Fraction 1, b. p. 98–110°, consists mainly of unreacted methylcyclohexane.

Fraction 3, b. p. 180–185°, identified as **1,3-dimethyl-5-propylcyclohexane.** *Anal.* Calcd. for $C_{11}H_{22}$: C, 85.63; H, 14.37; mol. wt., 154. Found: C, 85.36; H, 14.52. n^{20}_D 1.4422, d^{20}_4 0.8012, mol. wt., 150. The dehydrogenated product was oxidized with dilute nitric acid ($1HNO_3$: $2H_2O$) at 130°. It yielded trimesic acid, identified as trimethyl trimesate, m. p. 141°. The mixed melting point with a known sample showed no depression.

Fraction 5a, b. p. 240–245°, was obtained on redistillation of fraction 5. It consists probably of dimethylcyclohexyl. *Anal.* Calcd. for $C_{14}H_{26}$: C, 86.60; H, 13.40; mol. wt. 194. Found: C, 86.44; H, 13.43; n^{20}_D 1.4672; d^{20}_4 0.8581; mol. wt., 195.

Acknowledgment.—The authors wish to express their thanks to Mr. Bruno Kvetinskas for the assistance he rendered.

Summary

The reaction analogous to the destructive alkylation of aromatics with paraffins is described with hexahydroaromatic hydrocarbons.

Paraffinic hydrocarbons with branched chains such as 2,2,3-trimethylpentane, 2,2,4-trimethylpentane, and 3,4-dimethylhexane react with cyclohexane or methylcyclohexane in the presence of aluminum halides. Isobutane is formed in each case. The alkylated hydrocarbons produced consist of polymethylcyclohexanes, methylethylcyclohexanes and dicyclic compounds. 2,2,3-Trimethylbutane and *n*-octane do not react with cyclohexane under similar conditions.

RIVERSIDE, ILLINOIS RECEIVED JANUARY 3, 1939

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF IOWA STATE COLLEGE]

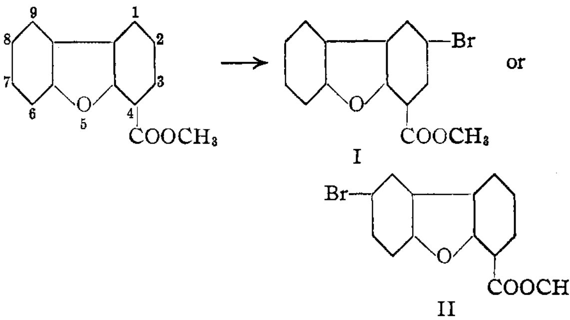
Dibenzofuran. VIII. Heteronuclear Substitution

BY HENRY GILMAN, MARIAN WESTON VAN ESS AND DAN M. HAYES

Introduction

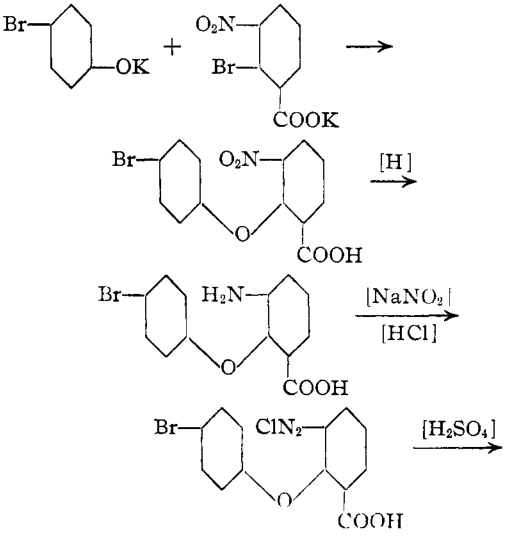
The 4- or 4,6-substituted dibenzofurans appear at this time to be the most significant dibenzofuran types from a biological viewpoint. Among the more accessible compounds having a water-solubilizing group is 4-dibenzofurancarboxylic acid, which is readily available by metalation of dibenzofuran followed by carbonation.[1] Preliminary to the examination of the effect of additional groups, it was necessary to establish the positions of nuclear substituents.

Bromination of methyl 4-dibenzofurancarboxylate gives a bromo-ester which, subsequent to hydrolysis and decarboxylation, yields 2-bromodibenzofuran. Accordingly, the bromo-ester might be methyl 2-bromo-4-dibenzofurancarboxylate (I), formed by homonuclear substitution; or methyl 2-bromo-6-dibenzofurancarboxylate (II), formed by heteronuclear substitution.



2-Bromo-4-methyldibenzofuran was synthesized by a series of reactions resulting in ring closure, described in the Experimental Part. Unfortunately, this compound could not be oxidized to the corresponding 2-bromo-4-dibenzofurancarboxylic acid, and thus comparison with (I) was precluded.

Then (II) was synthesized by the following transformations, and the product shown to be identical with that obtained by bromination of methyl 4-dibenzofurancarboxylate.



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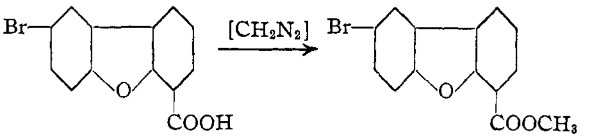
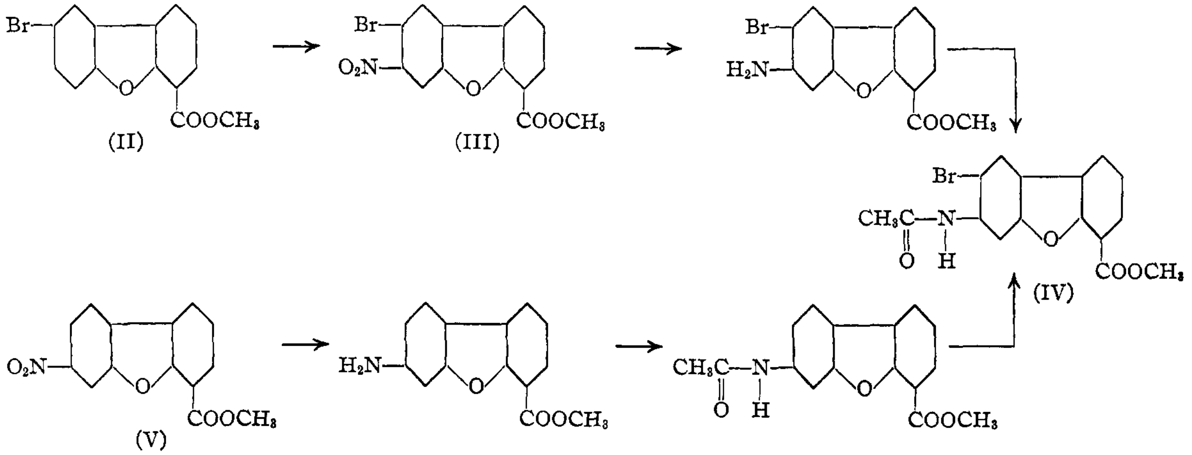
(1) Gilman and Young, THIS JOURNAL, **56**, 1415 (1934); **57**, 1121 (1935).

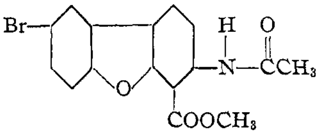


These ring closure reactions illustrate the wide applicability of this mode of synthesis, now applied for the first time for the preparation of 4-substituted dibenzofurans and for a carboxydibenzofuran. The arrangement of substituents in the phenyl ether appears to be of decisive importance in ring closure to 4-substituted dibenzofurans. The nitro group through which the ring ultimately is closed by reduction and diazotization must be in the same nucleus with the group which is to be the 4-substituent of the dibenzofuran product. Thus far, at least, success has attended every synthesis in which these conditions were fulfilled, and every attempt in which these conditions were not met has ended in failure.[2]

Nitration of methyl 4-dibenzofurancarboxylate gave two isomeric methyl nitro-4-dibenzofurancarboxylates. One of these gave 3-nitrodibenzofuran after hydrolysis and decarboxylation. The other gave 2-nitrodibenzofuran by a similar series of reactions. The more important nitro-ester is the one which gave 3-nitrodibenzofuran, for that nitro-ester invariably was formed and in yields up to 60% of highly purified product. The nitro-ester giving 3-nitrodibenzofuran could have its nitro group in either the 3- or the 7-position. By a series of reactions it was shown that the nitro-ester was methyl 3-nitro-6-dibenzofurancarboxylate (V). First, a structural relationship was established between the nitro-ester of unknown constitution and the bromo-ester whose structure was proved by ring closure. This was done by introducing a third substituent into the nitro-ester and the bromo-ester. In the following reactions the structures of all compounds other than [II] are assumed.



Each of these series of transformations was found to give the same bromo-acetamino ester. This, however, does not establish the structure of (IV) inasmuch as all the facts could be explained equally well by the isomeric



To prove structure (IV) it was only necessary to show that the bromo and the acetamino (or amino or nitro) groups were *ortho* to each other. The simplest approach was to start with the bromo-nitro-ester (III) and convert it by hydrolysis and then decarboxylation to a known bromonitrodibenzofuran. The ester was hydrolyzed without difficulty; but decarboxylation, in the usual manner, by treating the acid in quinoline with copper bronze, yielded 3-nitrodibenzofuran and none of an expected bromo-nitrodibenzofuran. This apparently negative result was still useful in establishing the relative positions of the bromine and the nitro group. It is evident that if decarboxylation is the first reaction, the bromo-nitro acid must yield intermediately either 2-bromo-3-nitrodibenzofuran or 2-bromo-7-nitrodibenzofuran. It seemed probable that one of these isomers suffered replacement of bromine by hydrogen more rapidly than the other under the conditions of decarboxylation.

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[2] (a) McCombie, Macmillan and Scarborough, *J. Chem. Soc.*, 529 (1931); (b) also, unpublished observations by P. R. Van Ess and P. T. Parker.

Accordingly, authentic specimens of 2-bromo-3-nitrodibenzofuran and 2-bromo-7-nitrodibenzofuran were treated under identical conditions with quinoline and copper. It was found that 2-bromo-3-nitrodibenzofuran was converted to 3-nitrodibenzofuran, whereas 2-bromo-7-nitrodibenzofuran was recovered unchanged. The ease with which the halogen is removed from 2-bromo-3-nitrodibenzofuran is in accord with the labilizing effect of a meta-directing group on substituents ortho and para to it.[3] These interrelated transformations establish the correctness of structure (IV), and prove that the bromo-nitro acid is 2-bromo-3-nitro-6-dibenzofurancarboxylic acid (see (III)). It follows that heteronuclear substitution takes place when methyl 4-dibenzofurancarboxylate is brominated or nitrated. Unquestionably, heteronuclear substitution will be found to predominate in other nuclear substitution reactions of methyl 4-dibenzofurancarboxylate such as sulfonation and the Friedel-Crafts reaction.[4]

There remains to be considered the structure of the second and isomeric nitro-ester obtained by nitration of methyl 4-dibenzofurancarboxylate. This nitro-ester, which gave 2-nitrodibenzofuran subsequent to hydrolysis and decarboxylation, must be either methyl 2-nitro-6-dibenzofurancarboxylate or methyl 2-nitro-4-dibenzofurancarboxylate. The former structure seems more likely for two reasons. First, all available evidence shows that a meta directing group[5] anywhere in one nucleus gives predominantly heteronuclear substitution. Second, the introduction of a second substituent in a ring already occupied by a "de-activating" group, as in the nitration of methyl 2-bromo-6-dibenzofurancarboxylate, requires considerably harsher conditions than hetero-substitution of a monosubstituted dibenzofuran. The two nitro-esters obtained from methyl 4-dibenzofurancarboxylate were formed under mild conditions.

Experimental Part

Methyl 4-Dibenzofurancarboxylate.—4-Dibenzofurancarboxylic acid was obtained by customary procedures.[1] The yield of acid from 4-dibenzofuryllithium, prepared by means of phenyllithium, ranged between 30–35%; and the yield when *n*-butyllithium (prepared from *n*-butyl chloride or bromide) was used was 34%.

The methyl ester was prepared both from methanol and the acid chloride, and by saturating a methanol solution of the acid with hydrogen chloride. The latter procedure, which gave yields of 97% (m. p. 92–94°), is recommended.

Di-4-dibenzofuryl Ketone.—In the carbonation of 4-dibenzofuryllithium there is always obtained varying quantities of an alkali-insoluble material. This was extracted with petroleum ether (b. p. 60–68°) to remove dibenzofuran, and then crystallized from boiling ethanol to give needles melting at 172–173°.

Anal. Calcd. for $C_{25}H_{14}O_3$: C, 82.85; H, 3.90. Found: C, 82.58; H, 3.89.

The formation of ketones incidental to the carbonation of organolithium compounds may be a predominant reaction under some conditions.[6]

Nitration of Methyl 4-Dibenzofurancarboxylate.—The reaction between 5.67 g. (0.025 mole) of methyl 4-dibenzofurancarboxylate and 20 cc. of concd. nitric acid was allowed to proceed for eighteen hours. The reaction mixture was poured upon ice, and the insoluble material obtained in this way was fractionally crystallized from glacial acetic acid to give 1 g. of compound melting at 205–205.5° and 2 g. of compound melting at 156–158°, or a total yield of 50.9%.

The compound melting at 205–205.5° was subsequently shown to be methyl 2-nitro-6-dibenzofurancarboxylate.

Anal. Calcd. for $C_{14}H_9O_5N$: N, 5.17. Found: N, 5.50.

The compound melting at 156–158° was subsequently shown to be methyl 3-nitro-6-dibenzofurancarboxylate.

Anal. Calcd. for $C_{14}H_9O_5N$: N, 5.17. Found: N, 5.27.

In some subsequent experiments, the only nitro-ester isolated was methyl 3-nitro-6-dibenzofurancarboxylate, and the yields were 60% of highly purified compound.

Incidental to developing the nitration procedure some polynitro compounds were isolated. A methyl dinitro-4-dibenzofurancarboxylate melted at 230–231°.

Anal. Calcd. for N, 8.86. Found: N, 8.75 and 9.06.

A methyl trinitro-4-dibenzofurancarboxylate melted at 208–210°.

Anal. Calcd. for N, 11.60. Found: N, 11.58 and 11.95.

In one nitration experiment an interesting complex was isolated. This melted at 170–172° and analyzed for one molecule of methyl nitro-4-dibenzofurancarboxylate and one molecule of methyl 4-dibenzofurancarboxylate.

Anal. Calcd. for $C_{14}H_9O_5N + C_{14}H_{10}O_3$: N, 2.59. Found: N, 2.54, 2.25. Molecular weight (Rast method) for one-half the complex: calcd., 249; found, 247.

2-Nitro-6-dibenzofurancarboxylic Acid and 3-Nitro-6-dibenzofurancarboxylic Acid.—Each of the nitro-esters was hydrolyzed quantitatively by refluxing 1 g. for three hours with 100 cc. of a mixture of equal volumes of glacial acetic acid and concd. hydrochloric acid. The acids decomposed with gas evolution at elevated temperatures: the 2-nitro-6-dibenzofurancarboxylic acid decomposing in the range 300–305°, and the 3-nitro-6-dibenzofurancarboxylic acid in the range 260–265°.

Neutralization equivalents: Calcd. for $C_{13}H_7O_5N$: 257. Found for 2-nitro-acid, 262; for 3-nitro-acid, 260.

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[3] Schöpf, *Ber.*, **22**, 900 (1889).

[4] A sole possible exception may be metalation, assuming that metalation can occur without the carboalkoxy group participating. See Gilman, Langham and Jacoby, THIS JOURNAL, **61**, 106 (1939), and Wittig, Pockels and Dröge, *Ber.*, **71**, 1903 (1938).

[5] Halogen has the same effect to a somewhat lesser extent.

[6] Gilman and Van Ess, THIS JOURNAL, **55**, 1258 (1933).

Decarboxylation of Nitro-acids.—Decarboxylation was effected by Johnson's[7] procedure with quinoline and powdered copper. Starting with 1 g. of nitro-acid in each case, the yield of nitrodibenzofuran was 72%. The 2-nitrodibenzofuran and 3-nitrodibenzofuran were identified by mixed m. p. determinations with authentic specimens.[8]

Bromination of Methyl 4-Dibenzofurancarboxylate.—To a solution of 10 g. (0.044 mole) of methyl 4-dibenzofurancarboxylate in 30 cc. of carbon tetrachloride was added 7.04 g. (0.044 mole) of bromine in 10 cc. of carbon tetrachloride. After refluxing for six hours at 60–70°, the mixture was worked up in the customary manner: first washing with bisulfite, and then steam distilling. The yield was 10 g. or 81.5%, and the methyl 2-bromo-6-dibenzofurancarboxylate melted at 166–167° after crystallizing first from acetic acid and then from methanol.

Anal. Calcd. for $C_{14}H_9O_3Br$: Br, 26.21. Found: Br, 26.50, 26.30.

2-Bromo-6-dibenzofurancarboxylic Acid and its Decarboxylation.—A quantitative yield of 2-bromo-6-dibenzofurancarboxylic acid, melting at 263–264°, was obtained when 5 g. of methyl 2-bromo-6-dibenzofurancarboxylate was refluxed for three hours with a mixture of 75 cc. of acetic acid and 25 cc. of concd. hydrochloric acid. *Neutralization equivalent:* Calcd. for $C_{13}H_7O_3Br$: 291; found, 293.

Decarboxylation was effected in the usual manner by heating with quinoline and copper. The purification of the resulting 2-bromodibenzofuran was effected by crystallization from the mixture of solvents used earlier by P. T. Parker: namely, a 75:25 by volume mixture of ethanol and carbon tetrachloride. Identification was completed by a mixed m. p. determination with an authentic specimen.

Preparation of 2-Bromo-6-dibenzofurancarboxylic Acid by Ring Closure.—2-Bromo-3-nitrobenzoic acid was prepared by the following sequence of reactions: (1) phthalic acid to 3-nitrophthalic acid[9]; (2) 3-nitrophthalic acid to anhydro-2-hydroxymercuri-3-nitrobenzoic acid[10]; and (3) conversion of the mercuri compound by bromine to 2-bromo-3-nitrobenzoic acid.[11] The 2-bromo-3-nitrobenzoic acid was converted to its potassium salt by dissolving in a saturated methyl alcoholic potassium hydroxide solution. A part of the salt precipitated out directly and the precipitation was completed by adding dry ether.

The synthesis of the substituted phenyl ether was effected as follows. One and fifty-four hundredths grams (0.025 mole) of potassium hydroxide was dissolved in the least amount of hot methanol, the solution cooled, and 5.19 g. (0.03 mole) of *p*-bromophenol, 7.1 g. (0.025 mole) of the potassium salt of 2-bromo-3-nitrobenzoic acid, and 0.5 g. of copper bronze added. The mixture was heated gradually in an oil-bath to 170° to expel the alcohol and water, after which this temperature was maintained for two hours. The cooled product was shaken with ether and water. The filtered aqueous layer when acidified precipitated a brown oily solid which was dissolved in the least amount of hot benzene and then was reprecipitated by the addition of petroleum ether (b. p. 60–68°). The 5 g. or 59% yield of product obtained in this way melted at 165–167°, and recrystallization raised the m. p. to 167.5–168.5°. *Neutralization equivalent:* Calcd. for $C_{13}H_8O_5NBr$, 338; found, 333.

The nitro group was reduced in accordance with the procedure of Schmidt and Kämpf.[12] To a warm suspension of 8.4 g. (0.025 mole) of 2-nitro-6-carboxy-4'-bromophenyl ether in 60 cc. of concd. hydrochloric acid was added 12 g. (0.1 g. atom) of granulated tin in several portions. Heating on a water-bath was continued until all of the metal dissolved. At the completion of the reaction, the greenish yellow amine hydrochloride was filtered, and washed with concd. hydrochloric acid and then with water. The dried product, 5.04 g. or a 67% yield, melted with decomposition at 190–200°. The compound was crushed and suspended in 100 cc. of 10% hydrochloric acid, cooled to 0°, and the calculated quantity of sodium nitrite, 1.04 g. or 0.015 mole, was added gradually, and the mixture allowed to stand at 0° for three hours. Diazotization was slow because of the slight solubility of both the amine hydrochloride and the diazonium compound.

The suspension of the diazonium compound was added to 100 cc. of boiling 50% sulfuric acid, and boiling was continued for three hours at constant volume. After working up in the customary manner,[12a] there resulted 0.5 g. of 2-bromo-6-dibenzofurancarboxylic acid which melted at 260–262° and showed no depression in a mixed m. p. determination with the acid obtained by bromination (followed by hydrolysis) of methyl 4-dibenzofurancarboxylate. The identity of the acid was confirmed further by converting it to its methyl ester by means of diazomethane. This methyl 2-bromo-6-dibenzofurancarboxylate was shown to be identical with the bromo-ester obtained by brominating methyl 4-dibenzofurancarboxylate.

Methyl 3-Acetamino-6-dibenzofurancarboxylate from Methyl 3-Nitro-6-dibenzofurancarboxylate.—A solution of 17.4 g. (0.078 mole) of stannous chloride hydrate in 115 cc. of concd. hydrochloric acid was added slowly to 6.78 g. (0.025 mole) of methyl 3-nitro-6-dibenzofurancarboxylate dissolved in 250 cc. of boiling glacial acetic acid, and then the mixture was heated at reflux temperature for two minutes. Cooling deposited 7.0 g. (quantitative yield) of the amine hydrochloride which turned brown but did not melt at 240°. An aqueous solution of the amine hydrochloride was converted by ammonium hydroxide to the free amine. The methyl 3-acetamino-6-dibenzofurancarboxylate was obtained by acetylating the amine in hot benzene with acetic anhydride. When recrystallized from a mixture of methanol and glacial acetic acid the yellow needles of acetaminoester melted at 245–246°.

Anal. Calcd. for $C_{16}H_{13}O_4N$: N, 4.95. Found: N, 5.17 and 5.34.

Preparation of 2-Bromo-3-acetamino-6-dibenzofurancarboxylic Acid. A. From 3-Acetamino-6-dibenzofurancarboxylic Acid.—An 81% yield of 2-bromo-3-acetamino-6-dibenzofurancarboxylic acid was obtained by brominating 0.0018 mole of the acetamino ester in acetic acid with

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(7) Shepard, Winslow and Johnson, THIS JOURNAL, **52**, 2083 (1930).

(8) The authors are grateful to W. H. Kirkpatrick and G. E. Brown for authentic samples.

(9) Culhane and Woodward, *Org. Syntheses*, Coll. Vol. I, p. 399.

(10) Whitmore, Culhane and Neher, *ibid.*, p. 48.

(11) Culhane, *ibid.*, p. 120.

(12) Schmidt and Kämpf, *Ber.*, **36**, 3738 (1903).

(12a) Cold aqueous sodium hydroxide was used to dissolve impurities, leaving undissolved the salt of the desired acid.

an equivalent amount of bromine. The product crystallized from glacial acetic acid as fine needles melting at 247–247.5°. Although this melting point is only two degrees higher than the original acetamino ester, the two compounds are different as shown by mixed m. p. and analysis.

Anal. Calcd. for $C_{16}H_{12}O_4NBr$: N, 3.87. Found: N, 3.77, 3.77.

B. From Methyl 2-Bromo-3-nitro-6-dibenzofurancarboxylate.—A solution of 0.45 g. (0.0013 mole) of methyl 2-bromo-3-nitro-6-dibenzofurancarboxylate in 15 cc. of boiling acetic acid was reduced by the slow addition of 0.7 g. (0.0031 mole) of stannous chloride hydrate in 5 cc. of concd. hydrochloric acid. After refluxing for five minutes, the solution was cooled, whereupon crystals of the tin salt complex of the amine hydrochloride were deposited. By the usual procedures involving successive treatments with sodium hydroxide, hydrogen chloride and ammonium hydroxide, the free amine was obtained in a 50% yield. From the 0.2 g. of amine was obtained 0.1 g. of the methyl 2-bromo-3-acetamino-6-dibenzofurancarboxylate, identical with the compound prepared by the bromination of methyl 3-acetamino-6-dibenzofurancarboxylate.

Nitration of Methyl 2-Bromo-6-dibenzofurancarboxylate. A. Dinitration.—When 1.25 g. (0.0041 mole) of methyl 2-bromo-6-dibenzofurancarboxylate was added slowly to 4 cc. of fuming nitric acid (d. 1.50) at room temperature, the ester dissolved, but after standing for thirty minutes the entire mass solidified. Crystallization from glacial acetic acid, followed by a second crystallization from benzene and petroleum ether (b. p., 60–68°) gave a 60% yield of pale yellow methyl dinitro-2-bromo-6-dibenzofurancarboxylate, melting at 259.5–260.5°.

Anal. Calcd. for $C_{14}H_7O_7N_2Br$: N, 7.09. Found: N, 7.17, 7.45.

B. Mononitration.—Methyl 2-bromo-6-dibenzofurancarboxylate was not nitrated by treating for thirty minutes with fuming nitric acid in acetic acid at 75°. Nitration with mixtures of concd. nitric and fuming nitric acids gave poor results because of the formation of a mixture of mono- and dinitration products. The best yields of the mononitration product were obtained by treating the ester with concd. nitric acid at steam-bath temperatures. To 7 cc. of concd. nitric acid (*d.* 1.42) was added 2.5 g. (0.0082 mole) of methyl 2-bromo-6-dibenzofurancarboxylate, and the mixture was heated with stirring for one hour. The product obtained by pouring on ice was filtered, dried and then extracted with hot methanol to remove all unchanged methyl 2-bromo-6-dibenzofurancarboxylate. The methyl 2-bromo-3-nitro-6-dibenzofurancarboxylate was obtained in 28% yield as small, pale yellow needles melting at 205–206° after recrystallization from acetic acid. The inconvenience of the low yield is in part compensated for by the easy recovery of unattacked bromo-ester. Attempts to increase the yield of mononitro-ester resulted in the formation of the dinitro derivative, and this made purification very difficult.

Anal. Calcd. for $C_{14}H_8O_5NBr$: N, 4.00. Found: N, 3.93 and 3.90.

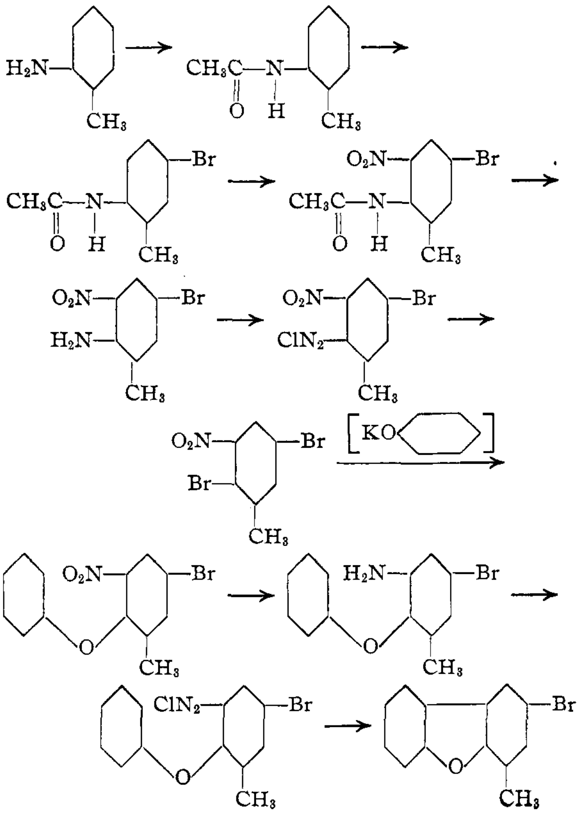
Hydrolysis of Methyl 2-Bromo-3-nitro-6-dibenzofurancarboxylate.—A 70% yield of 2-bromo-3-nitro-dibenzofurancarboxylic acid was obtained by refluxing the bromo-nitro-ester for three hours with a mixture of acetic acid and concd. hydrochloric acid. The acid was obtained from acetic acid as yellow needles melting at 331–334°. The acid and its salts are quite insoluble in water.

Decarboxylation of 2-Bromo-3-nitro-6-dibenzofurancarboxylic Acid.—A mixture of 0.24 g. of the bromo-nitro-acid, 1 g. of copper bronze and 5 cc. of freshly distilled quinoline was heated in a test-tube immersed in a metal bath. Vigorous bubbling began at 180°, and heating was continued for thirty minutes at 200–210°. The product isolated was 3-nitrodibenzofuran, and the yield was 0.04 g. Decarboxylation in the presence of copper sulfate hydrate instead of copper bronze required a higher temperature, but also gave 3-nitrodibenzofuran.

An authentic specimen[13] of 2-bromo-3-nitrodibenzofuran (0.1 g.) under corresponding conditions gave 3-nitrodibenzofuran (0.04 g.).

An authentic specimen[13] of 2-bromo-7-nitrodibenzofuran (0.1 g.) was treated in a manner identical with that used with 2-bromo-3-nitrodibenzofuran, and 0.06 g. of the original compound was isolated. In this experiment, no product came over in steam distillation. The 3-nitrodibenzofuran was obtained in the preceding experiment by steam distillation subsequent to a treatment with 10% sulfuric acid.

2-Bromo-4-methyldibenzofuran.—The method for the preparation of 2-bromo-4-methyldibenzofuran from a substituted phenyl ether was based on related syntheses of McCombie, Macmillan and Scarborough.[2a] A schematic representation of the several transformations follows



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(13) Kindly provided by Dr. Glen Bywater.

From the acetylation of 134 g. (1.25 moles) of *o*-toluidine in benzene by acetic anhydride there was obtained 135 g. of the acet-*o*-toluidide melting at 108°. Bromination in about 50-g. lots, by the procedure of Bogert and Hand,[14] gave an 80% yield of the bromo-acet-*o*-toluidide. This was nitrated by fuming nitric acid.[15] The acetyl group was removed by hydrolyzing 25-g. lots of the nitrated product with 30 cc. of concd. hydrochloric acid in 120 cc. of ethyl alcohol, and the yield was 52 g. of bromo-amine melting at 134° (all the initial 135 g. of acet-*o*-toluidide being used in the successive reactions). The amino group was then replaced by bromine in essential accordance with the procedure of Holleman,[16] to give 23 g. of 2,5-dibromo-3-nitrotoluene melting at 68–69° after crystallization from petroleum ether (b. p. 60–68°).

A mixture of 14.2 g. (0.048 mole) of 2,5-dibromo-3-nitrotoluene and 6.86 g. (0.052 mole) of potassium phenoxide was heated for three hours at 170°. The cooled reaction mixture was shaken with ether and water, and the residue obtained by evaporation of the ether was crystallized from petroleum ether (b. p. 60–68°) to give 12 g. or an 81% yield of 2-nitro-4-bromo-6-methylphenyl ether melting at 92–94°. The nitro group was reduced by dissolving 12 g. (0.039 mole) of the compound in 150 cc. of dry ether to which 20.85 g. (0.093 mole) of stannous chloride had been added, and then saturating the resulting solution with hydrogen chloride at 0°. The hydrochloride separated as a light brown solid (10.9 g.), and this was diazotized without further purification. Finally, the diazonium solution was added slowly to 150 cc. of boiling 50% sulfuric acid contained in a 500-cc. distilling flask which was connected to a condenser so that volatile products could be collected by steam distillation during the addition of the diazonium solution. The yield of 2-bromo-4-methyldibenzofuran was 4 g., and the compound crystallized from alcohol in the form of needles melting at 106–106.5°.

Anal. Calcd. for $C_{13}H_9OBr$: Br, 30.62. Found: Br, 30.43, 30.23.

2-Bromo-4-methyldibenzofuran was converted quantitatively to 4-methyldibenzofuran by shaking with hydrogen in the presence of palladium–calcium carbonate catalyst. The authors are grateful to Jack Swislowsky for this experiment.

The bromomethyl compound was unaffected by refluxing for four days with alkaline potassium permanganate, a mixture of potassium permanganate and dilute nitric acid at 180° for eight hours, and an alkaline solution of potassium ferrocyanide at reflux temperature for twelve hours. When treated with an acetic acid solution of chromic acid for four hours at 50°, the compound was partially destroyed but no acid could be isolated, and some unchanged compound was recovered. In the same solution at the boiling point, the compound was completely destroyed. The use of chromic acid in dilute sulfuric acid also destroyed the compound without stopping at the desired dibenzofurancarboxylic acid.

Summary

It has been shown that bromination and nitration of methyl 4-dibenzofurancarboxylate give heteronuclear substitution products.

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[14] Bogert and Hand, THIS JOURNAL, **27**, 1479 (1905).

[15] Wroblewski, *Ann.*, **192**, 206 (1878). See, also, Niementowski, *Ber.*, **25**, 869 (1892).

[16] Holleman, *Rec. trav. chim.*, **27**, 155 (1908).

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The Reduction of Silver Ions by Hydroquinone

BY T. H. JAMES

No detailed investigation of the mechanism of the reaction between silver ions and hydroquinone appears to have been made, although the reaction is of considerable interest in connection with the study of the mechanism of photographic development and fogging action. In the present investigation, we have studied the reaction in gelatin and in gum arabic solutions. The use of a protective colloid served both to facilitate the study of the catalytic phenomena involved and to allow a somewhat closer approach to conditions which would exist in the case of a reaction between free silver ions and hydroquinone in the development process.

Materials and Procedure

Hydroquinone and Silver Nitrate.—The Eastman Kodak Company preparations were purified further by recrystallization.

Buffer Salts.—General Chemical Company reagent grade. Both acetate and phosphate buffers were used, although the low solubility of silver phosphate limited the use of the latter to low silver nitrate concentrations.

Colloidal Silver.—Carey Lea's, dextrin reduction.

Colloidal Gold.—Red sol, phosphorus reduction, 0.0728 g. gold per liter.

The solutions were prepared in two parts, the first containing the silver nitrate and stabilizing colloid (gelatin or gum arabic) and the second containing the hydroquinone and buffer. A total solution volume of 150 ml. was employed. After the solutions had attained the temperature of the thermostat (20 ± 0.05°, unless otherwise specified) they were mixed quickly. At regular intervals, 10-ml. samples were pipetted off and rapidly added to 10 ml. of 30% sodium thiosulfate solution, which effectively stopped the reaction. The time required for emptying the pipet was two seconds. Density determinations were made by means of a photronic cell turbidimeter within two minutes after addition of the reaction mixture to the thiosulfate. No significant destruction of silver by re-