138.4–138.8°. Neither the color nor the melting point was improved by chromatographic adsorption using activated alumina.

Anal. Calcd. for $C_{19}H_{14}$: C, 94.18; H, 5.83. Found: C, 94.20; H, 5.93.

Summary

A rather general method is described for the synthesis of 1,2-benzanthracenes containing a substituent at the meso position 9. This method involves the following steps: reaction of 1-naphthylmagnesium bromide with phthalic anhydride (or 3-methylphthalic anhydride); addition of methylmagnesium bromide to the ketonic carbonyl group of the resulting keto acid; reduction of the resulting lactone to an acid; and cyclization and reduction to the hydrocarbon. In this manner, 5,9-dimethyl-1,2-benzanthracene and 9-methyl-1,2-benzanthracene have been prepared for the purpose of comparing their possible carcinogenic activity with that of 10-methyl-1,-2-benzanthracene and that of 3,4-benzpyrene.

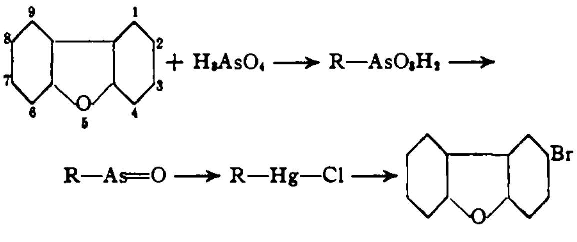
COLUMBUS, OHIO RECEIVED APRIL 3, 1937

[CONTRIBUTION FROM THE AVERY LABORATORY OF CHEMISTRY, UNIVERSITY OF NEBRASKA]

Arsenicals Containing the Dibenzofuran Nucleus

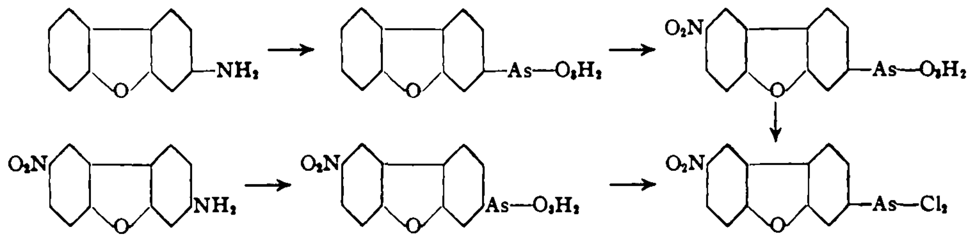
BY BENJAMIN F. SKILES[1] AND CLIFF S. HAMILTON

Dibenzofuran was arsonated directly by heating it with arsenic acid. The structure of the arsonic acid formed was problematical for, in the case of dibenzofuran, the nature of the entering groups has a marked effect upon the position assumed by nuclear substituents. Nitration involves principally the 3-position;[2] sulfonation,[3] and halogenation[4] favor the 2-position exclusively, while in metalation[5] the substituent enters the 4-position. The following sequence of reactions was used to prove that dibenzofuran on direct arsonation yields 2-dibenzofurylarsonic acid.[3,6]



3-Dibenzofurylarsonic acid[7] was prepared by means of a Bart[8] reaction utilizing 3-aminodibenzofuran as a starting material. The product was nitrated to yield nitro-3-dibenzofurylarsonic acid, and then converted into nitro-3-dibenzofuryldichloroarsine which on heating to 350° with mercuric acetate gave 2-nitrodibenzofuran. This indicated that the nitro group entered either the 2- or the 8-position. Since the arsono group is a meta director in the benzene ring, and 3-nitrodibenzofuran on nitration yields 3,8-dinitrodibenzofuran, the latter structure seemed the more probable. The nitration product was shown to be 8-nitro-3-dibenzofurylarsonic acid by preparing a sample of this acid having a known structure and converting it into the dichloroarsine which was identical with the one prepared from the nitration product (mixed m. p.).

3-Dibenzofurylarsonic acid on sulfonation gave sulfo-3-dibenzofurylarsonic acid. The structure of this compound has not been established but it is probably 8-sulfo-3-dibenzofurylarsonic acid.



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(1) Parke, Davis and Company Fellow.

(2) Cullinane, *J. Chem. Soc.*, 2267 (1930).

(3) Gilman, Smith, and Oatfield, THIS JOURNAL, 56, 1412 (1934).

(4) Mayer and Krieger, *Ber.*, 55, 1659 (1922).

(5) Gilman and Young, THIS JOURNAL, 56, 1415 (1934).

(6) Gilman has shown that replacement of the Hg–Cl group by bromine is reliable under the experimental conditions used in this reaction.

(7) Since the completion of this investigation, an article by Davies and Othen has appeared recording the preparation of dibenzofurylarsonic acids containing the arsono group in the 2-, 3- and 4-positions; *J. Chem. Soc.*, 1236 (1936).

(8) Bart, *Ann.*, 429, 55 (1922).

Experimental

2-Dibenzofurylarsonic Acid.—An intimate mixture of 30 g. of arsenic acid and 30 g. of dibenzofuran was heated at 175° for three hours with constant stirring. The temperature was then increased to 220° for ten minutes, the mixture becoming very tarry. This mass was extracted first with water and then with *N* sodium hydroxide. The alkaline solution was made neutral to litmus with hydrochloric acid and the precipitated tar filtered off. Acidification of the filtrate to Congo red paper precipitated 2-dibenzofurylarsonic acid; purified by extraction with hot concentrated hydrochloric acid and crystallization from glacial acetic acid; yield 6 g., not melted at 250°.

Anal. Calcd. for $C_{12}H_9O_4As$: As, 25.68. Found: As, 25.52, 25.57.

2-Dibenzofurylarsine Oxide.—Five grams of 2-dibenzofurylarsonic acid was suspended in 50 cc. of boiling glacial acetic acid and 5 cc. of phosphorus trichloride, dissolved in 20 cc. of glacial acetic acid, was added slowly. The solution was refluxed for thirty minutes and then cooled in an ice-bath, the 2-dibenzofuryldichloroarsine separating as an oil which solidified on standing. This product was not isolated, but was hydrolyzed to the arsine oxide by refluxing with boiling water for two hours. The water-insoluble product was recrystallized from a methyl cellosolve–water mixture; yield 80%, not melted at 250°.

Anal. Calcd. for $C_{12}H_7O_2As$: As, 28.96. Found: 29.02, 29.00.

Structure Proof.—Two grams of 2-dibenzofurylarsine oxide and 5 g. of mercuric acetate were dissolved in 150 cc. of glacial acetic acid and refluxed for one hour. Addition of a glacial acetic acid solution of calcium chloride gave a white precipitate of 2-dibenzofurylmercuric chloride which was extracted with water and recrystallized with acetone; yield 80%, m. p. 235° (checks value in literature[3]).

Gilman's method[3] was used to convert the 2-dibenzofurylmercuric chloride to 2-bromodibenzofuran. The product obtained was identified by means of a mixed melting point with a known sample of 2-bromodibenzofuran prepared by brominating dibenzofuran.[4]

3-Dibenzofurylarsonic Acid.—Eighteen grams of 3-aminodibenzofuran was diazotized in 1.0 liter of *N* hydrochloric acid and the solution added slowly to a mechanically stirred mixture containing 19 g. of sodium arsenite, 0.25 g. of copper sulfate, and 300 g. of sodium carbonate dissolved in 8.0 liters of water and cracked ice. The resulting solution was stirred for four hours, allowed to stand at room temperature for twelve hours, and then filtered through a charcoal mat. Acidification of the filtrate with concd. hydrochloric acid precipitated the 3-dibenzofurylarsonic acid; yield 70%. Recrystallization from glacial acetic acid gave a white crystalline compound, not melted at 275°.

Anal. Calcd. for $C_{12}H_9O_4As$: As, 25.68. Found: As, 25.55, 25.58.

3-Dibenzofuryldichloroarsine.—An 85% yield of this compound was obtained by adding slowly a solution of 10 cc. of phosphorus trichloride, dissolved in 25 cc. of glacial acetic acid, to a boiling suspension of 3-dibenzofurylarsonic acid in 75 cc. of glacial acetic acid, and refluxing the resulting solution for thirty minutes. On cooling, the dichloroarsine crystallized out as a white solid; an additional amount was obtained by adding 10 cc. of concd. hydrochloric acid to the mother liquor; m. p. 130°, after recrystallization from glacial acetic acid.

Anal. Calcd. for $C_{12}H_7OAsCl_2$: As, 23.96; Cl, 22.68. Found: As, 24.00, 24.04; Cl, 22.44, 22.52.

3-Dibenzofurylarsine Oxide.—A theoretical yield of the oxide was obtained by boiling 3-dibenzofuryldichloroarsine for two hours with water. Recrystallization from a methyl cellosolve–water mixture gave a white solid, not melted at 250°.

Anal. Calcd. for $C_{12}H_7O_2As$: As, 28.96. Found: As, 29.03, 29.01.

8-Nitro-3-dibenzofurylarsonic Acid.—This compound was prepared by two different methods. In one, 8-nitro-3-aminodibenzofuran served as the starting compound, while in the other 3-dibenzofurylarsonic acid was used.

Method I.—Four grams of 8-nitro-3-aminodibenzofuran[9] dissolved in 120 cc. of glacial acetic acid was diazotized with 3 g. of sodium nitrite dissolved in 20 cc. of water. This solution was diluted with 200 cc. of aqueous 2 *N* hydrochloric acid and added slowly to a mechanically stirred solution containing 10 g. of sodium arsenite, 0.25 g. of copper sulfate, and 200 g. of sodium carbonate dissolved in 1.0 liter of water and cracked ice. The solution was stirred for three hours and after standing for twelve hours at room temperature was filtered through a charcoal mat. On acidification of the filtrate with hydrochloric acid 8-nitro-3-dibenzofurylarsonic acid separated; yield 35%; purified by extraction with glacial acetic and concd. hydrochloric acids followed by solution in alkali, filtration and precipitation with hydrochloric acid; yellow solid, not melted at 280°.

Anal. Calcd. for $C_{12}H_8O_6NAs$: As, 22.26. Found: As, 22.35, 22.37.

Method II.—Nine grams of 3-dibenzofurylarsonic acid was treated for two hours at 5° with fuming nitric acid (d. 1.48) and the resulting solution poured into 400 cc. of ice water. The arsonic acid separated as yellow solid; purified as above; yield 70%.

8-Nitro-3-dibenzofuryldichloroarsine.—Twenty grams of 8-nitro-3-dibenzofurylarsonic acid was suspended in 100 cc. of boiling glacial acetic acid and 20 cc. of phosphorus trichloride, dissolved in 30 cc. of glacial acetic acid, was added slowly. The solution was refluxed for thirty minutes and on cooling the dichloroarsine precipitated as a yellow solid. An additional amount was obtained by adding 125 cc. of concd. hydrochloric acid to the mother liquor. Recrystallization from glacial acetic acid gave an 80% yield; m. p. 152°.

Two preparations of 8-nitro-3-dibenzofuryldichloroarsine were made by this procedure. In one, the 8-nitro-3-dibenzofurylarsonic acid prepared from 8-nitro-3-aminodibenzofuran was used. In the other the product, obtained when 3-dibenzofurylarsonic acid was nitrated, served as the starting material. The dichloroarsines obtained from these two reactions were identical (mixed melting points).

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(9) Cullinane, *J. Chem. Soc.*, 2365 (1932).

Anal. Calcd. for $C_{12}H_6O_3NAsCl_2$: As, 20.95; Cl, 19.83. Found: As, 21.05, 21.04; Cl, 19.57, 19.61.

Structure Proof.—An intimate mixture of 15 g. of 8-nitro-3-dibenzofuryldichloroarsine and 15 g. of mercuric acetate was fused for ten minutes at 350°. An acetic acid extract of this melt on dilution with water gave 1 g. of a yellow solid, m. p. 149° after crystallization from an alcohol–acetone mixture. It was identified as 2-nitrodibenzofuran by means of a mixed melting point.[9] Reduction of this compound gave 2-aminodibenzofuran, m. p. 125°, and acetylation of the amine produced 2-acetamino-dibenzofuran, m. p. 162°.

8-Nitro-3-dibenzofurylarsine Oxide.—A quantitative yield of the oxide was obtained by the hydrolysis of 2 g. of 8-nitro-3-dibenzofuryldichloroarsine with boiling water for four hours; light orange product after crystallization from methyl cellosolve, not melted at 250°.

Anal. Calcd. for $C_{12}H_6O_4NAs$: As, 24.75. Found: 24.67, 24.65.

8-Amino-3-dibenzofurylarsonic Acid.—A quantitative yield of this acid was obtained by reducing an alkaline solution of 8-nitro-3-dibenzofurylarsonic acid with hydrogen using the Raney catalyst.[10] Acidification to litmus with concd. hydrochloric acid produced a white precipitate of the amine which was recrystallized from dilute hydrochloric acid; not melted at 250°.

Anal. Calcd. for $C_{12}H_{10}O_4NAs$: As, 24.43. Found: As, 24.48, 24.44.

Sulfo-3-dibenzofurylarsonic Acid.—A suspension of 9 g. of 3-dibenzofurylarsonic acid in 60 cc. of concd. sulfuric acid was heated over a steam-bath for two hours. The solution was then cooled in an ice-bath and diluted with water until a heavy white precipitate was formed; not melted at 300° after recrystallization from water. The structure of this compound has not been proved but it is probably 8-sulfo-3-dibenzofurylarsonic acid.

Anal. Calcd. for $C_{12}H_9O_7SAs$: As, 20.16. Found: As, 20.30, 20.27.

Sulfo-3-dibenzofurylarsine Oxide.—An 80% yield of the oxide was obtained by bubbling sulfur dioxide through a solution of 0.5 g. of potassium iodide, and 1 g. of sulfo-3-dibenzofurylarsonic acid in 150 cc. of 2 *N* hydrochloric acid. At the end of twenty minutes the precipitated arsine oxide was filtered out and purified by salting it out of a water solution, not melted at 275°.

Anal. Calcd. for $C_{12}H_7O_6SAs$: As, 22.19. Found: As, 22.39, 22.37.

Summary

1. Direct arsonation of dibenzofuran gives 2-dibenzofurylarsonic acid as shown by structure proof; its oxide is described.

2. 3-Dibenzofurylarsonic acid has been prepared through the diazo reaction and converted into the dichloroarsine and oxide by reduction. Nitration of 3-dibenzofurylarsonic acid gives the 8-nitro derivative and from this the corresponding amine compound has been obtained by catalytic reduction.

3. 3-Dibenzofurylarsonic acid has been sulfonated directly.

LINCOLN, NEBRASKA RECEIVED MARCH 18, 1937

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[10] Raney, U. S. Patent 1,628,190 (1927).

[CONTRIBUTION FROM THE BIOCHEMICAL LABORATORY, STATE UNIVERSITY OF IOWA, AND THE INSTITUTE OF EXPERIMENTAL BIOLOGY, UNIVERSITY OF CALIFORNIA]

Antioxidants and the Autoxidation of Fats. IX. The Antioxidant Properties of the Tocopherols

BY H. S. OLCOTT AND O. H. EMERSON

The unsaponifiable fraction of some vegetable oils exhibits marked antioxidant properties when small amounts are added to lard. Olcott and Mattill[1] have recorded some of the characteristics of the active principles which they called inhibitols. When wheat germ oil or cottonseed oil was used as the source, the inhibitol concentrates contained a large amount of vitamin E from which the inhibitols could not be separated. The successful isolation of three individual compounds possessing vitamin E activity from these oils by Evans, Emerson and Emerson[2-4] provided an opportunity for ascertaining the relationship between the inhibitols and tocopherols.

The three tocopherols and their allophanates were assayed for antioxidant activity by the oxygen absorption method previously described.[5] The tocopherols were effective antioxidants in lard and oleo oil, but had no activity in esters prepared from hydrogenated cottonseed oil (Table I). Since the inhibitol concentrates from wheat germ oil and cottonseed oil behave similarly,[6] it seems apparent that they owe at least part, and possibly all, of their antioxidant activity to the tocopherols. However, the inhibitols obtained

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[1] Olcott and Mattill, THIS JOURNAL, 58, 1627 (1936).

[2] Evans, Emerson and Emerson, *J. Biol. Chem.*, 113, 319 (1936).

[3] Emerson, Emerson and Evans, *Science*, 83, 421 (1936).

[4] Emerson, Emerson, Mohammed and Evans, in press.

[5] French, Olcott and Mattill, *Ind. Eng. Chem.*, 27, 724 (1935).

[6] Olcott and Mattill, THIS JOURNAL, 58, 2204 (1936).