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THE MERCURATION OF NAPHTHOIC ACIDS. I. 1-NAPHTHOIC ACID

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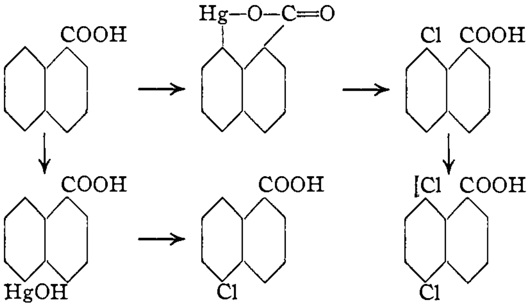
The present paper is a continuation of the studies on mercuration and the preparation of organic mercury compounds of higher molecular weight which have been carried on in this Laboratory during the past ten years.

1-Naphthoic acid reacts readily with mercuric acetate to give a mixture of mercurated acids substituted in the 5- and 8-positions. The structure of the mercurated products was determined by replacement of the mercury by chlorine. The structure of the 8-chloro-1-naphthoic acid was confirmed by chlorination to give 5,8-dichloro-1-naphthoic acid.



A considerable by-product of the mercuration was an alkali-insoluble organic mercury compound formed with the loss of carbon dioxide. This product contained two mercury atoms probably in the 1,5-positions.

In the course of the study anhydro-8-hydroxymercuri-1-naphthoic acid obtained from naphthalic acid was changed to the 8-chloro- and the 8-bromo acids. This is the best available way to obtain the 8-halogen-1-naphthoic acids in quantity and in a high degree of purity.

Experimental Part

Preparation of 1-Naphthoic Acid.—Several methods were studied. Fusion of sodium 1-naphthalene sulfonate with sodium formate gave a 6 to 8% yield. Heating the same materials in kerosene gave none of the desired acid. The use of the calcium salt in the fusion with sodium formate gave a 9% yield. Passage of the vapors of 1-bromonaphthalene over heated potassium ferrocyanide gave no naphthonitrile. Treatment of 1-naphthylamine by the Sandmeyer reaction gave none of the nitrile.

The best methods of preparing 1-naphthoic acid were found to be through its nitrile formed by fusion of sodium 1-naphthalene sulfonate with sodium cyanide and from 1-bromonaphthalene through the Grignard reagent and treatment with carbon dioxide.

Sodium 1-naphthalene sulfonate was prepared by sulfonating naphthalene with concentrated sulfuric acid at 40–50°, neutralization with calcium hydroxide, treatment with sodium carbonate solution, removal of calcium carbonate by filtration and evaporation of the filtrate to crystallization.

A mixture of 920 g. (4 moles) of dry sodium 1-naphthalene sulfonate and 196 g. (4 moles) of sodium cyanide was prepared by grinding the materials together in a meat grinder and passing the mixture several times through a sieve. The retort used was a 3-inch iron pipe about 3 feet long with one end closed by a cap and the other provided with a flange fitted to another flange bearing a half-inch bent pipe about 6 inches long. The large pipe was placed on end and a stick about $^3/_4$ inch in diameter was placed in it. The mixture for fusion was then filled into the pipe to within about 6 inches of the top. A hard asbestos gasket was stuck to the flange with sodium silicate solution. The iron pipe with the stick at the top was then placed horizontally in a gas-heated combustion furnace. The stick was withdrawn, leaving a free space above the whole length of the mixture. The other flange was bolted on and the small pipe was connected with a flask set in an air-bath. This flask was connected with a vertical condenser and five wash bottles containing benzene. The end of the system was connected with a water pump. The combustion furnace was turned on full force. The nitrile started to distil almost immediately. Several runs were made without emptying the receiving system. The crude cyanide was separated from a small amount of water and distilled. The main fraction boiled at 285–300°. A considerable amount was recovered from the benzene wash bottles.

The 1-naphthonitrile was hydrolyzed by the method of Kamm,[1] refluxing 50 g. of nitrile with 100 cc. each of sulfuric acid, acetic acid and water for four hours. Treatment of the precipitated product with ammonium hydroxide dissolved all except 3 g. The filtrate from this material was acidified with hydrochloric acid and the solid collected on a filter; m. p. 145–155°; wt., 55 g. (98% yield). With considerable difficulty the acid was purified to its true melting point of 161° by crystallization from dilute acetic acid, dilute ethyl alcohol or xylene. The best method of purification was by esterification and vacuum distillation of the ethyl ester with subsequent hydrolysis; boiling point of ethyl 1-naphthoate, 183–186° (20 mm.).

The Grignard reagent prepared from 103.5 g. (0.5 mole) of 1-bromonaphthalene and 12 g. (0.5 g. atom) of magnesium in 1.5 liters of dry ether was treated under vigorous stirring with dry carbon dioxide gas. The Grignard addition product adhered to the walls of the flask as a green tar. The ether was decanted for use in another run. The tar was treated with dilute hydrochloric acid with the formation of crude 1-naphthoic acid. It was dissolved in ammonium hydroxide, boiled with decolorizing carbon and fuller's earth and filtered. The filtrate was allowed to stand for twenty-four hours to allow a small amount of a very troublesome tar to separate. After the addition of a little fuller's earth and filtration, the light green or straw-colored solution was acidified with hydrochloric acid. Pure white 1-naphthoic acid separated; m. p. 148–152°; wt., 40–45 g. (46–52% yield).

Mercuration of 1-Naphthoic Acid.—The mercuration of this acid took place with extreme ease but the products were most unmanageable. A total of 1357 g. of 1-naphthoic acid was mercurated in 39 experiments with a systematic variation of solvent,

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[1] Private communication.

concentration, temperature and time of heating. The results of all the experiments were roughly similar. Only one will be given here.

A solution of 172 g. (1 mole) of 1-naphthoic acid in 210 cc. of 5 *N* sodium hydroxide and 2 liters of water was placed in a flask provided with a dropping funnel, a mercury seal stirrer and a reflux condenser connected with weighed potassium hydroxide traps to catch the carbon dioxide evolved. The stirrer was started and the mixture was heated to boiling. A solution of 318 g. (1 mole) of mercuric acetate in 1.5 liters of water and 60 cc. of acetic acid was added gradually. A white granular precipitate formed at once. Gas was evolved slowly. The mixture was refluxed for forty-four hours. The apparatus was then swept out with air free from carbon dioxide. The carbon dioxide absorbed by the potassium hydroxide was 4.98 g. The cream-colored precipitate in the flask was treated with 280 cc. of 5 *N* sodium hydroxide. Part of it dissolved and the rest turned black, due to the presence of mercurous compounds. The insoluble portion weighed 80 g. The alkaline filtrate was saturated with carbon dioxide. The precipitate formed was filtered and redissolved in sodium hydroxide solution. It was again precipitated by carbon dioxide; wt., 240 g. The filtrate from the mercurated product gave 34 g. of unchanged 1-naphthoic acid when acidified with hydrochloric acid.

As will be shown below the chief product consisted of hydroxymercuri-1-naphthoic acids having the mercury in the 5- and 8-positions. The alkali-insoluble product was mainly a dimercurated naphthalene.

The above mercuration experiment can be summarized as follows

1-Naphthoic acid recovered unchanged, g.	34
1-Naphthoic acid equivalent to 240 g. of Hg compound, g.	110.5
1-Naphthoic acid equivalent to 80 g. of Hg_2 compound, g.	24.5
1-Naphthoic acid not accounted for, g.	3
1-Naphthoic acid started with, g.	172

The amount of mercurous compound formed by oxidation–reduction reactions was not determined. The amount of carbon dioxide recovered was only 80% of the amount calculated from the amount of alkali-insoluble dimercurated product obtained.

Purification and Identification of Mercury Compounds Obtained from 1-Naphthoic Acid.—Literally hundreds of experiments were carried out to separate the mixture of hydroxymercuri-1-naphthoic acids into pure chemical individuals. Many fractionations were obtained by the use of a variety of solvents. In almost all cases fractions were obtained which contained 44 to 55% of mercury (calcd. for anhydro-hydroxymercuri-1-naphthoic acid, Hg, 54.05).

It was finally decided to convert the mixture of mercury compounds to a mixture of halogenated 1-naphthoic acids and to separate these.

Attempts to obtain iodonaphthoic acids by treatment with a chloroform solution of iodine gave only tarry products.

Replacement by bromine was more successful. A solution of 60 g. of the mixed hydroxymercuri-1-naphthoic acids in 60 cc. of 5 *N* sodium hydroxide and 300 cc. of water was heated with decolorizing carbon, filtered and barely acidified with hydrochloric acid. The chloromercuri compound was separated and suspended in 800 cc. of acetic acid and treated with 28 g. of bromine dissolved in sodium bromide solution. As the bromine solution was added, the color disappeared until the last was added when the red color remained. On boiling, the solution became clear but the color of bromine persisted. This was removed by treatment with a little sodium bisulfite. After boiling with decolorizing carbon and filtering, the solution was cooled. Crystals were obtained which melted at 226–230°. After several crystallizations from glacial acetic acid, the product melted at 248–250°. It was 5-bromo-1-naphthoic acid.[2] The mother liquors gave more of this acid and another acid which was not successfully purified.

Although the replacement of mercury by chlorine is not generally used in determinations of structure, it was decided to attempt it in this case.

An alkaline solution of 132.5 g. of the mixed hydroxymercuri-1-naphthoic acids was treated with 20 g. of sodium chloride, boiled for a few minutes, barely acidified with hydrochloric acid and filtered. The chloromercuri compound after drying in the air weighed 140 g. It was stirred with 400 cc. of glacial acetic acid and treated at room temperature with a glacial acetic acid solution of 24 g. of chlorine. Reaction took place at once and most of the material went into solution. The mixture was heated to boiling and filtered from a slight residue. The filtrate on cooling and on concentration gave mixtures of acids which were separated by a careful series of fractional crystallizations using as solvents glacial acetic acid, water and xylene. The acid obtained in largest amount melted at 241–242°. This was 5-chloro-1-naphthoic acid. Its melting point was not lowered by mixing with some of the known acid.[3] Smaller amounts of 8-chloro-1-naphthoic acid[4] melting at 171–171.5° were obtained. A known sample of this acid was prepared by treating with chlorine anhydro-8-hydroxymercuri-1-naphthoic acid obtained from naphthalic acid.[5] It melted at 170–170.5°. A mixture of the two melted at 169–170°. Examination of the optical properties of the two samples by means of the polarizing microscope also showed their identity. 8-Bromo-1-naphthoic acid, m. p. 176–179°, was made by a similar process.

The mother liquors from the 5-chloro and 8-chloro acids may have contained other acids but none could be isolated.

In a further search for other acids in the mixture it was decided to resort to a fractional distillation of the esters; consequently, 320 g. of the hydroxymercuri-1-naphthoic acids was treated with chlorine as above. The mixed acids were then refluxed with absolute methanol and dry hydrogen chloride for eleven hours. The oil left after the removal of the excess of methanol was washed with sodium carbonate solution. The acid obtained by acidifying the sodium carbonate solution was again treated with methanol and hydrogen chloride. Most of it failed to esterify; wt., 25 g. Several crystallizations from dilute acetic acid and from xylene gave crystals melting at 165–166°. A mixture with a slightly impure sample of known 8-chloro-1-naphthoic acid of m. p. 166–167° melted at 164.5–166.5°. A crystallographic examination proved the identity of the two materials. The interference colors were identical; both were biaxial. One axis of each had an index of refraction of 1.572 ± 0.003, while each had an index of refraction for the other axis between 1.635 and 1.740. To further prove the structure of this acid, a sample was chlorinated at room temperature in acetic acid using iodine as a catalyst. The product was 5,8-dichloro-1-naphthoic acid[6] melting at 186–187°.

The oily esters insoluble in sodium carbonate solution were dried by mixing with dry benzene and distilling off the benzene. The dry ester mixture was submitted to three

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[2] Hausemann, *Ber.*, 9, 1520 (1876).

[3] Ekstrand, *ibid.*, **11**, 1604 (1878).

[4] Ekstrand, *J. prakt. Chem.*, [2] **38**, 148 (1889).

[5] Leuck, Perkins and Whitmore, THIS JOURNAL, **51**, 1831 (1929).

[6] Ekstrand, *J. prakt. Chem.*, [2] **38**, 151, 255 (1889).

careful fractionations at 6-mm. pressure and a fourth at 4-mm. pressure. In this way four fractions were obtained.

FRACTION I. 6.2 g., b. p. 120–125° (4 mm.).—Hydrolysis gave mainly 1-naphthoic acid, m. p. 160–161°. A careful series of fractional crystallizations from boiling water failed to give any other acid. A mixture with known 1-naphthoic acid of m. p. 159° melted at 159–160°. The identity of the known 1-naphthoic acid and the acid from the ester fraction was further determined by crystallographic studies. Both crystallized from xylene in needles. Each had an extinction axis parallel to the long axis of the crystal. Each gave the same type of interference colors. Each had an index of refraction for one axis of 1.550 and for the other axis one above 1.740. A mixture of the acid with a sample of 8-chloro-1-naphthoic acid of m. p. 166–167° melted completely below 150°.

FRACTION II. 5.3 g., b. p. 125–130° (4 mm.).—This proved to be mainly impure 1-naphthoic acid. No other acid was isolated.

FRACTION III. 10.8 g., b. p. 131–133° (4 mm.).—On hydrolysis this gave mainly 5-chloro-1-naphthoic acid, m. p. 236–240°.

FRACTION IV. 10.8 g., b. p. 140–143° (4 mm.).—This gave 5-chloro-1-naphthoic acid, m. p. 244–245°. A mixture with known pure 5-chloro-1-naphthoic acid of m. p. 245–246° melted at 244–246°.

The alkali-insoluble product from the mercuration of 1-naphthoic acid was next studied. It reacted violently with an almost equal weight of bromine. From the tarry product there was obtained only a very small amount of a bromine compound, m. p. 124–146°. This *may* be impure 1,5-dibromonaphthalene. No other product could be separated from the tar.

Summary

1. Two satisfactory methods have been developed for making 1-naphthoic acid in quantity.

2. 1-Naphthoic acid is readily mercurated in the 5- and 8-positions, chiefly in the former.

3. During the mercuration some of the product loses carbon dioxide with the formation of an alkali-insoluble di-mercurated product of unknown structure.

4. 5-Bromo-1-naphthoic acid, 5-chloro-1-naphthoic acid and 8-chloro-1-naphthoic acid have been prepared from the mercury compounds.

5. 8-Chloro-1-naphthoic acid cannot be esterified even by long treatment with absolute methanol and dry hydrogen chloride.

6. A useful method has been developed for making 8-halogen-1-naphthalic acids from the mercuration product of naphthalic acid.

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