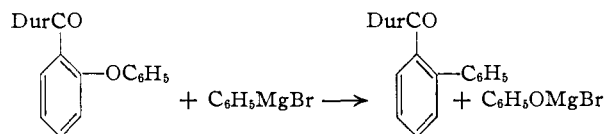


from an *ortho* position in such ketones is not influenced greatly by the nature of the Grignard reagent. The displacement of the phenoxy group is illustrative.



Interest in the displacement of the phenoxy group refers primarily to its low donor capacity, which might be expected to render less likely the intervention of a coordination compound involving both oxygen atoms. On the other hand, the high order of stability of the phenoxide ion would lead to the prediction that displacement would be facilitated. Experiment showed that displacement is practically quantitative.

Since the phenoxy group is displaced more readily than the methoxy, it seemed probable that, in the sulfur series, phenylmercapto might be displaced more easily than methylmercapto. Experiment bore out this prediction; displacement of phenylmercapto occurred in 61% yield while with the methylmercapto group the yield was only 37%.

This ratio reversed itself in the corresponding sulfones, the phenyl and methylsulfonyl groups being displaced in yields of 68 and 94%, respectively. Since the sulfones, as well as the ethers and thioethers, are capable of forming cyclic coordination complexes it is not clear to what extent, if at all, the displacement depends on this factor.

The behavior of the methyl sulfone is of special interest since it should be able to form a Grignard reagent³ which in turn might undergo ring closure or bring about displacement. The high yield of the phenylated product makes the occurrence of such reactions seem improbable.

Experimental⁴

The various displacement reactions were all carried out under similar conditions; a description of the general procedure follows. A solution of phenylmagnesium bromide was prepared in ether and then filtered through glass wool into boiling ether. The substituted duryl phenyl ketone, dissolved in benzene, was then added. During this addition and the early stages of the reflux period very intense color changes usually were noted. After several hours of refluxing the mixtures were poured into dilute hydrochloric acid; the organic layers were separated, washed with a saturated sodium chloride solution and finally dried over

TABLE I
DISPLACEMENT OF A IN *o*-AC₆H₄CODur^a

Ketone A = (mole)	Phenyl- mag- nesium bromide, mole	Ether, ml.	Ben- zene, ml.	Time, hr.	Yield of <i>o</i> - duroyl- bi- phenyl, %
OC ₆ H ₅ (0.0091)	0.027	115	50	4	99
SC ₆ H ₅ (0.0145)	.03	110	50	10.5	61
SCH ₃ (0.007)	.015	50	40	14	37
SO ₂ C ₆ H ₅ (0.004)	.01	60	50	4	68
SO ₂ CH ₃	.02	80	60	17.5	94

^a For the methods of preparation of the ketones see R. C. Fuson and W. S. Friedlander, *THIS JOURNAL*, **76**, 4989 (1954).

(3) L. Field and J. W. McFarland, *THIS JOURNAL*, **75**, 5582 (1953).

(4) All melting points are corrected.

sodium sulfate. Evaporation of the solvents left clear viscous oils from which the product, *o*-duroylbiphenyl, could be induced to crystallize by the addition of methanol. The *o*-duroylbiphenyl melted at 130.5–131.5° when crystallized from ethanol or isopropyl alcohol, and after sublimation melted at 136.5–137.5°.

Anal. Calcd. for C₂₃H₂₂O: C, 87.86; H, 7.05. Found: C, 87.83; H, 6.78.

A mixed melting point of this compound with a sample of *o*-duroylbiphenyl prepared by the addition of phenyllithium to duryl phenyl ketone⁵ was not depressed.

Experimental details are shown in Table I.

(5) R. C. Fuson, G. P. Speranza and R. Gaertner, *J. Org. Chem.*, **15**, 1155 (1950).

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Some 1,2-, 2,3- and 3,4-Disubstituted Dibenzofurans

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A number of *ortho* disubstituted dibenzofurans has been described in the literature.^{1–3} The methods of synthesis employed for the preparation of these compounds were, in general, those which have been used for the synthesis of *ortho* derivatives of monosubstituted benzenes.

An earlier paper^{1a} from this Laboratory has discussed at some length the homonuclear substitution of dibenzofuran. Available evidence indicated that the strong *ortho-para* directing functions orient an incoming group to the same nucleus, there being two positions available for the introduction of the second substituent.

In the course of further studies concerned with orientation in the dibenzofuran series, we have prepared a variety of 1,2-, 2,3- and 3,4-disubstituted dibenzofurans. The results of our work confirm the previous observations in regard to the orientation tendencies shown by monosubstituted dibenzofurans.

Although 2-diacetamidodibenzofuran is brominated in the 3-position,^{1a} reaction of the free amine with bromine yields the 2-amino-1-bromo compound.⁴ The structure of the latter compound was proven by its deamination to the known 1-bromodibenzofuran.^{1c}

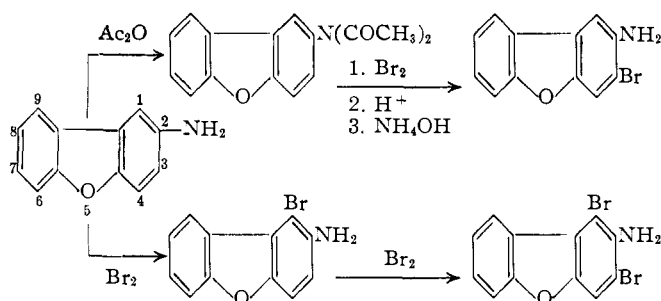
A by-product of the bromination reaction was a dibromo derivative. It was identical with both the bromination product of 2-amino-3-bromodibenzofuran and that of 1-bromo-2-aminodibenzofuran; hence, the dibromo compound must be 1,3-dibromo-2-aminodibenzofuran.

(1) (a) H. Gilman, G. E. Brown, W. G. Bywater and W. H. Kirkpatrick, *THIS JOURNAL*, **56**, 2473 (1934); (b) H. Gilman, A. L. Jacoby and J. Swislow, *ibid.*, **61**, 954 (1939); (c) H. Gilman and P. R. Van Ess, *ibid.*, **61**, 1365 (1939); (d) H. Gilman, P. T. Parker, J. C. Bailie and G. E. Brown, *ibid.*, **61**, 2836 (1939); (e) H. Gilman and M. W. Van Ess, *ibid.*, **61**, 3146 (1939).

(2) R. J. Moulam and K. Venkataraman, *J. Sci. Ind. Research*, **3**, 447 (1945) [*C. A.*, **39**, 4605 (1945)].

(3) K. Schimmelschmidt, *Ann.*, **566**, 184 (1950).

(4) Because the ring-activating amino group (protected by acetylation) in an aminodibenzofuran always has been found to direct an incoming group to the same ring, the structure which we have assigned here to the bromoamine seems more probable than that of the hetero-substituted amine, *i.e.*, 1-bromo-8-aminodibenzofuran.



The Fries rearrangement as carried out with 2-acetoxydibenzofuran yielded two isomeric phenolic methyl ketones. The higher melting of the two was converted by methylation and oxidation to the known 2-methoxy-3-dibenzofurancarboxylic acid.^{1c} The methylation product of the other rearrangement product analyzed correctly for a methoxyacetyldibenzofuran. Presumably, this compound is 1-acetyl-2-methoxydibenzofuran, the other possible *ortho* rearrangement product.

We have been able to isolate but one product, 3-acetyl-4-hydroxydibenzofuran, as a result of the Fries rearrangement of 4-acetoxydibenzofuran. The hydroxyacetyl compound secured was converted to its methoxy derivative and then to the oxime. This oxime underwent a Beckmann rearrangement to give an amide which was hydrolyzed to 3-amino-4-methoxydibenzofuran, a known compound.^{1b}

The low yield of 3-acetyl-4-hydroxydibenzofuran obtained (42%) suggests that an isomeric hydroxy ketone may have been formed but escaped detection. (It should be noted here that from the Claisen rearrangement of 2-allyloxydibenzofuran only one product, 1-allyl-2-hydroxydibenzofuran, was isolated.^{1c} The low yield (34%) makes it appear likely that rearrangement to the other *ortho* position took place, but this isomer was not isolated.)

A number of derivatives of these and other dibenzofuran compounds are reported here for the first time.

Experimental⁵

1-Bromo-2-aminodibenzofuran.—To a solution of 4.0 g. (0.0218 mole) of 2-aminodibenzofuran^{1a} in 100 ml. of glacial acetic acid was added 2.0 g. of sodium carbonate. By means of a slow stream of air, 3.3 g. (0.0206 mole) of bromine was entrained and introduced through an inlet tube beneath the surface of the rapidly stirred solution. The addition required 3.5 hours. Dilution of the solution with water and filtration gave 4.0 g. of material, m.p. 100–114°. Recrystallization from methanol yielded 1.75 g. (32%), m.p. 120–121°, of a monobromoamine.

Anal. Calcd. for C₁₂H₈BrNO: Br, 30.48; N, 5.34. Found: Br, 30.68, 30.79; N, 5.31.

A small amount of the crude material melting from 100–114° was insoluble in methanol. This was filtered from the hot solution of the bromoamine and recrystallized from 95% ethanol. The product obtained, 0.5 g. (6.7%), m.p. 180–181°, was found by mixed melting point determination to be 1,3-dibromo-2-aminodibenzofuran, the preparation of which is described below.

The isolation of a monobromoamine was possible only when the entrainment method of bromination was employed. Dropwise addition of bromine in acetic acid gave only 1,3-dibromo-2-aminodibenzofuran (48%) and unreacted 2-aminodibenzofuran.⁶

(5) All melting points are uncorrected.

(6) Experiment carried out by J. R. Thirtle.

Deamination of 1-Bromo-2-aminodibenzofuran.—Five-tenths of a gram (0.0019 mole) of the bromoamine was deaminated (as the diazonium chloride) by 50% hypophosphorous acid according to the method of Mai.⁷ Three recrystallizations from petroleum ether (b.p. 60–86°) gave 0.2 g. (43%) of compound, m.p. 64–65°. A mixed melting point with an authentic sample of 1-bromodibenzofuran^{1c} showed no depression.

1,3-Dibromo-2-aminodibenzofuran. A. From 2-Amino-3-bromodibenzofuran.⁸—A solution of 1.13 g. (0.0043 mole) of 2-amino-3-bromodibenzofuran^{1a} in 100 ml. of glacial acetic acid was stirred at room temperature while 25 ml. of an acetic acid solution containing 0.005 mole of bromine was added dropwise. After the addition was completed, the reaction mixture was stirred for 30 minutes, then filtered. The crude product weighed 1.45 g. and melted at 176–179°. Recrystallization from 200 ml. of ethanol gave 1.21 g. (82%) of 1,3-dibromo-2-aminodibenzofuran, m.p. 181–182°. A mixed melting point with the compound obtained incidental to the preparation of the monobromoamine was not depressed.

Anal. Calcd. for C₁₂H₇Br₂NO: Br, 46.92; N, 4.11. Found: Br, 46.57, 46.55; N, 4.18.

B. From 1-Bromo-2-aminodibenzofuran.—To 0.7 g. (0.00267 mole) of 1-bromo-2-aminodibenzofuran dissolved in 40 ml. of glacial acetic acid was added dropwise, with stirring, 2.67 ml. of a 1 M solution of bromine in glacial acetic acid. After the addition of all the brominating solution, the reaction mixture was heated to dissolve the precipitate which had formed. Cooling and filtration gave 0.7 g. (77%) of needles, m.p. 180–181°. There was no depression of melting point of an admixture of this material with that obtained as a by-product in the preparation of 1-bromo-2-aminodibenzofuran.

2-Acetoxydibenzofuran.⁸—Sixteen grams (0.0869 mole) of 2-hydroxydibenzofuran^{1c} was suspended in 50 ml. (54.1 g., 0.53 mole) of acetic anhydride and 3 drops of concd. sulfuric acid added. The mixture was refluxed for 10 minutes and then cooled and filtered. Sixteen grams (81%) of white plates, m.p. 111–113°, was obtained. Dilution of the mother liquor with water gave an additional 5.0 g. of ester. The combined fractions were recrystallized from *n*-propyl alcohol to give 17.4 g. (88%) of 2-acetoxy compound, m.p. 115–116°. Recrystallization from ethanol did not raise the melting point.

Anal. Calcd. for C₁₄H₁₀O₃: C, 74.3; H, 4.46. Found: C, 74.2; H, 4.89.

Fries Rearrangement with 2-Acetoxydibenzofuran.⁹—Five grams (0.0221 mole) of 2-acetoxydibenzofuran was dissolved in 30 ml. of *sym*-tetrachloroethane and the solution heated to 60°, whereupon 3.2 g. (0.0240 mole) of anhydrous aluminum chloride was added in small quantities. The mixture was heated to 140° for 1 hour, vigorous stirring being employed, and then allowed to cool, stirring being continued for 7 hours. Following hydrolysis, the solvent was removed by steam distillation. The residue was dissolved in boiling 10% sodium hydroxide solution. On cooling to room temperature, bright yellow plates separated. Acidification of a suspension of these plates in water yielded 1.0 g. (20%) of yellow crystals, m.p. 165–166.5°. Recrystallization from ethanol-*n*-propyl alcohol-water raised the melting point to 168–169°. The color of this compound was not altered by distillation (b.p. 227° (7 mm.)) or by repeated treatments with decolorizing charcoal in ethanol.

Anal. Calcd. for C₁₄H₁₀O₃: C, 74.35; H, 4.47. Found: C, 74.14; H, 4.42.

Subsequent methylation and oxidation (see below) of this compound to the known 2-methoxy-3-dibenzofurancarboxylic acid showed this compound to be 2-hydroxy-3-acetyldibenzofuran.

(7) J. Mai, *Ber.*, **35**, 162 (1902); see also N. Kornblum in R. Adams, "Organic Reactions," Vol. II, John Wiley and Sons, Inc., New York N. Y., 1944, pp. 277–282.

(8) K. Schimmelschmidt, see ref. 3, has reported a melting point of 118–119° for this compound, but no analytical data or preparative details were given. See also, J. Swislow, *Iowa State Coll. J. Sci.*, **14**, 92 (1939) [C. A., **34**, 6273 (1940)].

(9) This procedure was adapted from that of D. H. Hey and E. R. B. Jackson, *J. Chem. Soc.*, 802 (1936), for the Fries rearrangement of the benzoate of 4-hydroxybiphenyl.

The material which had been retained in the 10% sodium hydroxide solution on cooling, was precipitated by acidification. There was obtained 2.4 g. (48%) of a pale yellow solid, m.p. 105–110°. Because of difficulties experienced in the attempted purification of this compound by recrystallization, it was converted to its methyl ether.

A solution of 18 ml. (24.0 g., 0.190 mole) of dimethyl sulfate, 1.5 g. of crude rearrangement product (m.p. 105–110°) and 28 ml. of acetone was heated at reflux while 14 ml. of a 60% potassium hydroxide solution was added dropwise with stirring. After the addition was completed, heating was continued for 30 minutes; then the solution was cooled. A colorless oil separated which was taken up in dilute ethanol and allowed to stand in the refrigerator for several weeks. About 0.1 g. of colorless cubic crystals, m.p. 114–118°, was deposited. Recrystallization from petroleum ether (b.p. 60–68°) raised the melting point to 121–122°.

Anal. Calcd. for $C_{14}H_{12}O_3$: C, 74.98; H, 5.03; methoxyl, 12.92. Found: C, 74.84, 74.86; H, 5.04, 5.05; methoxyl, 12.78.

Presumably, this ether is 1-acetyl-2-methoxydibenzofuran.

2-Methoxy-3-acetyldibenzofuran.—Seven-tenths of a gram (0.0031 mole) of 2-hydroxy-3-acetyldibenzofuran was dissolved in 100 ml. of 3% sodium hydroxide solution and 40 ml. of acetone. To this was added 10 ml. (13.3 g., 0.106 mole) of dimethyl sulfate, and the mixture was allowed to stand overnight. Water was added to the reaction mixture, and the resulting precipitate was filtered off. The product was washed with warm 5% sodium hydroxide solution. There remained 0.72 g. (97%) of white crystals, m.p. 112–113°. Recrystallization from ethanol yielded needles, m.p. 113–114°.

Anal. Calcd. for $C_{15}H_{12}O_3$: C, 74.98; H, 5.03. Found: C, 74.60; H, 4.93.

2-Methoxy-3-dibenzofurancarboxylic Acid.—One tenth of a gram of 2-methoxy-3-acetyldibenzofuran in 2 ml. of dioxane and 2 ml. of 10% sodium hydroxide solution was treated with a solution of iodine in potassium iodide. The addition was carried out slowly with agitation until an iodine color persisted. The mixture was acidified with hydrochloric acid and, after a few crystals of sodium bisulfite were added to destroy excess iodine, the whole was filtered. The yellow residue, which smelled strongly of iodoform, was extracted with dilute sodium hydroxide solution. Acidification of the filtered alkaline solution yielded very fine white needles melting at 206–207° after recrystallization from 70:30 ethanol-water solution. There was no depression in the melting point of an admixture of this compound with authentic 2-methoxy-3-dibenzofurancarboxylic acid.¹⁰

4-Acetoxydibenzofuran.—Ten drops of concd. sulfuric acid was added to a stirred suspension of 75 g. (0.407 mole) of 4-hydroxydibenzofuran¹⁰ in 45 g. (0.441 mole) of acetic anhydride. The exothermic reaction caused dissolution of the phenol to take place. The solution was heated on a water-bath for 1 hour, then poured into a large volume of water. The crude acetoxy compound was filtered off and washed well with water. The dried material was distilled under reduced pressure (b.p. 181° (4 mm.)) and the distillate recrystallized twice from ethanol to give 60.0 g. (65%) of ester, m.p. 99–100°.

Anal. Calcd. for $C_{14}H_{10}O_3$: C, 74.34; H, 4.46. Found: C, 74.22; H, 4.68.

Fries Rearrangement of 4-Acetoxydibenzofuran.—Several variations of the Fries reaction were employed, but even the use of elevated temperatures¹¹ failed to cause the formation of the *para* isomer, 1-acetyl-4-hydroxydibenzofuran. *sym*-Tetrachloroethane proved to be less satisfactory as a solvent than nitrobenzene. The following procedure was the most successful of the several tried.

To a solution of 30.0 g. (0.133 mole) of 4-acetoxydibenzofuran in 150 ml. of dry nitrobenzene was added in small portions, 22.5 g. (0.169 mole) of aluminum chloride. During the addition, the temperature was not allowed to exceed 35°. After stirring for 12 hours at room temperature, the solution was poured onto an ice-hydrochloric acid mixture. The nitrobenzene was removed by steam distillation,

and the solid residue was refluxed with decolorizing charcoal in 5% potassium hydroxide solution. Filtration and acidification of the filtrate gave 24.0 g. of a dark brown solid. Several recrystallizations from large volumes of ethanol yielded 12.0 g. (40%) of lemon-yellow crystals, m.p. 180–181.5°. The identity of this compound was established (see below) as 3-acetyl-4-hydroxydibenzofuran by Beckmann rearrangement of the oxime of the methoxy derivative to an amide which gave the known 3-amino-4-methoxydibenzofuran on hydrolysis.

Anal. Calcd. for $C_{14}H_{10}O_3$: C, 74.34; H, 4.46. Found: C, 74.51; H, 4.73.

Excess hydroxylamine hydrochloride and a solution of 5.0 g. of potassium acetate in 10 ml. of water were added to a solution of 4.0 g. (0.0177 mole) of 3-acetyl-4-hydroxydibenzofuran in 350 ml. of ethanol. The solution was refluxed for 6 hours and then poured into a large volume of water. The precipitate was recrystallized from ethanol to give 4.1 g. (96%) of 3-acetyl-4-hydroxydibenzofuran oxime, m.p. 233–237° dec. An analytical sample recrystallized from ethanol, from methanol and from water (as the sodium salt) melted at 236–237° dec.

Anal. Calcd. for $C_{14}H_{11}NO_3$: N, 5.81. Found: N, 5.70.

3-Acetyl-4-methoxydibenzofuran.—To a refluxing solution of 5.8 g. (0.0256 mole) of 3-acetyl-4-hydroxydibenzofuran and 9.7 g. (0.0769 mole) of dimethyl sulfate in 25 ml. of acetone was added, dropwise, with stirring, 2 ml. of a 60% solution of potassium hydroxide. After the addition was completed, the reaction mixture was refluxed for 1 hour and then poured into 300 ml. of water. The oil which separated soon solidified and was recrystallized from 70:30 ethanol-water solution to give 5.5 g. (89%) of 3-acetyl-4-methoxydibenzofuran, m.p. 70.5–71.5°.

Anal. Calcd. for $C_{15}H_{12}O_3$: C, 74.98; H, 5.03; methoxyl, 12.92. Found: C, 74.96, 75.07; H, 5.11, 5.03; methoxyl, 12.70.

Five grams (0.0208 mole) of 3-acetyl-4-methoxydibenzofuran was treated with hydroxylamine hydrochloride according to standard procedure¹² to give 3.2 g. (60%) of 3-acetyl-4-methoxydibenzofuran oxime, m.p. 163–165°, after several recrystallizations from ethanol.

Anal. Calcd. for $C_{15}H_{13}NO_3$: N, 5.50. Found: N, 5.48.

3-Acetamido-4-methoxydibenzofuran.—To a solution of 0.12 g. of 3-acetyl-4-methoxydibenzofuran oxime in 20 ml. of dry benzene was added in small portions, 0.13 g. of phosphorus pentachloride. The solution turned green in color and became quite warm. The reaction mixture was shaken for 5 minutes, then poured onto ice. The mixture was made alkaline with sodium carbonate and then was acidified with acetic acid. The benzene was distilled off and the residual gum dissolved in aqueous ethanol. After treatment with decolorizing charcoal at the boiling point of the solution and filtration, the solution deposited on cooling, 30 mg. of needles. Two recrystallizations from 60:40 ethanol-water solution yielded pink crystals, m.p. 135–136°, with a change in crystalline form observed at 65° by means of a microscope.

Anal. Calcd. for $C_{15}H_{13}NO_3$: N, 5.50. Found: N, 5.30.

Five milligrams of this amide was refluxed for 4 hours with 2 ml. of concd. hydrochloric acid. The solution was diluted with water, decolorizing charcoal added and the mixture filtered. Addition of ammonium hydroxide until the solution was basic precipitated an amine, m.p. 73–74°. The identity of this amine was confirmed to be 3-amino-4-methoxydibenzofuran by mixed melting point with an authentic sample.^{1b}

3-(α -Aminoethyl)-4-methoxydibenzofuran Hydrochloride.—One hundred and twenty grams of 2.5% sodium amalgam was added in small portions to a solution of 4.0 g. (0.0157 mole) of 3-acetyl-4-methoxydibenzofuran oxime in 75 ml. of warm absolute ethanol. Glacial acetic acid was added concurrently with the amalgam in such quantities that the reaction mixture was at all times slightly acidic. The solution was stirred and refluxed for an additional 90 minutes after completion of the addition; then the solution was decanted from the residual mercury into 400 ml. of water.

(10) H. Gilman and R. J. Young, *THIS JOURNAL*, **57**, 1121 (1935).

(11) A. H. Blatt in R. Adams, "Organic Reactions," Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1942, p. 344.

(12) Procedure 42B in R. L. Shriner and R. C. Fuson, "The Systematic Identification of Organic Compounds," 3rd. ed., John Wiley and Sons, Inc., New York, N. Y., 1948, p. 202.

The solution was extracted twice with ether to remove unreacted oxime. Ammonium hydroxide was added until the solution was basic, and the solution was again extracted twice with ether. The ethereal extracts containing the free base were combined and dried over anhydrous sodium sulfate. Subsequent to filtration of the drying agent, the filtrate was saturated with dry hydrogen chloride. The precipitated amine hydrochloride was recrystallized twice from dilute hydrochloric acid to give 3.0 g. (69%), m.p. 223–223.5°.

Anal. Calcd. for $C_{15}H_{16}ClNO_2$: N, 5.06. Found: N, 5.12.

Acetylation of 3-Acetyl-4-hydroxydibenzofuran Oxime.—A suspension of 3.5 g. (0.0146 mole) of 3-acetyl-4-hydroxydibenzofuran oxime in acetic anhydride was refluxed until solution was effected. Upon cooling, there was obtained 3.6 g. (87%) of product, m.p. 165–171° dec. Recrystallization from acetic anhydride raised the melting point to 169–171.5° dec. The compound decomposed somewhat on exposure to light.

Anal. Calcd. for $C_{16}H_{15}NO_4$: N, 4.95. Found: N, 4.85.

3-Methylbenzofuro[3,2-g]-1,2-benzisoxazole.—The method employed for the preparation of this compound was essentially that used by Lindemann and Romanoff¹³ for the preparation of 3-methylindoxazine.

Two and one-half grams (0.0089 mole) of 3-acetyl-4-hydroxydibenzofuran acetyloxime was heated at 200° for 15 minutes. Rapid decomposition of the compound took place, and vapors having the sharp odor of acetic acid were evolved. After the reaction mixture had cooled, concd. hydrochloric acid was added and the mixture was refluxed 1 hour. The mixture was filtered and the solid collected was dissolved in a minimum amount of hot ethanol. Decolorizing charcoal was added and the mixture filtered. Cooling yielded tan needles, recrystallization of which from petroleum ether (b.p. 60–68°) gave 0.62 g. (31%) of faintly pink needles, m.p. 172–174°.

Anal. Calcd. for $C_{14}H_9NO_2$: N, 6.28. Found: N, 6.38.

1-Bromo-2-acetoxydibenzofuran.¹⁴—Two drops of concd. sulfuric acid was added to a suspension of 9.2 g. (0.035 mole) of crude 1-bromo-2-hydroxydibenzofuran¹⁶ (m.p. 103–112°) in 15 ml. of acetic anhydride. The mixture was refluxed for 10 minutes, cooled to room temperature and diluted with water. The precipitated product, m.p. 133–135°, was recrystallized twice from ethanol to give 7.8 g. (73%) of ester, m.p. 135–136°.

Anal. Calcd. for $C_{14}H_9BrO_2$: Br, 26.3. Found: Br, 26.1, 26.2.

1-Methyl-2-methoxydibenzofuran.—To 4.7 g. (0.017 mole) of 1-bromo-2-methoxydibenzofuran¹⁶ in 75 ml. of dry benzene was added 0.0154 mole of *n*-butyllithium¹⁵ in ether under an atmosphere of nitrogen. There was an immediate evolution of heat with the development of a slightly reddish color. After 15 minutes of vigorous stirring, 10 ml. of dimethyl sulfate was added dropwise as rapidly as the rate of reflux permitted. Following 2 hours stirring, the reaction mixture was allowed to stand overnight; then the white precipitate which had formed was filtered off. The filtrate was washed with 10% sodium hydroxide solution and then with water. After separation of the layers, the ether–benzene solution was dried over anhydrous sodium sulfate and then the solvents removed by distillation. The residual oil solidified on standing. Two recrystallizations from petroleum ether (b.p. 60–86°) gave 2.0 g. (56%) of product, m.p. 60–61°.

Anal. Calcd. for $C_{14}H_{12}O_2$: C, 79.2; H, 5.67. Found: C, 79.1; H, 5.73.

1-Methyl-2-hydroxydibenzofuran.—One and one-half grams (0.007 mole) of the above methyl ether was refluxed in a mixture of 10 ml. of 47% hydrobromic acid and 10 ml. of glacial acetic acid for 10 hours. The reaction mixture was diluted with water, and the product which initially came down as an oil, was filtered off upon solidification. Recrystallization from petroleum ether (b.p. 60–86°) gave 0.9 g. (65%) of needles, m.p. 135–136°.

(13) H. Lindemann and S. Romanoff, *J. prakt. Chem.*, **122**, 214 (1929).

(14) This experiment was carried out by F. A. Yeoman.

(15) H. Gilman, J. A. Beel, C. G. Brannen, M. W. Bullock, G. E. Dunn and L. S. Miller, *THIS JOURNAL*, **71**, 1499 (1949).

Anal. Calcd. for $C_{13}H_{10}O_2$: C, 78.7; H, 5.05. Found: C, 78.5; H, 5.00.

1-Methyl-2-acetoxydibenzofuran.—Two drops of concd. sulfuric acid was added to a solution of 0.7 g. (0.0035 mole) of 1-methyl-2-hydroxydibenzofuran in 5 ml. of acetic anhydride. The solution was refluxed for 30 minutes and then was poured into a large volume of water. Two recrystallizations of the precipitate from petroleum ether (b.p. 60–86°) yielded 0.63 g. (75%) of crystals, m.p. 80–81°. In spite of the narrow melting point range this material was somewhat impure as indicated by the analysis.

Anal. Calcd. for $C_{15}H_{12}O_3$: C, 74.98; H, 5.03. Found: C, 75.6; H, 4.9.

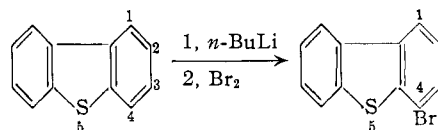
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Some Derivatives of Dibenzothiophene

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In connection with studies of some heterocycles, several derivatives of dibenzothiophene have been prepared and certain of their reactions studied. The preparation of 4-bromodibenzothiophene-5-dioxide was achieved readily by the oxidation of 4-bromodibenzothiophene with hydrogen peroxide in glacial acetic acid. 4-Bromodibenzothiophene¹ was prepared easily by treating 4-dibenzothiophenyl-lithium with bromine. Contrary to the bromination of the organolithium compound, no bromodibenzothiophene was isolated by a similar bromine treatment of the product obtained from the reaction of phenylcalcium iodide with dibenzothiophene. It has been established^{1,6} that dibenzothiophene is metalated in the 3-position by phenylcalcium iodide and not in the 4-position as in the case of *n*-butyllithium.



Nitration of 2,8-dibromodibenzothiophene with warm, fuming nitric acid yielded a dinitro-2,8-dibromodibenzothiophene-5-oxide tentatively established as 2,8-dibromo-3,7-dinitrodibenzothiophene-5-oxide on the basis of general considerations of the nitration reactions of dibenzofuran, dibenzothiophene and their derivatives. Attempts to nitrate 2,8-dibromodibenzothiophene-5-dioxide by similar procedures were unsuccessful. The preparation of 2,8-dibromodibenzothiophene-5-dioxide was accomplished readily by the oxidation of 2,8-dibromodibenzothiophene with hydrogen peroxide in glacial acetic acid.

Experimental²

4-Bromodibenzothiophene.—To a stirred solution of 27.6 g. (0.15 mole) of dibenzothiophene in 250 ml. of ether was added 140 ml. of a 1.32 *M* ether solution of *n*-butyllithium³

(1) This compound has been prepared in a different manner; H. Gilman and A. L. Jacoby, *J. Org. Chem.*, **3**, 108 (1938).

(2) All melting points are uncorrected.

(3) H. Gilman, J. A. Beel, C. G. Brannen, M. W. Bullock, G. E. Dunn and L. S. Miller, *THIS JOURNAL*, **71**, 1499 (1949). A similar procedure has been used successfully for the preparation of *n*-propyllithium in yields in excess of 80%. Some initial experiments on the metalation of dibenzothiophene have indicated that *n*-propyllithium reacts at a much faster rate than *n*-butyllithium and gives on carbona-