

The hot solution was clear and on cooling gave 13 g. of what was shown by halogen analysis and melting point to be triethyllead chloride.

The author is indebted to Professor C. S. Marvel for many helpful suggestions.

Summary

Diaryl lead dichlorides react in some cases with mercury diaryls to form the aryl mercuric chloride and a triaryl lead chloride.

Triaryl or alkyl lead halides disproportionate on heating to form a tetra-substituted lead derivative and a disubstituted lead dihalide. Diaryl or alkyl lead dihalides react with their corresponding tetraaryl or alkyl derivatives to form trisubstituted lead halides in good yields.

URBANA, ILLINOIS

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

SUBSTITUTION PRODUCTS OF ALPHA-NAPHTHOYL-ORTHO-BENZOIC ACID

BY E. H. JOHNSON,¹ V. WEINMAYR² AND ROGER ADAMS

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The formation of anthraquinone and its substitution products through the condensation of phthalic anhydride with benzene and its derivatives has found wide commercial application. Among the variations of this general procedure certain substituted anthraquinones, otherwise difficult to obtain, can be prepared by substituting the intermediate benzoyl-*o*-benzoic acids and subsequently closing the ring to the anthraquinone.

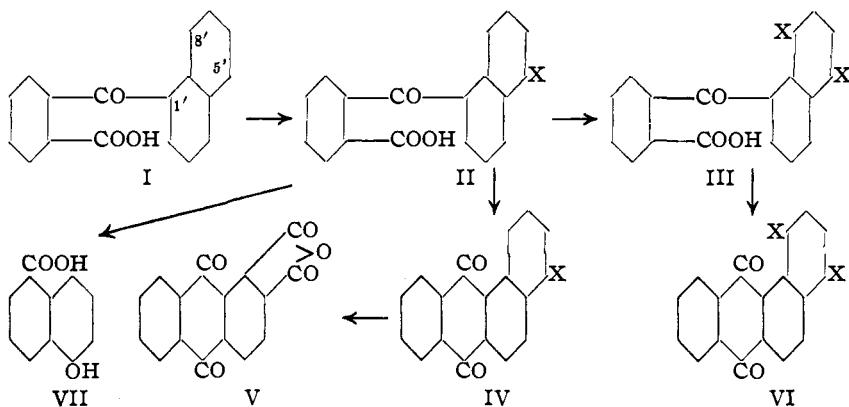
Benzanthraquinones have likewise been prepared from phthalic anhydride or substituted phthalic anhydrides with naphthalene or substituted naphthalenes,³ though more difficulties are encountered so far as isomers are concerned than appear in the benzene series. The substitution of the intermediate α -naphthoyl-*o*-benzoic acids with subsequent conversion to the benzanthraquinones, however, has not been previously described. A number of such reactions are reported in this communication.

¹ This communication is an abstract of a thesis submitted by E. H. Johnson in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Chemistry at the University of Illinois.

² Dr. V. Weinmayr, in the Laboratories of the Organic Chemicals Department, Dyestuffs Division of the du Pont Company, carried out the experiments on the chlorine derivatives.

³ Ador and Crafts, *Bull. soc. chim.*, **34**, 531 (1880); Elbs, *Ber.*, **19**, 2209 (1886); Gabriel, *ibid.*, **33**, 446 (1900); Scholl, *ibid.*, **44**, 2992 (1911); *ibid.*, **44**, 2370 (1911); *Monatsh.*, **32**, 997 (1911); **33**, 507 (1913); **41**, 583 (1920); Graebe, *Ann.*, **340**, 249 (1905); **340**, 259 (1905); Heller, *Ber.*, **41**, 3672 (1908); **45**, 665 (1912); Groggins, *Ind. Eng. Chem.*, **22**, 157 (1930); U. S. Patent 941,320 (1910); German Patent 234,917 (1911); Waldmann, *J. prakt. chem.*, **127**, 185 (1930); **127**, 201 (1930); Dziewonski, *Bull. Int. Acad. Pol.*, **3A**, 181 (1927); U. S. Patent 968,533.

α -Naphthoyl-*o*-benzoic acid (I) was readily chlorinated or brominated in glacial acetic acid either to a monochloro or monobromo (II) derivative. By further halogenation of the monohalogen products or by using two molecular equivalents of halogen with the α -naphthoyl-*o*-benzoic acid, dihalogen substitution products (III) resulted. With sulfuric acid as a solvent, the reaction proceeds rapidly toward the production of the dihalogen compound without stopping at the monohalogen state.

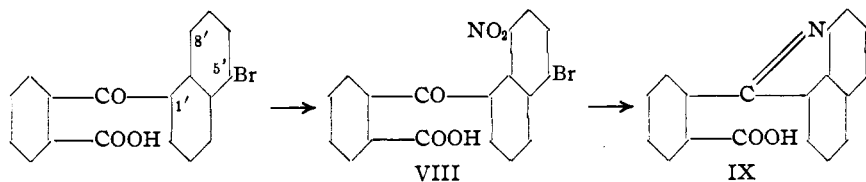


The position of the monosubstituted bromine compound was established. Upon oxidation with potassium permanganate of the bromo-1,2-benzanthraquinone (IV) obtained by ring closure of the bromo- α -naphthoyl-*o*-benzoic acid, anthraquinone-1,2-dicarboxylic acid anhydride (V) resulted which indicated that the bromine must be located in the original naphthalene nucleus. Its exact position was shown by fusing the bromo- α -naphthoyl-*o*-benzoic acid (II) with a mixture of sodium and potassium hydroxide at 200°. From the fusion 5-hydroxy-1-naphthoic acid (VII) was isolated and identified by its melting point and the melting point of its acetyl derivative, thus showing the original compound to be 5'-bromo-1'-naphthoyl-2-benzoic acid. It is fair to assume that the chlorine occupies the same position. The positions 5', 8' might be expected for the dihalogen compounds and by analogy to the structure of the nitro compounds discussed below these positions appear reasonably certain.

The monochloro- or bromo-1'-naphthoyl-2-benzoic acids were readily converted to the corresponding benzantraquinones (IV) by means of sulfuric acid with or without boric acid. The dihalogen compounds were, in a similar manner, converted to benzantraquinones (VI). A single dibromobenzanthraquinone was isolated, but from the dichloronaphthoyl-benzoic acid, two isomeric dichlorobenzanthraquinones were obtained. It would appear that during the dehydration, migration of the halogens must have occurred to some extent. As a consequence, the exact structure of these dihalogen benzantraquinones is not certain. It is probable,

however, that the dibromo and one of the dichloro compounds are 5', 8' disubstitution products.

The chloro- and bromo-1'-naphthoyl-2-benzoic acids were nitrated to mononitro derivatives (VIII). The 8'-position for this nitro group might be anticipated and subsequent experiments showed this to be the case. Upon reduction, the nitrobromo-1'-naphthoyl-2-benzoic acid gave a product, not an amine but obviously a secondary product (IX) acid in character with water eliminated. This could have formed only if the nitro were in the 8' position. This is a product analogous to that reported by



Scholl and Wolodkowitsch⁴ upon reduction of bz-1-nitro-1,2-benzanthraquinone.

The 5'-bromo-1'-naphthoyl-2-benzoic acid may also be nitrated in acetic anhydride. Under these conditions the product proved to be a dinitro- α -naphthoyl-*o*-benzoic acid. Bromine had been eliminated completely. It seems probable that the first nitro group was introduced in the 8'-position as in the mononitro monobromo compound, and since the bromine is eliminated, it is a natural conclusion that the second nitro has probably taken its place, leading to 5',8'-dinitro-1'-naphthoyl-2-benzoic acid.

Experimental

α -Naphthoyl-*o*-benzoic Acid.—This product was made by the procedure of Heller and Schulke⁵ as modified by Groggins and Newton.⁶ The only modification which was followed was in the purification. It was found that, in the laboratory at least, it could be crystallized readily from a large volume of toluene and purified much more readily than through the ammonium salt as previously recommended. The crude material obtained by following directions specified gave a product melting at 153–165° which, upon two recrystallizations from toluene gave a melting point of 173–173.5°. By evaporating the toluene mother liquors from the crystallizations there was no difficulty in recovering essentially all of the α -naphthoyl-*o*-benzoic acid present.

5'-Bromo-1'-naphthoyl-2-benzoic Acid (II).—To 100 g. of α -naphthoyl-*o*-benzoic acid in a 500-cc., round-bottomed flask fitted with a glass-jointed reflux condenser, were added 100 cc. of glacial acetic acid and 36 cc. (115 g.) of bromine and the mixture was refluxed for four hours. The reaction mixture was then cooled in an ice-salt bath until it had all solidified. On warming the flask to room temperature, a precipitate of 5'-bromo-1'-naphthoyl-2-benzoic acid was present. This was filtered out and dried; yield, 89.2 g. (69.5%). The compound was purified by two recrystallizations from toluene, m. p. 203–204°.

⁴ Scholl and Wolodkowitsch, *Ber.*, **44**, 2370 (1911).

⁵ Heller and Schulke, *ibid.*, **41**, 3670 (1908).

⁶ Groggins and Newton, *Ind. Eng. Chem.*, **22**, 157 (1930).

Anal. Calcd. for $C_{15}H_{11}O_3Br$: neut. equiv., 355; Br, 22.51. Found: neut. equiv., 350; Br, 22.35.

5',8'-Dibromo-1'-naphthoyl-2-benzoic Acid.—In a mortar 5 g. of pure α -naphthoyl-*o*-benzoic acid was ground with a trace of ferric chloride and a trace of iron powder and placed in a 125-cc. Erlenmeyer flask. Five cc. of bromine was allowed to drop slowly onto this mixture. After the bromine was all added, the reaction mixture was allowed to stand for three to four hours at room temperature and was then treated with dilute sodium hydroxide solution. All of the product dissolved in the boiling solution leaving a residue of ferric hydroxide. This was filtered off and on cooling a small amount of the sodium salt precipitated. The solution was acidified with dilute hydrochloric acid and a white precipitate was produced; yield, 4.5 g. (57.3%). The dibromo compound was purified by crystallization from toluene or glacial acetic acid. It formed fine white needles, m. p. 260–261°.

Anal. Calcd. for $C_{15}H_{10}O_3Br_2$: Br, 36.84. Found: Br, 36.72.

An alternate procedure is to dissolve 276 g. of α -naphthoyl-*o*-benzoic acid in 1370 g. of 93% sulfuric acid at 50°, and to add 160 g. of bromine slowly at this temperature, which is maintained for twenty-two hours longer. The temperature is then raised slowly to 70° to complete the reaction. The mass is now poured into 4 liters of ice water and the yellow precipitate is filtered and washed. The cake is extracted with dilute sodium hydroxide (to separate it from a considerable amount of ring-closed product) and the clear solution is run into ice and acid. The product is purified as described above and melts at 260–261°. The mixed melting point of the products made by the two methods was unchanged.

Anal. Calcd. for $C_{15}H_{10}O_3Br_2$: Br, 36.84. Found: Br, 36.68.

Proof of the Position of Bromine Atom in Bromo- α -naphthoyl-*o*-benzoic Acid

1. Oxidation⁷ of the Benzantraquinone from Bromo- α -naphthoyl-*o*-benzoic Acid.—A solution of 10 g. of monobromobenzantraquinone in 160 g. of concentrated sulfuric acid was poured into 400 cc. of water so that the product was precipitated in a finely divided form. This suspension was then heated to boiling and 75 g. of potassium permanganate was added in small portions. This was followed by solid oxalic acid until the black color was entirely gone. The hot solution was filtered, leaving a light yellow residue on the filter paper. More of this light colored solid precipitated when the hot filtrate had cooled. The precipitate from the hot filtration was treated with dilute aqueous ammonia, filtered, then acidified, when fine needles precipitated. This precipitate was then united with the one obtained from the cooling of the original oxidation solution and recrystallized twice from acetic anhydride (V). Light yellow needles were formed, m. p. 322–324°. This substance was shown to be anthraquinone-1,2-dicarboxylic acid anhydride by comparing it with an authentic sample prepared by oxidation of 1,2-benzantraquinone.⁷

2. 5-Hydroxy-1-naphthoic Acid by Fusion of Monobromo- α -naphthoyl-*o*-benzoic Acid with Potassium Hydroxide.—A mixture of 100 g. of sodium hydroxide, 100 g. of potassium hydroxide, and 25 g. of potassium nitrate was placed in a 500-cc., two-necked flask and heated until melting took place. A stirrer and condenser were placed in the center neck while a thermometer was placed in the side-neck. The stirrer was started and the flask was cooled to 200°. This temperature was maintained throughout the reaction. With continuous stirring 10 g. of bromo- α -naphthoyl-*o*-benzoic acid was added in small portions. When all had been added, the reaction mixture was stirred for fifteen minutes longer and then allowed to cool. The melt was dissolved in

⁷ General Method of Scholl and Schwinger, *Ber.*, **44**, 2992 (1911); Scholl and Graz, German Patent 241,624.

water and poured into a large volume of iced dilute hydrochloric acid. This solution was then extracted with ether. The ether extract was evaporated to a small volume and poured into a large volume of petroleum ether. A reddish-purple tar was precipitated. The liquid was decanted after standing, during which more tar appeared, was decanted again and then evaporated to dryness. The yellow residue thus obtained was dissolved in boiling water and treated with norite for a few minutes. The solution was filtered while hot and on cooling a white precipitate appeared. This was recrystallized twice from water to a constant m. p. of 236–237°. This is the melting point given in the literature for 5-hydroxy-1-naphthoic acid (VII).⁵

Some of this precipitate was then refluxed for two hours with acetic anhydride. The acetic anhydride was distilled off under reduced pressure and the resulting residue was recrystallized three times from water. It was a white solid, m. p. 198–201°. This is the melting point of the acetyl derivative of 5-hydroxy-1-naphthoic acid.⁵

5'-Chloro-1'-naphthoyl-2-benzoic Acid.—A solution of 414 g. of α -naphthoyl-*o*-benzoic acid in 500 g. of glacial acetic acid was treated at 114–118° with chlorine gas until it increased in weight by about 53 g. The red solution was poured onto a large amount of ice and water and the precipitate filtered. It weighed 440 g. (94.4%). White crystals, m. p. 179–180°, formed after purification from toluene.

Anal. Calcd. for $C_{15}H_{11}O_3Cl$: Cl, 11.42. Found: Cl, 11.35.

5',8'-Dichloro-1'-naphthoyl-2-benzoic Acid.—Into a solution of 276 g. of α -naphthoyl-*o*-benzoic acid in 1370 g. of 93% sulfuric acid at 30–70°, chlorine was passed until it had gained 87 g. in weight. The solution was then poured onto ice and water. The filtered mass was extracted with hot dilute sodium hydroxide, which left about 92 g. of chlorinated benzantraquinones. The alkaline solution was acidified and the product recrystallized from glacial acetic acid. White crystals of 5',8'-dichloro-1'-naphthoyl-2-benzoic acid, m. p. 242°, were obtained.

Anal. Calcd. for $C_{15}H_9O_3Cl_2$: Cl, 20.60. Found: Cl, 20.54.

The chlorination in glacial acetic acid gives the same dichloro compound as the chlorination in sulfuric acid but in much poorer yields.

Halogenated 1,2-Benzanthraquinones

Bz-4-bromo-1,2-benzanthraquinone (IV).—A solution of 20 g. of 5'-bromo-1'-naphthoyl-2-benzoic acid in 400 cc. of concentrated sulfuric acid was heated for exactly fifteen minutes at 115–117° and then was poured into a large volume of ice and water. The total reaction time was twenty minutes. A yellow precipitate was produced which was filtered off and treated with dilute sodium hydroxide solution to dissolve any unreacted material. The product was recrystallized from glacial acetic acid and gave greenish-yellow bulky needles, m. p. 231–232°; yield, 10.8 g.

Anal. Calcd. for $C_{15}H_9O_2Br$: Br, 23.71. Found: Br, 23.08, 23.39.

Bz-1,4-dibromo-1,2-benzanthraquinone (VI).—A solution of 4.8 g. of 5',8'-dibromo-1'-naphthoyl-2-benzoic acid in 30 cc. of concentrated sulfuric acid was heated at 122–124°, with or without 3 g. of boric acid, for twenty minutes. The sulfuric acid solution was immediately poured into a large volume of ice and water. A yellow precipitate was produced. This was filtered out, washed several times with water and then heated to the boiling point in 1300 cc. of dilute sodium hydroxide solution. Most of the yellow precipitate did not dissolve and after the solution cooled, it was filtered off; yield, 2.5 g. (54.3%). The product was purified by crystallization from benzene and gave a bright yellow solid, m. p. 265–266°.

Anal. Calcd. for $C_{15}H_7O_2Br_2$: Br, 38.44. Found: Br, 38.16.

⁵ Royle and Schedler, *J. Chem. Soc.*, **123**, 1647 (1923).

Bz-4-chloro-1,2-benzanthraquinone.—A solution of 45 g. of 5'-chloro-1'-naphthoyl-2-benzoic acid in 450 g. of 100% sulfuric acid containing 45 g. of boric acid was heated to 115–120° and held for twenty minutes. The ring-closed mass was poured onto a large amount of ice and water. The yellow precipitate was filtered, washed and extracted with hot dilute caustic solution. The yield was 38 g. (90.5%). Upon crystallization from glacial acetic acid, bright yellow needles were formed which melted at 232°.

Anal. Calcd. for $C_{18}H_9OCl$: Cl, 12.13. Found: Cl, 12.10.

Bz-dichloro-1,2-benzanthraquinones.—Seventy grams of 5',8'-dichloro-1'-naphthoyl-2-benzoic acid melting at 242° was added to a solution of 70 g. of boric acid in 700 g. of 100% sulfuric acid, heated to 160° and held for thirty minutes at 160–165°. The solution was cooled quickly to 100°, then poured onto a large amount of ice and water. The yellow precipitate was filtered, washed and extracted with hot dilute caustic solution. The yield was 30 g. (45.2%) of product melting at 240–300°.

Twenty-eight grams of the dry ring-closed product was extracted twice with 80 cc. of hot chlorobenzene. On cooling the extract, fine yellow needles separated which were filtered and recrystallized from 100 cc. of toluene. The fraction (7 g.) melted at 237–238°.

Anal. Calcd. for $C_{18}H_8O_2Cl_2$; Cl, 21.70. Found: Cl, 21.47.

The residue insoluble in chlorobenzene was further extracted hot with 380 cc. of chlorobenzene and 55 cc. of nitrobenzene. The precipitate from these extractions was filtered and recrystallized from 250 cc. of chlorobenzene. Five grams of dark yellow needles was obtained melting at 304°.

Anal. Calcd. for $C_{18}H_8O_2Cl_2$; Cl, 21.70. Found: Cl, 21.57.

8'-Nitro-5'-bromo-1'-naphthoyl-2-benzoic Acid. (VII.)—A solution of 97 g. of 5'-bromo-1'-naphthoyl-2-benzoic acid in 550 g. of 100% sulfuric acid was cooled to 10° and nitrated under agitation with 90 g. of a mixed acid containing 21% nitric acid and 69% sulfuric acid at 5–10°. After stirring for an hour, a test showed no nitric acid. Upon dilution with water the nitro compound precipitated (yield, 112 g.). It was purified by crystallization from hot nitrobenzene or *n*-butyl alcohol. The product consisted of white crystals, m. p. 228–230°.

Anal. Calcd. for $C_{18}H_{10}O_2NBr$: Br, 19.97; N, 3.50. Found: Br, 19.98; N, 3.51.

Reduction of 8'-Nitro-5'-bromo-1'-naphthoyl-2-benzoic Acid.—A solution of 4 g. of 8'-nitro-5'-bromo-1'-naphthoyl-2-benzoic acid in 100 cc. of acetic anhydride was reduced with 0.05 g. of platinum-oxide platinum black at 2.5 atm. pressure and a temperature of 80°. The catalyst was filtered and the acetic anhydride was distilled off under reduced pressure. A deep red tar remained in the flask which was washed with ether several times. An oil apparently dissolved in the ether leaving a brown solid. The solid was recrystallized twice from *n*-butyl alcohol to give a light brown amorphous product. It had no melting point, but merely turned black gradually.

Anal. Calcd. for $C_{18}H_{10}O_2NBr$: Br, 22.70. Found: Br, 22.18.

The same product is formed if iron and acid are used as a reducing agent.

8'-Nitro-5'-chloro-1'-naphthoyl-2-benzoic Acid.—A solution of 109 g. of 5'-chloro-1'-naphthoyl-2-benzoic acid in 600 g. of 100% sulfuric acid at 20–25° was cooled to 0–5° and nitrated with 110 g. of nitrating mixture containing 20% nitric acid and 69% sulfuric acid. The product was poured into water and ice; yield, 130 g. The compound is readily purified from chlorobenzene, m. p. 233–234°.

Anal. Calcd. for $C_{18}H_{10}O_2NCl$: Cl, 10.0; N, 3.94. Found: Cl, 10.78; N, 3.74.

5',8'-Dinitro-1'-naphthoyl-2-benzoic Acid.—Into a solution of 30 g. of 5'-bromo-1'-naphthoyl-2-benzoic acid in 160 cc. of acetic anhydride was dropped slowly with stirring 30 cc. of concentrated nitric acid. The temperature of the reaction was not allowed to go above 30°. The solution was stirred for eight hours after the nitric acid

had all been added, during which time an appreciable quantity of the yellow 5',8'-dinitro-1'-naphthoyl-2-benzoic acid precipitated and was filtered. The acetic anhydride filtrate was poured into a large volume of water and allowed to stand overnight to decompose the acetic anhydride. A yellow precipitate was produced which was filtered and dried at room temperature. The precipitate was then crystallized twice from boiling toluene; yield, 10 g. (32%) of yellow plates. If heated rapidly it melted sharply at 262-263° (decomp.).

Anal. Calcd. for $C_{18}H_{10}O_7N_2$: C, 59.0; H, 2.43. Found: C, 59.9; H, 2.52.

Summary

1. A study of the substitution of α -naphthoyl-*o*-benzoic acid has been made. By the action of chlorine or bromine, either the 5'- or 5',8'-substitution derivatives are obtained which may readily be dehydrated to the corresponding benzantraquinones.

2. Proof of the 5'-position of the monobromo derivative was established by oxidation of the bromobenzanthraquinone to anthraquinone-1,2-dicarboxylic acid and by fusion of the bromo- α -naphthoyl-*o*-benzoic acid with sodium and potassium hydroxide to yield 1-hydroxy-5-naphthoic acid.

3. Nitration of 5'-chloro- or bromo-1'-naphthoyl-2-benzoic acid gave the 8'-nitro derivative, as shown by the fact that on reduction a ring structure was produced characteristic of 1-keto-8-aminonaphthalenes. Further nitration gave a halogen-free dinitro compound, probably 5',8'-dinitro-1'-naphthoyl-2-benzoic acid.

URBANA, ILLINOIS

[CONTRIBUTION FROM THE LABORATORY OF ORGANIC CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

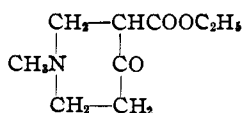
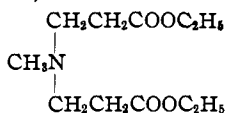
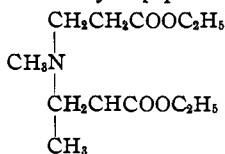
THE DEAMINATION OF ETHYL BETA-METHYLAMINOPROPIONATE

BY W. B. THOMAS AND S. M. McELVAIN

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In an attempt to prepare β -carbethoxyethyl- β -carbethoxypropylmethylamine (I), ethyl β -methylaminopropionate was treated with ethyl β -bromoisobutyrate. Instead of the desired compound the product which was obtained was β,β' -dicarbethoxydiethylmethylamine¹ (II) as shown by the fact that it was converted by sodium ethoxide into 1-methyl-3-carbethoxy-4-piperidone¹ (III).



¹ McElvain, THIS JOURNAL, 46, 1721 (1924).