

these data are not quite in agreement with those given in the literature for 4,5-benzpyrene⁶ (m. p. 178–179°, picrate 229–230°), we believe that the structure is correct.

peri-Naphthindone from α -Naphthol.— α -Naphthol (72 g.) and acrolein (56 g.) were added simultaneously, within forty minutes, to anhydrous hydrofluoric acid (530 g.) at 15–20°. A sample of the condensation mass soon showed the bright green fluorescence in sulfuric acid, characteristic for *peri*-naphthindone. A precipitate formed in the hydrofluoric acid, while the reaction mass was agitated overnight. The condensation mass was poured onto ice, and the suspension filtered and washed. A brown powder (105 g.) was obtained, which was soluble in sulfuric acid with a yellow color and a strong green fluorescence. Fifty grams of this product was extracted with 500 cc. of boiling dichlorobenzene. The solvent extract was steam distilled to remove the solvent. *peri*-Naphthindone crystallized from the water layer (4000 cc.) in light yellow crystals. Much tarry matter also was obtained. The *peri*-naphthindone was identified by its melting point (151°), mixed melting point with a sample prepared according to German Patent 283,066, by its color and fluorescence in sulfuric acid. Similarly, *peri*-naphthindone was obtained from β -naphthol.

Condensation of Acenaphthene with Acrolein.—Acrolein (28 g.) and acenaphthene (30.8 g.) were added to an-

(5) J. W. Cook, C. L. Hewett and I. Hieger, *J. Chem. Soc.*, 395 (1933).

hydrous hydrofluoric acid (370 g.) at 15–18° in ten minutes, and this solution was agitated for one hour at 10–15°. Acenaphthene showed no coloration in sulfuric acid, but the condensation product which formed as soon as acrolein was added dissolved in sulfuric acid with a brilliant green color. A finely divided precipitate formed while the charge was agitated at 15–20° for one hour. The reaction product isolated (51 g., light brown powder) after decomposition with ice had no melting point, dissolved in sulfuric acid with brilliant green color, and was only sparingly soluble in organic solvents with yellow color, and without appreciable fluorescence. A low melting product was isolated by extraction in a Soxhlet apparatus but could not be crystallized or identified.

Summary

“*Peri*” condensations which are not possible in sulfuric acid were performed in anhydrous hydrofluoric acid. “*Peri*” condensations obtained in sulfuric acid also could be performed in hydrofluoric acid. Perylene was obtained from phenanthrene and 1,10-trimethylene-9-hydroxyphenanthrene, 4,5-benzpyrene from 9,10-dihydroanthracene, and *peri*-naphthindone from α - and β -naphthol.

WILMINGTON, DEL.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE COLLEGE]

Dibenzofuran. IX. Metalation of Some Derivatives*

BY HENRY GILMAN, LEE C. CHENEY AND H. B. WILLIS

Introduction

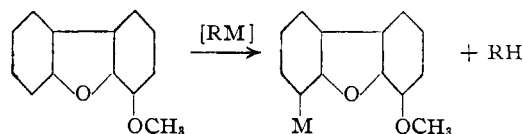
Metalation of dibenzofuran by a wide variety of metalating agents has given invariably a product having the metal in the 4-position, or ortho to the ether linkage.¹ Also, dimetalation has involved the positions ortho to the ether linkage to give 4,6-dimetalated dibenzofurans.^{1b} It was shown subsequently that metalation of a variety of other ethers took place in an ortho position.²

Several substituted dibenzofurans have been metalated. With 4-methyldibenzofuran and with 4-methoxydibenzofuran, the metal enters the 6-position when *n*-butylsodium is used as the metalating agent.^{1b}

(*) Paper VIII, Gilman, Van Ess and Hayes, *THIS JOURNAL*, **61**, 643 (1939).

(1) (a) Gilman and Young, *ibid.*, **56**, 1415 (1934); (b) Gilman and Young, *ibid.*, **57**, 1121 (1935).

(2) (a) Gilman and Jacoby, *J. Org. Chem.*, **3**, 108 (1938); (b) Gilman and Bradley, *THIS JOURNAL*, **60**, 2333 (1938); (c) Wittig, Pockels and Dröge, *Ber.*, **71**, 1903 (1938); (d) Gilman, Langham and Jacoby, *THIS JOURNAL*, **61**, 106 (1939); (e) Gilman and Bebb, *ibid.*, **61**, 109 (1939).

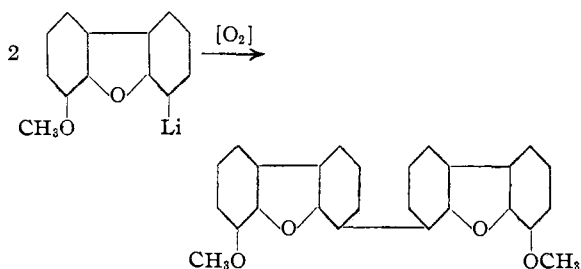


The first dibenzofuran derivative whose metalation did not involve an available 4- or 6-position was 2-methoxydibenzofuran.^{2e} Two products were characterized in this case: a 1-metalated- and a 3-metalated-2-methoxydibenzofuran.

Later, we had need of large quantities of 4-hydroxy-6-methoxydibenzofuran and intended to prepare it by metalation of 4-methoxydibenzofuran with *n*-butyllithium followed by oxidation of the metalation product. However, after oxidation two isomeric hydroxy-4-methoxy-dibenzofurans were isolated. One of these was the expected 4-hydroxy-6-methoxydibenzofuran and the other was shown to be 3-hydroxy-4-methoxydibenzofuran by a diazo reaction on 3-amino-4-methoxydibenzofuran, the synthesis of

which is described in the following paper.³ Accordingly, metalation invariably takes place ortho to an ether linkage, but need not involve an available 4- or 6-position, as was assumed in earlier studies.

From the oxidation of the metalated 4-methoxydibenzofuran, there was always isolated some neutral compound. This was finally shown to be a coupling product: for example, bi-(6-methoxy-4-dibenzofuryl) from 6-methoxy-4-dibenzofuryllithium.



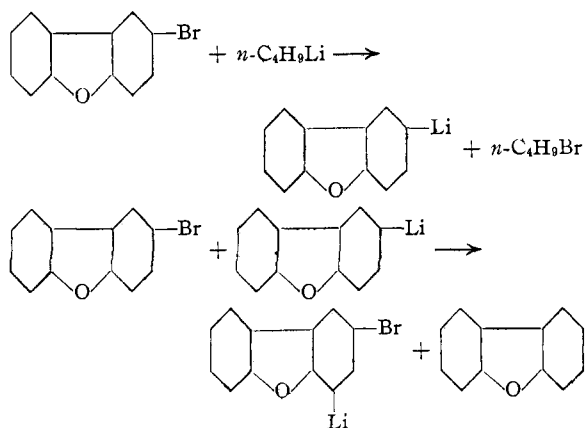
The reaction appears to be general, for re-examination of the products of oxidation of 4-dibenzofuryllithium revealed the presence of some bi-(4-dibenzofuryl). Wooster,⁴ in a review of organoalkali compounds, mentions unpublished observations on the oxidation of benzohydrylsodium, in liquid ammonia



and suggests that "the formation of an organic peroxide as an oxidation product is typical only of those organoalkali compounds which are derivatives of free radicals." Peroxides of some form or other have been generally postulated as intermediates in the oxidation of many types of organometallic compounds. Such peroxides may or may not have the formula ROOR, but it is interesting that oxidation of many RM compounds does give appreciable quantities of coupling or RR compound. Two illustrations may suffice: the oxidation of trimethylindium to give ethane,^{5a} and the oxidation of *p*-tolylmagnesium bromide to give *p*-bitolyl.^{5b} In the latter case there might be supplementary effects of water or other hydroxyl-containing compounds.⁶ Apropos the probable coupling influence of oxygen, it would be interesting to examine the effect of oxygen on the Wurtz-Fittig reaction which in-

volves, in part, the intermediate formation of organo-alkali compounds.

In connection with the proof of structure of the bromination product of 4-dibenzofurancarboxylic acid,⁷ we metalated 2-bromodibenzofuran and then carbonated the resulting lithium compound in the expectation of preparing the hetero-substituted 8-bromo-4-dibenzofurancarboxylic acid. The product obtained was different from the 8-bromo-4-dibenzofurancarboxylic acid obtained by ring closure. Metalation did take place in a 4- or 6-position because debromination yielded 4-dibenzofurancarboxylic acid. It was then confirmed that homonuclear metalation took place by treating the metalated product with dimethyl sulfate: the compound isolated was identical with 2-bromo-4-methyldibenzofuran, whose structure was established just previously by ring closure.⁷ This interesting reaction is now known to conform with recent observations on the metalation of halogen-containing nuclei.^{2a,c,d} As is the case with compounds like *p*-bromodiphenyl ether, metalation takes place in the halogen-containing nucleus rather than in the halogen-free nucleus. The reaction mechanism of metalation is still not clear, but it is significant that appreciable quantities of dibenzofuran were isolated. This indicates a possible interchange^{2c,d} followed by a metalation with 2-dibenzofuryllithium as one of the metalating agents.



The 2-dibenzofuryllithium may also have resulted, in part, from finely divided or colloidal lithium reacting with 2-bromodibenzofuran.

Experimental Part

4-Hydroxydibenzofuran.—A solution of 168 g. (1.0 mole) of dry dibenzofuran in 500 cc. of ether was metalated by an excess of *n*-butyllithium in 750 cc. of ether, by re-

(7) Gilman, Van Ess and Hayes, *ibid.*, **61**, 643 (1939).

(3) Gilman, Jacoby and Swislow, *THIS JOURNAL*, **61**, 954 (1939).

(4) Wooster, *Chem. Rev.*, **11**, 21 (1932).

(5) (a) Dennis, Work, Rochow and Chamot, *THIS JOURNAL*, **56**, 1047 (1934); (b) Gilman and Wood, *ibid.*, **48**, 806 (1926).

(6) Meyer and Tögel, *Ann.*, **347**, 55 (1906); Kharasch, Goldberg and Mayo, *THIS JOURNAL*, **60**, 2004 (1938).

fluxing and stirring for sixteen to eighteen hours in a nitrogen atmosphere. After adding one mole of *n*-butylmagnesium bromide in 450 cc. of ether,⁸ the mixture was cooled by an ice-salt bath, and oxygen was admitted over the surface of the cold, stirred solution until a negative color test⁹ showed the disappearance of RM compounds. Hydrolysis was effected by ice and hydrochloric acid; the ether was extracted free of phenolic compound by 2-5% sodium hydroxide solution. Acidification yielded almost colorless 4-hydroxydibenzofuran melting at 99-100° and pure enough for most synthetic purposes. The yields from several runs were: 47.6, 52.5, 40.0, 48.5 and 45.3%. One crystallization from petroleum ether (b. p. 77-115°) produced pale pink needles melting at 101-102°. The bi-(4-dibenzofuryl), isolated from the ether layer subsequent to the sodium hydroxide extraction, was identical (mixed m. p.) with the synthetic product described later in this report.

Metalation of 4-Methoxydibenzofuran with Subsequent Oxidation.—One mole of 4-methoxydibenzofuran was metalated by *n*-butyllithium in accordance with the directions given for the metalation of dibenzofuran. A red-brown color developed immediately. After stirring and refluxing for six hours, one mole of *n*-butylmagnesium bromide was added and then oxygen was passed in until a negative color test was obtained. Following hydrolysis, the ether-insoluble product was filtered. The two isomeric phenols were separated on the basis of the extreme difference in the solubilities of their sodium salts. Equal amounts of the total yellow ether layer were placed in two 2-liter flasks, and 350 cc. of 10% sodium hydroxide was added to each flask with shaking. The precipitated sodium salt of 4-hydroxy-6-methoxydibenzofuran was filtered by suction, dissolved in 3.5 liters of water, boiled with Norite, and filtered through a steam funnel. Acidification of the filtrate gave 49.4 g. of phenol melting at 101-106°; recrystallization from petroleum ether (b. p., 60-68°) yielded 42.5 g. (19.8%) of colorless needles melting at 111-112°. An alcoholic solution of the phenol gave a green color with ferric chloride.

The aqueous layer of the filtrate was separated from the ether layer, which was then extracted free of phenol. Acidification, followed by recrystallization from 30% ethanol, gave a 19.9% yield of 3-hydroxy-4-methoxydibenzofuran as silky needles melting at 109-110°. An alcoholic solution of this phenol gave a red-brown color with ferric chloride. A hot alcoholic solution has a pleasant cinnamon-like odor.

The ether-insoluble compound crystallized from acetic acid as colorless needles melting at 237-238°. The yield of this bi-(6-methoxy-4-dibenzofuryl) was 6.5 g. or 3.3%, and its identity was established by comparison with the authentic specimen described later. The mother liquors were not examined for bi-(4-methoxy-3-dibenzofuryl) and the possible unsymmetrical coupling product.

Bi-(4-dibenzofuryl).—To 0.012 mole of 4-dibenzofurylmagnesium bromide (prepared from 0.012 mole of 4-bromodibenzofuran)^{10a} was added 0.012 mole of anhydrous

cupric chloride. The yield of bi-(4-dibenzofuryl) was 85% and the compound melted at 191° after crystallization from acetic acid.

Anal. Calcd. for C₂₄H₁₄O₂: C, 86.2; H, 4.22. Found: C, 86.1; H, 4.29.

3-Hydroxy-4-methoxydibenzofuran from 3-Amino-4-methoxydibenzofuran.—Three-tenths of a gram of 3-amino-4-methoxydibenzofuran^{10b} was diazotized and the diazonium solution added to a boiling solution of 75 g. of copper sulfate in 300 cc. of water. The compound melted at 109-110° and was shown to be identical with the compound obtained by oxidation of the metalation product of 4-methoxydibenzofuran.

Anal. Calcd. for C₁₃H₁₀O₃: CH₂O, 14.5. Found: CH₂O, 14.1.

4 - Bromo - 6 - methoxydibenzofuran.—4 - Methoxydibenzofuran (193 g. or 0.975 mole) was metalated in the usual manner by *n*-butyllithium, and to the resulting organolithium compounds in ether cooled to -10° was added bromine vapor obtained by bubbling nitrogen through dry, warm liquid bromine. The temperature was kept at 0°, and a negative color test showed the reaction to be complete in several hours. The excess bromine was destroyed by the cautious addition of a saturated solution of sodium bisulfite. The fraction distilling between 176-184° (4 mm.) melted over the range 75-91° and weighed 69.9 g. Recrystallizations from petroleum ether (b. p. 77-115°) gave 19.7 g. or a 7.3% yield of 4-bromo-6-methoxydibenzofuran melting at 114°.

Anal. Calcd. for C₁₃H₉O₂Br: Br, 28.85. Found: Br, 28.98.

Amination of this compound gave an amino-methoxydibenzofuran unlike the known 3-amino-4-methoxydibenzofuran. Inasmuch as metalation of 4-methoxydibenzofuran involves the 3- and 6-positions only, the compound must be, therefore, 4-bromo-6-methoxydibenzofuran. Accidental loss of the remaining mixture during distillation prevented isolation of the isomeric 3-bromo-4-methoxydibenzofuran.

Bi-(6-methoxy-4-dibenzofuryl).—To an ether solution of 6-methoxy-4-dibenzofurylmagnesium bromide (prepared from 0.4 g. of 4-bromo-6-methoxydibenzofuran) was added 0.5 g. of anhydrous cupric chloride to give a 61.5% yield of the coupling product, which crystallized as needles from acetic acid and melted at 237-238°.

Anal. Calcd. for C₂₆H₁₈O₄: C, 79.2; H, 4.60; mol. wt., 394. Found: C, 79.5; H, 4.52; mol. wt., 381.

Bi-(6-hydroxy-4-dibenzofuryl).—It is interesting that the methoxyl groups in bi-(6-methoxy-4-dibenzofuryl) are not cleaved under the conditions of the usual Zeisel determinations, probably because of the extreme insolubility in that medium. However, a 77% yield of the dihydroxy compound was obtained when a suspension of 2.0 g. of bi-(6-methoxy-4-dibenzofuryl) in 20 cc. of hydrobromic acid (sp. gr. 1.49) and 50 cc. of acetic acid was refluxed for 29 hours. Bi-(6-hydroxy-4-dibenzofuryl) crystallized from dil. ethanol as small, shiny plates melting at 285-286°.

Anal. Calcd. for C₂₄H₁₄O₄: C, 78.67; H, 3.85. Found: C, 78.4; H, 4.16. A Zerewitinoff analysis gave 2.05 active hydrogens (calcd., 2).

(8) In accordance with the general suggestion of Ivanoff, *Bull. soc. chim.*, **39**, 47 (1926), for improving the yields of phenols in the oxidation of arylmagnesium halides.

(9) Gilman and Schulze, *THIS JOURNAL*, **47**, 2002 (1925).

(10) (a) Prepared by George E. Brown from 4-dibenzofuryllithium and bromine; (b) kindly provided by Arthur L. Jacoby.

2-Bromo-4-dibenzofurancarboxylic Acid.—Five hundredths mole of *n*-butyllithium, prepared in the usual manner,¹¹ was added to 12.4 g. (0.05 mole) of 2-bromodibenzofuran dissolved in 50 cc. of ether. After refluxing this solution for one hour, an equal volume (150 cc.) of benzene was added and the refluxing continued, with stirring, for nine hours. Subsequent to carbonation and crystallization from acetic acid there was obtained 3.5 g. (24% yield) of 2-bromo-4-dibenzofurancarboxylic acid, m. p. 285–286°.

Anal. Calcd. for C₁₃H₇O₃Br: neut. equiv., 291.1. Found: neut. equiv., 291.6.

In addition, dibenzofuran was isolated. The weight of crude product was 2.1 g., and from this was obtained 1 g. or a 12% yield of pure dibenzofuran.

The authors are grateful to W. Langham for suggestions concerning this metalation reaction.

Methyl 2-Bromo-4-dibenzofurancarboxylate.—Fifteen-tenths gram of 2-bromo-4-dibenzofurancarboxylic acid, dissolved in 100 cc. of dry ether, was methylated with an excess of diazomethane. Crystallization from glacial acetic acid gave 0.45 g. (87%) of methyl 2-bromo-4-dibenzofurancarboxylate which melted at 189–189.5°.

Anal. Calcd. for C₁₄H₉O₃Br: Br, 26.11. Found: Br, 26.13. Methyl 2-bromo-6-dibenzofurancarboxylate melts at 165–166°.⁷

Debromination of 2-Bromo-4-dibenzofurancarboxylic Acid.—One-tenth gram of 2-bromo-4-dibenzofurancarboxylic acid, suspended in 20 cc. of absolute ethanol with 1 g. of palladium-calcium carbonate catalyst,¹²

(11) Gilman, Zoellner and Selby, *THIS JOURNAL*, **55**, 1252 (1933).

(12) Busch and Stöve, *Ber.*, **49**, 1063 (1916).

was allowed to stand at room temperature under hydrogen at a gage pressure of 30 pounds for twelve hours. The dehalogenation was quantitative, and the 4-dibenzofurancarboxylic acid obtained melted at 106–107°. A mixed melting point determination with an authentic specimen of 4-dibenzofurancarboxylic acid showed no depression.

2-Bromo-4-methyldibenzofuran.—One-tenth mole (12.6 g.) of dimethyl sulfate was added dropwise to a cooled reaction mixture obtained from the metalation of 0.05 mole of 2-bromodibenzofuran by *n*-butyllithium. After thirty minutes of refluxing the excess dimethyl sulfate was destroyed by sodium hydroxide and, following removal of the solvent, the product was subjected to fractional distillation under reduced pressure. From the fraction which boiled at 145–180° at 6 mm. (6 g.), there was obtained after repeated crystallizations from petroleum ether, 0.1 g. (0.8%) of 2-bromo-4-methyldibenzofuran melting at 105–106°. A mixed melting point determination with an authentic sample showed no depression.

Summary

Metalation of dibenzofurans invariably takes place ortho to an ether linkage, but need not involve an available 4- or 6-position.

Homonuclear metalation occurs with 2-bromodibenzofuran to give 2-bromo-4-dibenzofuryllithium.

Oxidation of some aryllithium compounds gives coupling or biaryl products.

AMES, IOWA

RECEIVED FEBRUARY 3, 1939

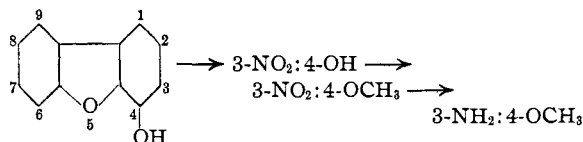
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE COLLEGE]

Dibenzofuran. X. Aminohydroxy Derivatives

BY HENRY GILMAN, ARTHUR L. JACOBY AND JACK SWISLOWSKY

Introduction

The 3-amino-4-methoxydibenzofuran necessary to establish the structure of 3-hydroxy-4-methoxydibenzofuran described in the preceding paper¹ was synthesized as follows



3-Nitro-4-hydroxydibenzofuran was also prepared by means of a diazo reaction of 3-nitro-4-aminodibenzofuran which, in turn, was synthesized by the following sequence of reactions:

(1) Paper IX, Gilman, Cheney and Willis, *THIS JOURNAL*, **61**, 951 (1939).

4-NHCOCH₃ → 3-NO₂:4-NHCOCH₃ → 3-NO₂:4-NH₂. The nitro group in the nitro-4-aminodibenzofuran was shown to be in the 3-position by replacing the amino group by hydrogen via diazotization and establishing the identity of the resulting 3-nitrodibenzofuran. Obviously, this does not tell whether the nitro group was in the same ring with the amino group or in the other benzenoid nucleus. This question was answered by reducing the nitro-amine to the diamine and then forming the phenazine derivative with phenanthraquinone.

Although 4-hydroxydibenzofuran directs the entering nitro group to the ortho or 3-position, the related 4-methoxydibenzofuran orients the nitro group to the para or 1-position to give 1-nitro-