boiling with 90% alcohol.

Anal. Calcd. for $C_7H_4O_2Hg$: Hg, 56.1. Found: Hg, 55.8, 55.9.

Summary

1. Terephthalic acid has been mercurated in the 2-position.

2. The salts of the mercurated terephthalic acid are only slightly less hydrolyzed than those of mercurated benzoic acid.

3. A method has been developed for purifying mercurated aromatic acids.

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