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

THE MERCURATION OF ANTHRAQUINONEDICARBOXYLIC ACIDS

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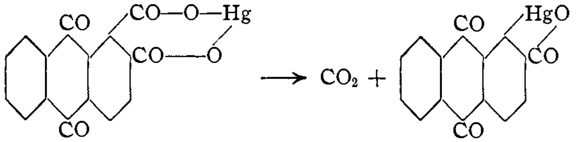
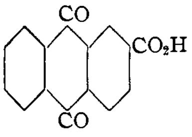
RECEIVED OCTOBER 15, 1928 PUBLISHED MARCH 6, 1929

The purposes of the present research were to make available mercurated carboxylic acids of relatively high molecular weight and to study further the replacement of one of two ortho carboxyl groups by mercury.[2]

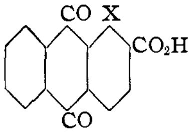
1,2-Anthraquinonedicarboxylic acid was converted to the mercury salt, which was heated dry until no more carbon dioxide was evolved and until ionizable mercury was absent.



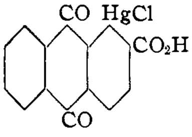
The position of the mercury was proved by treatment with acid, yielding pure anthraquinone-2-carboxylic acid (I) which was shown to be identical with some of the acid prepared by the oxidation of β-methylanthraquinone. Replacement of the mercury by halogen gave the known 1-iodo-anthraquinone-2-carboxylic acid (II) and the hitherto unknown 1-bromo-anthraquinone-2-carboxylic acid (II). The anhydro hydroxymercuri compound was also converted to 1-chloromercuri-anthraquinone-2-carboxylic acid (III).



I



II



III

There was no evidence that any of the β-carboxyl was replaced by mercury with the formation of a derivative of anthraquinone-1-carboxylic acid. In other words, the carboxyl replaced was the one between the quinone group and the other carboxyl group.

2,3-Anthraquinonedicarboxylic acid was prepared from the 2,3-dimethyl compound obtained from o-xylene and phthalic anhydride. The mercury salt heated dry decomposed considerably more readily than that of the 1,2-acid.

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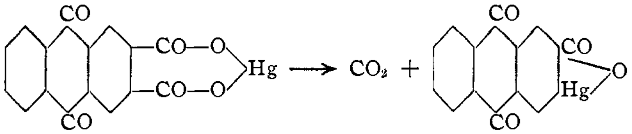
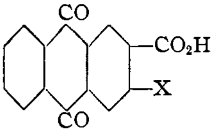
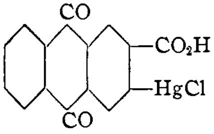
[2] This well-known method of introducing mercury into organic compounds was discovered by Pesci, *Atti accad. Lincei*, [5] **10**, I, 362 (1901).



Treatment of the mercurated product with acid and halogens gave anthraquinone-2-carboxylic acid (I), the known 3-bromo-anthraquinone-2-carboxylic acid (IV) and the new 3-iodo-anthraquinone-2-carboxylic acid (IV). The chloromercuri acid was also prepared (V).



IV



V

Experimental Part

Preparation of Anthraquinone-1,2-dicarboxylic Acid.—Naphthalene and phthalic anhydride were condensed in benzene solution in the presence of anhydrous aluminum chloride to form *α*-naphthoyl-*o*-benzoic acid. Through the elimination of water from this compound by means of concd. sulfuric acid benz-1,2-anthraquinone was obtained. The oxidation of the latter substance with potassium permanganate in strongly acid solution gave anthraquinone-1,2-dicarboxylic acid. Purification of the acid was effected by recrystallization from glacial acetic acid until the melting point was 270°.

Formation of the Mercury Salt of Anthraquinone-1,2-dicarboxylic Acid.—To a hot solution of 10 g. of the dibasic acid in 300 cc. of water and 5 g. of potassium hydroxide was added a solution of 7 g. of mercuric oxide in 40 cc. of 50% acetic acid. The resulting mixture contained a slight excess of the dibasic acid and was slightly acid with acetic acid. The mercury salt was immediately precipitated as a slightly yellow powder upon mixing the two solutions. It was filtered off, thoroughly washed with hot water, dried and pulverized. The yield was about 95%.

Establishment of a Carbon-Mercury Linkage in Anthraquinone-1,2-dicarboxylic Acid.—Refluxing of suspensions of the mercury salt in dilute acetic acid solution did not split out carbon dioxide to form a carbon-mercury linkage. Attempts were made under a wide range of conditions. To effect the desired result, it was found necessary to heat the dry mercury salt at 235°. No evolution of carbon dioxide was perceptible at lower temperatures.

The pulverized mercury salt was placed in a small flask which was immersed in a fused salt bath (potassium nitrate and sodium nitrite) held at 235°. A convenient amount of the mercury salt for a 200-cc. flask was 15 g. The material was frequently stirred in order to insure a uniform product. Small amounts of the material were tested from time to time for the presence of inorganic mercury by suspending in dilute acetic acid and adding a bright piece of copper wire. An amalgamation of the surface of the copper on heating the above mixture to boiling was taken to indicate the presence of inorganic mercury. This test was the most reliable one available. A minimum of eight hours' heating at 235° was required to obtain a product giving no test for inorganic mercury. The material thus obtained was almost entirely alkali-soluble, though long boiling with alkali was necessary to effect solution. Longer heating of the mercury salt gave a larger amount of alkali-insoluble material. The mercuration product as obtained in this way was a bright yellow powder. It did not melt and decomposed only on heating above 300°.

A suspension of 2 g. of the finely pulverized mercuration product in 400 cc. of water was boiled for five minutes with 25 cc. of concd. hydrochloric acid. The undissolved material was filtered and washed with hot water. It was then boiled with a dilute solution of ammonia for one minute. The material unchanged by this treatment was filtered and thoroughly washed with hot water. This treatment should suffice to eliminate both acidic and basic impurities. The material was then dried and analyzed.

Anal. Subs., 0.2517, 0.2310: Hg, 0.1128, 0.1030. Calcd. for $C_{15}H_6O_4Hg$: Hg, 44.5. Found: Hg, 44.8, 44.6.

Treatment of the Mercuration Product with Hydrochloric Acid.—A mixture of 10 g. of the mercuration product and 500 cc. of concd. hydrochloric acid was boiled for twenty-four hours. The reaction mixture was diluted with twice its volume of water and filtered. The residue was washed with warm water and extracted with dilute sodium hydroxide.

The alkali-insoluble material did not change on further boiling with concd. hydrochloric acid. It contained no mercury. On boiling with *aqua regia* anthraquinone was formed. The presence of this alkali-insoluble material was perhaps due to the action of hydrochloric acid on the monobasic anthraquinone acid. The 2-acid on boiling with concd. hydrochloric acid forms an alkali-insoluble product. Anthraquinone itself even on long boiling with concd. hydrochloric acid is unchanged.

The alkali-soluble material was precipitated from solution by the addition of hydrochloric acid. This material on drying weighed 4.25 g. (76.6% yield). It melted at 281–282° without further purification. The melting point after two crystallizations from glacial acetic acid was 285–285.5°. Investigation of the various fractions from the acetic acid crystallizations failed to show the presence of any other product.

Preparation of Anthraquinone-2-carboxylic Acid.—A solution of 40 g. of β-methylanthraquinone in 800 cc. of concd. sulfuric acid was added to 1600 cc. of hot water in a 3-gallon crock with vigorous mechanical stirring. To the suspension of β-methylanthraquinone thus produced was gradually added 60 g. of finely-powdered potassium permanganate. The reaction was allowed to continue with vigorous mechanical stirring for ten minutes after the addition of all of the permanganate. The mixture was then decolorized by the addition of a hot solution of oxalic acid. The insoluble material was collected on a filter and extracted with hot dilute ammonia solution. The insoluble residue from this treatment was unchanged β-methylanthraquinone. The ammoniacal solution was acidified with hydrochloric acid and the precipitated material filtered off. The crude acid was treated with decolorizing carbon in boiling glacial acetic acid. The solution was filtered and allowed to crystallize. The first crop of crystals melted at 285–286°. The melting point was unchanged by further recrystallization from glacial acetic acid. A mixed melting point of this acid with that obtained by the action of hydrochloric acid on the mercuration product was 285–286°, an indication of the identity of the two materials.

Formation of 1-Iodo-anthraquinone-2-carboxylic acid.—The position of the mercury in the anhydro compound was further established by the formation of this acid on replacing mercury by iodine. A mixture of 6.75 g. (0.015 mole) of the mercurated product, 7.47 g. (0.045 mole) of potassium iodide and 3.81 g. (0.015 mole) of iodine and 200 cc. of water was heated at 70° for about three hours, or until the iodine was entirely used up. The presence of about 3 cc. of chloroform was found to be very helpful in the estimation of the amount of iodine present at any time. When the iodine had all reacted, the mixture was filtered while hot. The filtrate was acidified with hydrochloric acid and the deep yellow precipitate was collected on a filter. This was washed with a little potassium iodide solution and then with warm water. On crystallization from 95% ethyl alcohol the substance was obtained in very fine, deep yellow needle crystals which became orange colored on standing; melting point 266–268°. The melting point given in the literature is 266–267°.

Anal. Subs., 0.2518, 0.2606: 0.100 *N* $AgNO_3$, 6.72 cc., 6.94 cc. Calcd. for $C_{15}H_7O_4I$: I, 33.6; Found: I, 33.9, 33.8.

Preparation of 1-Bromo-anthraquinone-2-carboxylic Acid.—This previously undescribed acid was obtained in a fashion analogous to that used for the iodo acid. A suspension of 5 g. of the mercurated product in 500 cc. of water was heated at 50° for three hours with an excess of bromine in sodium bromide solution. At the end of this time the excess bromine was boiled off. The mixture was filtered while hot. The filtrate on acidification with hydrochloric acid gave a slightly yellow flocculent precipitate. This was filtered off, washed with warm water and dried, yield, 1.37 g. Apparently only a part of the mercury had been replaced, since 2.15 g. of the original material was recovered apparently unchanged. Crystallization from alcohol gave yellow needles, melting at 267–268°. As in the case of the corresponding iodo acid the needles were extremely fine.

Anal. Subs., 0.1589: 0.100 *N* $AgNO_3$, 4.80 cc. Calcd. for $C_{15}H_7O_4Br$: Br, 24.1. Found: Br, 24.2.

Preparation of 1-Chloromercuri-anthraquinone-2-carboxylic Acid.—A mixture of 5 g. of the mercurated product, 20 g. of sodium hydroxide and 500 cc. of water was heated just below boiling for twelve hours. The mixture was filtered hot and made barely acid with hydrochloric acid at the boiling point of the solution. After standing for a few minutes, it was made alkaline with 2 *N* sodium hydroxide solution and then just acid with hydrochloric acid. These operations were all carried out at the boiling point; otherwise filtration was very difficult and the precipitate likely to be very impure. The precipitated material was filtered off, washed thoroughly with hot water, dried and pulverized. The compound as thus obtained was a light yellow powder.

Anal. Subs., 0.2017, 0.2006: Hg, 0.0824, 0.0820. Subs., 0.1978, 0.2012: 4.00, 4.18 cc. of 0.100 *N* $AgNO_3$. Calcd. for $C_{15}H_7O_4ClHg$: Hg, 41.2; Cl, 7.28. Found: Hg, 40.9, 40.9; Cl, 7.16, 7.37.

Preparation of Anthraquinone-2,3-dicarboxylic Acid.—*o*-Xylene was condensed with phthalic anhydride in the presence of anhydrous aluminum chloride, high boiling naphtha being used as a diluent. The *o*-xyloyl-*o*-benzoic acid thus formed gave 2,3-dimethylanthraquinone on dehydration with 15–20% fuming sulfuric acid. Dimethylanthraquinone was oxidized to the dibasic acid as follows.

A solution of 40 g. of 2,3-dimethylanthraquinone in 800 g. of concd. sulfuric acid was added with vigorous mechanical stirring to 1600 g. of hot water in a 3-gallon crock. To the suspension of dimethylanthraquinone thus obtained was added in small portions 120 g. of finely-powdered potassium permanganate. The addition was made at such a rate as to maintain the temperature at 90–95°. The reaction was allowed to continue for ten minutes with mechanical stirring after the addition of all the permanganate. The excess oxidizing agent was then removed by oxalic acid. The insoluble material was filtered off and washed with hot water. It was transferred to a beaker and the acid dissolved in hot dilute ammonia solution. The residue of unchanged dimethylanthraquinone was removed by filtration. The dibasic acid was precipitated from the filtrate by the addition of hydrochloric acid. The material was filtered, thoroughly washed with hot water and dried; yield, 7.5 g. The amount of recovered dimethylanthraquinone was 21 g. The yield of the acid was 31.6%, based on the material which reacted. Purification was effected by crystallization from glacial acetic acid. The melting point of the material thus obtained was 340–342°.

Preparation of the Mercury Salt of Anthraquinone-2,3-dicarboxylic Acid.—To a hot solution of 7.5 g. of the acid in 500 cc. of water and 50 cc. of 2 N potassium hydroxide was added a solution of 5.25 g. of mercuric oxide in 30 cc. of 50% acetic acid. The mercury salt was immediately precipitated as a slightly yellow powder. The above procedure provided for a slight excess of the dibasic acid and the resulting mixture was slightly acid with acetic acid. The material was filtered off, washed with a large quantity of hot water, dried and pulverized. The yield was about 95%.

Establishment of a Carbon-Mercury Linkage in Anthraquinone-2,3-dicarboxylic Acid.—In a 200-cc. flask was placed 11 g. of the finely-powdered mercury salt of anthraquinone-2,3-dicarboxylic acid. The flask was heated in a fused salt-bath. The evolution of carbon dioxide was tested for from time to time as the temperature was raised. At 210–215° the evolution of carbon dioxide was first noticed. At this temperature the gas came off quite rapidly. The contents of the flask were stirred from time to time to insure uniform treatment of the material. At the end of four or five hours, no test could be obtained for inorganic mercury by the previously described copper wire method. The product was a bright yellow powder. Sublimed yellow needles and free mercury were evidence that some decomposition took place under the conditions used. The amount of material recovered was 8.72 g.

The mercurated product required purification before analysis, since it was not at all homogeneous. The possible impurities such as the original acid, anthraquinone and mercuric oxide are soluble in glacial acetic acid. Accordingly, 2 g. of the mercurated product was boiled for five minutes with 50 cc. of glacial acetic acid. The material undissolved by this treatment was filtered, dried and analyzed.

Anal. Subs., 0.2308, 0.2333: Hg, 0.1015, 0.1027. Calcd. for $C_{15}H_6O_4Hg$: Hg, 44.5. Found: Hg, 44.0, 44.0.

As in the case of the 1,2-dibasic acid, the formation of a mercuri-*bis* acid or a double mercuri-*bis* compound might be possible. No evidence was obtained for the formation of such products. The mercurated product after the above treatment was almost entirely soluble in alkali, though solution was very slow. The formation of two isomeric anhydro-*o*-hydroxymercuri acids was not possible here as in the case of the 1,2-dibasic acid.

Treatment of the Mercuration Product with Hydrochloric Acid.—A mixture of 3.00 g. of the mercurated product and 150 cc. of concd. hydrochloric acid was refluxed for fifteen hours. The reaction mixture was diluted with twice its volume of water, allowed to stand for a short time and filtered. The insoluble material was extracted with dilute ammonium hydroxide. The extract was acidified with hydrochloric acid. A slightly yellow flocculent substance was precipitated. The mixture was allowed to digest on the steam-bath for about an hour. The precipitated material was filtered off, washed with warm water and dried; yield, 1.49 g. The various filtrates were collected and evaporated to dryness together.

The material insoluble in ammonia was boiled with glacial acetic acid. Its original weight was 0.12 g. The amount soluble in acetic acid was 0.06 g. This was probably a substance formed by the action of hydrochloric acid on the anthraquinone acid. The insoluble material was probably unchanged mercury compound.

The material soluble in ammonia solution was the main product. It was dissolved in boiling glacial acetic acid and treated with decolorizing carbon and filtered. The filtrate on cooling deposited small felted crystals of a slightly yellow color; melting point, 280–281°. Further crystallization from the same solvent raised the melting point to 284–285°. A mixture with the 2-acid from the oxidation of β-methylanthraquinone melted at 284.5–285.5°.

The residue from the evaporation of the various filtrates was taken up in 25 cc. of water slightly acidulated with hydrochloric acid. The insoluble portion was collected on a filter. It weighed 0.10 g. It did not melt and seemed to consist largely of inorganic material.

The amount of the mercury compound reacting was 3.00 g. − 0.06 g. = 2.94 g. Assuming that the material insoluble in alkali but soluble in acetic acid is formed from an approximately equal weight of the 2-acid of anthraquinone, the amount of material accounted for is 1.49 g. + 0.06 g. = 1.55 g. The amount of the monobasic anthraquinone acid which would be formed from 2.94 g. of the anhydro compound is 1.65 g. The amount of material accounted for is thus about 94%.

Preparation of 3-Bromo-anthraquinone-2-carboxylic Acid.—A suspension of 2 g. of the mercury compound in 200 cc. of water was treated with an excess of bromine in potassium bromide. The mixture was heated at 50–60° for two hours under reflux to prevent the loss of bromine. The excess of bromine was then boiled off under a hood. The mixture was filtered and the filtrate acidified with hydrochloric acid. The mixture was allowed to digest on the steam-bath for about an hour. The product, after washing with warm water and drying, weighed 0.95 g. (yield 65%). After two crystallizations from 70% alcohol, it was obtained in very fine, almost colorless felted needles. These melted at 284–285.5°. The value given in the literature is 284°.

Anal. Subs., 0.1556: 0.100 *N* $AgNO_3$, 4.62 cc. Calcd. for $C_{15}H_7O_4Br$: Br, 24.1. Found: Br, 23.7.

Preparation of 3-Iodo-anthraquinone-2-carboxylic Acid.—The previously undescribed iodo acid was prepared in a fashion analogous to that for the corresponding bromine compound. To a solution of 1.27 g. of iodine and 2.50 g. of potassium iodide in 200 cc. of water was added 2.25 g. (0.05 mole) of the mercury compound. The mixture was heated at 60° under a condenser until the iodine had all reacted (three to four hours). The insoluble material, usually small in amount, was removed by filtration. The filtrate was acidified with hydrochloric acid. The precipitated material was filtered after digestion on the steam-bath for about an hour, washed with a little potassium iodide solution to insure the removal of mercuric iodide, then with water at about 60° and dried. The crude yield was 1.37 g. or 72.5%.

On crystallization from alcohol the substance was obtained in extremely fine felted crystals of a bright yellow color. These melted at 289–290°.

Anal. Subs., 0.2042: 0.100 *N* $AgNO_3$, 5.36 cc. Calcd. for $C_{15}H_7O_4I$: I, 33.6. Found: I, 33.3.

Preparation of 3-Chloromercuri-anthraquinone-2-carboxylic Acid.—A mixture of 2 g. of the mercury compound, 50 cc. of 2 *N* sodium hydroxide and 450 cc. of water was refluxed for twelve hours. Any residue was filtered off. The filtrate was heated to boiling and made strongly acid with hydrochloric acid. A flocculent yellow precipitate was formed. After standing for three minutes the mixture was neutralized with 2 *N* sodium hydroxide. It was then made slightly acid with hydrochloric acid to precipitate the chloromercuri acid, the procedure again being carried out at the boiling point. The precipitation had to be made at the boiling point; otherwise the material precipitated was very difficult to filter and to wash free of the impurities which it contained. The product was filtered off and thoroughly washed with hot water. After drying it was pulverized and boiled for five minutes with 25 cc. of glacial acetic acid. It was washed and dried. The chloromercuri acid is a light yellow powder. Its alkaline solution is a deep red color.

Anal. Subs., 0.1996, 0.2488: Hg,[3] 0.0818, 0.1015. Subs., 0.2500: 5.32 cc. of

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[3] In the usual gold crucible analysis an unusually high temperature was required for decomposition of this compound.

0.100 *N* $AgNO_3$. Calcd. for $C_{15}H_7O_4ClHg$: Hg, 41.2; Cl, 7.28. Found: Hg, 40.9, 40.8; Cl, 7.54.

All melting point temperatures given in this paper are uncorrected. The correction for temperatures used is about 4°.

All mercury analyses were made by the gold crucible method.[4]

In halogen analyses the materials were decomposed by the use of sodium peroxide as outlined in Kingscott and Knight, "Organic Analysis." The amount of halogen was then determined by the Volhard method.

Summary

1. The mercury salts of the 1,2- and the 2,3-dicarboxylic acids of anthraquinone lose carbon dioxide when heated above 200°. In each case a mercury–carbon linkage is established. In the 1,2-acid the replacement is limited to the carboxyl between the quinone group and the other carboxyl, that is, only the α-carboxyl is replaced.

2. The mercury salt of the 2,3-acid loses carbon dioxide more readily than that of the 1,2-acid.

3. The corresponding chloromercuri compounds have been prepared.

4. The mercury has been replaced by bromine and by iodine.

5. The following new compounds have been prepared: anhydro-1-hydroxymercuri-anthraquinone-2-carboxylic acid, 1-chloromercuri-anthraquinone-2-carboxylic acid, 1-bromo-anthraquinone-2-carboxylic acid, anhydro-3-hydroxymercuri-anthraquinone-2-carboxylic acid, 3-chloromercuri-anthraquinone-2-carboxylic acid, 3-iodo-anthraquinone-2-carboxylic acid.

6. A new method has been developed for preparing anthraquinone-2,3-dicarboxylic acid.

EVANSTON, ILLINOIS

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[4] Whitmore, "Organic Compounds of Mercury," Chemical Catalog Co., Inc., New York, **1922**, p. 365.