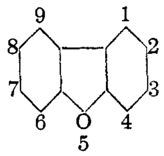
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE COLLEGE]

Dibenzofuran. IV. Orientation and Relative Aromaticities of the 2-, 3- and 4-Dibenzofuryl Radicals

BY HENRY GILMAN, W. GLEN BYWATER AND PAUL T. PARKER

Introduction

2-Nitrodibenzofuran.—Nitration of dibenzofuran takes place predominatingly in the 3-position. Other common nuclear substitution reactions (halogenation, sulfonation and the Friedel–Crafts reaction) introduce a substituent in the 2-position. However, a by-product of nitration is a so-called isomeric mononitro compound, melting at about 110°, and first isolated by Borsche and Bothe.[1] Originally it was suggested that the 110° compound was the 2-nitro isomer, but subsequent comparison with an authentic specimen of 2-nitrodibenzofuran (synthesized by Brumberg[2] from 2-nitro-3-aminodibenzofuran by replacement of the amino group by hydrogen) invalidated this postulate. More recently it has been proposed that the isomer is 4-nitrodibenzofuran.[3]



The substance is of more than ordinary significance in dibenzofuran orientation. From analogies based on nuclear substitutions of more common benzenoid types, as well as from present information on dibenzofuran,[4] it appeared altogether unlikely that we were dealing with a 4-isomer, and a 2-isomer was indicated. The confusion was due primarily to the belief that the 110° product was an individual substance. Actually it is a mixture of substances which so far has not been resolved into its components. The presence of some 2-nitrodibenzofuran in the mixture was established by indirect methods. The mixture was reduced to the amine or amines which were then acetylated to yield, after numerous recrystallizations, pure 2-acetaminodibenzofuran. Incidentally, this serves to establish that nitration and sulfonation of dibenzofuran are not wholly unlike, for both involve (to widely different degrees, to be sure) the 2-position.

3-Hydroxydibenzofuran by Pyrolysis of Resorcinol.—Tsuzuki[4a] obtained two hydroxydibenzofurans, one containing one hydroxyl and the other two hydroxyl groups, on passing resorcinol over tungstic oxide heated to 500–550°. Two alternative formulas were considered for the monohydroxy compound: namely, 1- and 3-hydroxydibenzofuran. Largely on the basis of a similarity of absorption curves for 2-hydroxydiphenyl and the hydroxydibenzofuran, it was concluded that the compound in hand was the 1-isomer. The formation of phenylmalonic acid by oxidation of the hexahydro derivative of the monohydroxydibenzofuran presents no definite evidence for either the 1- or 3-hydroxydibenzofuran. Present knowledge of dibenzofuran points to an extreme difficulty of introducing a substituent into the 1-position. Actually, no 1-isomer has as yet been isolated from nuclear substitution reactions even when substituents are present which would appear to favor such substitution.[4,5] On this as well as on other grounds it appeared more reasonable to prefer the 3- to the alternative 1-isomer. 3-Hydroxydibenzofuran was prepared and found to have a melting point like that of the supposed 1-isomer. A comparison of the authentic 3-hydroxy compound with the compound obtained by pyrolysis of resorcinol showed these compounds to be identical. The dihydroxydibenzofuran is, accordingly, probably the 3,7- rather than the 1,9-isomer.

After the manuscript was submitted an article appeared by Tatematsu and Kubota, *Bull. Chem. Soc.*, Japan, **9**, 448 (1934), in which the hydroxy compound was identified as the 3-isomer.

Relative Aromaticities of the 2-, 3- and 4-Dibenzofuryl Radicals.—If ease of nuclear substitution be a criterion of aromaticity, then the general behavior of dibenzofuran in a miscellany of typical nuclear substitution reactions indicates that this hetero-polynuclear system is more aro-

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(1) Borsche and Bothe, *Ber.*, **41**, 1940 (1908).

(2) Brumberg, Doctoral Dissertation, Göttingen, 1925.

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

(4) Gilman, Brown, Bywater and Kirkpatrick, THIS JOURNAL, **56**, 2473 (1934).

(4a) Tsuzuki, *Bull. Chem. Soc. Japan*, **2**, 79 (1927).

(5) The significant observation has been made very recently that 4-acetaminodibenzofuran on bromination gives 1-bromo-4-acetaminodibenzofuran. The 1-bromodibenzofuran obtained from the bromo-acetamino compound melts at 67°. Likewise 4-hydroxydibenzofuran directs bromine to the 1-position; and coupling of 4-hydroxydibenzofuran with benzene-diazonium chloride gives the 1-phenylazo-4-hydroxydibenzofuran.

Sulfonation of 1,2,3,4-tetrahydrodibenzofuran introduces a sulfonic group into the 7-position. This position appears to be favored by other substitution reactions of the tetrahydrodibenzofuran.

matic than benzene. One of the methods suggested for comparison of relative aromaticities involves the scission of organometallic compounds by hydrogen chloride.[6] For example, in a compound like ethyl-triphenyl-lead the more aromatic phenyl radical combines with hydrogen to give benzene.

$$(C_2H_5)(C_6H_5)_3Pb + HCl \longrightarrow (C_2H_5)(C_6H_5)_2PbCl + C_6H_6$$

The reaction appears to be of general usefulness for this purpose, although it is not free of some apparently anomalous or exceptional cases.[6c] The isomeric 2-, 3- and 4-dibenzofuryl-triphenyl-leads were prepared and then cleaved by hydrogen chloride. In each case the cleavage proceeded predominatingly in the direction of giving dibenzofuran. The 2-, 3- and 4-dibenzofuryl radicals are designated as **R** in the transformation

$$R(C_6H_5)_3Pb + HCl \longrightarrow (C_6H_5)_3PbCl + RH$$

Experimental Part

2- and 3-Hydroxydibenzofurans.—2-Hydroxydibenzofuran was prepared by oxidation of a mixture of Grignard reagents prepared from 7.2 g. (0.294 atom) of magnesium turnings, 36.5 g. (0.147 mole) of 2-bromodibenzofuran and 19.1 g. (0.14 mole) of *n*-butyl bromide in 700 cc. ether. The oxidation, effected with oxygen at −10° gave a 36.7% yield of the crude phenol which when purified by two crystallizations from alcohol melted at 134°. This procedure, suggested by Ivanoff,[7] has been used effectively by P. R. Van Ess for the oxidation of 4-dibenzofuryl-*lithium* in the presence of *n*-butylmagnesium bromide. The 2-hydroxydibenzofuran was also prepared by heating 2-dibenzofuryldiazonium borofluoride with acetic acid and then hydrolyzing the resulting acetate.[8]

A quantitative yield of 3-dibenzofuryldiazonium borofluoride was obtained by diazotizing 17.5 g. (0.08 mole) of 3-aminodibenzofuran hydrochloride in 25 cc. of concd. hydrochloric acid and then adding 28 g. of hydrofluoroboric acid solution (from 20 g. of 48% hydrofluoric acid and 8 g. of boric acid). Twelve grams of the diazonium borofluoride was heated in the customary manner[8] with acetic anhydride, and hydrolysis of the acetate by 10% sodium hydroxide gave 1.3 g. or 24% of 3-hydroxydibenzofuran melting at 138–139° after recrystallization from dilute acetic acid.

Anal. Calcd. for $C_{12}H_8O_2$: C, 78.26; H, 4.34. Found: C, 78.57 and 78.71; H, 4.68 and 4.64.

A Zerewitinoff determination gave 0.94 active hydrogen. More recently there appeared a patented preparation for the phenols by heating the diazonium compounds to about 200° with phosphoric acid.[9]

Unfortunately, a specimen of the hydroxydibenzofuran was not available for purposes of comparison. However, through the kindness of Professor Tsuzuki we obtained detailed directions for the pyrolysis of resorcinol over tungstic oxide, and succeeded in preparing the reported phenol, which melted at 137.5–138.5°. The yield of phenol, reported and found, is quite small and for this reason a check preparation was desirable. From the second preparation, starting with 15 g. of resorcinol, there was obtained 0.03 g. of the same phenol, which was shown to be 3-hydroxydibenzofuran (mixed m. p.). In addition, 0.2 g. of dibenzofuran was isolated.

2-Acetaminodibenzofuran.—One mole of once-distilled technical dibenzofuran was nitrated in 500 cc. of glacial acetic acid at 60–65° with 152 cc. of fuming nitric acid. These conditions favor the formation of the isomer. Vigorous stirring was maintained until the stirrer was stopped by the heavy precipitate of 3-nitrodibenzofuran, which is insoluble in the quantity of acetic acid used. The yield of 3-nitrodibenzofuran melting at 181–182° was 161.6 g. or 75.8%. On diluting the nitration mother liquor with two volumes of water, 57 g. of light yellow needles separated. Purification was attempted by extraction with petroleum ether (b. p. 60–68°) then recrystallization from methyl alcohol, dilute acetic acid, petroleum ether and benzene. The melting point was raised from 92° to 107–110°.

The mixture obtained in this manner was reduced by tin and hydrochloric acid to give a 71% yield of amine hydrochlorides. Subsequent to recrystallization from dilute hydrochloric acid, the light gray hydrochlorides were converted by ammonium hydroxide to the amines, which melted at 103–112° after three recrystallizations from aqueous alcohol. Three grams of the amines in benzene was acetylated by acetic anhydride. The solution was allowed to stand at room temperature for one-half hour; then concentrated by distillation of the solvent; and chilled to give 1.5 g. or 40.8% of crude 2-acetaminodibenzofuran melting at 141–144°. Purification was completed by recrystallizing five times from aqueous alcohol, extracting once with petroleum ether and finally recrystallizing five times from benzene to give fine white needles melting at 162–162.5° and shown to be identical with an authentic specimen.[4]

2-, 3- and 4-Dibenzofuryl-triphenyl-leads and their Cleavage by Hydrogen Chloride.—General directions were used for the preparation of the unsymmetrical lead compounds[6b] from triphenyl-lead chloride[10] and the appropriate organometallic compound, the analysis of the organolead compounds,[11] and their cleavage by hydrogen chloride.[6b,c] The 4-dibenzofuryl-triphenyl-lead was prepared from 4-dibenzofuryl-lithium,[12] a similar reaction having been used earlier by Austin.[13] 3-Bromodibenzofuran formed a Grignard reagent more readily than the isomeric 2-bromo compound, and the yields of these

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(6) (a) Kharasch and Flenner, This Journal, **54**, 674 (1932); (b) Gilman and Towne, *Rec. trav. chim.*, **51**, 1054 (1932): (c) Gilman, Towne and Jones, This Journal, **55**, 4689 (1933). It is interesting to note that the cleavage of anisyl-2-furyl-leads gives furan largely. This places the 2-furyl radical as the most electronegative or most aromatic radical of those radicals which have been given a definite position in such series.

(7) Ivanoff, *Bull. soc. chim.*, **39**, 47 (1926). See, also, Gilman and Wood, This Journal, **48**, 806 (1926).

(8) Haller and Shafer, *ibid.*, **55**, 4954 (1933).

(9) I. G. Farbenind. A.-G. German patent 591,213 [*C. A.*, **28**, 2366 (1934)].

(10) This Journal, **51**, 3112 (1929).

(11) *Ibid.*, **50**, 1714 (1928).

(12) Gilman and Young, *ibid.*, **56**, 1415 (1934).

(13) Austin, *ibid.*, **54**, 3726 (1932).

TABLE I

DIBENZOFURYL-TRIPHENYL-LEADS AND THE HYDROGEN CHLORIDE CLEAVAGE PRODUCTS

	$R(C_6H_5)_3Pb$ compounds					Cleavage products[a]	
				Pb, %			
R	Yield, %	Solvent for crystn.	M. p., °C.	Calcd.	Found	Phenyl-lead compounds, %	Dibenzofuran, %
2-Dibenzofuryl	71.4	Pet. ether	158.5–159.5	34.24	33.96, 33.74	56	53
3-Dibenzofuryl	53	Pet. ether	125–126	34.24	33.90	42.8	34[b]
4-Dibenzofuryl	[c]	[c]	99–100	34.24	34.19	47.2	24[d]

[a] The percentages of phenyl-lead compounds are those calculated from the sum of triphenyl-lead chloride and diphenyl-lead dichloride isolated. These values are lower than the quantities actually formed, for the yield of diphenyl-lead dichloride was based on the yield of pure tetraphenyl-lead formed after heating the non-melting diphenyl-lead dichloride with phenylmagnesium bromide. For example, from the cleavage of 2-dibenzofuryl-triphenyl-lead there was isolated from 2.42 g. (0.004 mole) of unsymmetrical lead compound, 0.8 g. of crude dibenzofuran which gave 0.36 g. or 53.8% of pure dibenzofuran. The yield of triphenyl-lead chloride was 0.4 g. or 21.1%, and that of diphenyl-lead dichloride was 0.6 g. or 34.7%. The yield of dibenzofuran based on the phenyl leads isolated was 96.5%. [b] 0.87 g. or 0.0014 mole of 3-dibenzofuryl-triphenyl-lead was used in the cleavage experiment. The yield of dibenzofuran based on the phenyl-leads isolated was 79.4%. [c] The 4-dibenzofuryl-triphenyl-lead was crystallized with difficulty, the product (after removing excess dibenzofuran by steam distillation) forming a colorless oil that partially solidified to a plastic mass on standing. An alcoholic solution that was allowed to stand for several days deposited the white crystals. 2.85 g. (0.0047 mole) of 4-dibenzofuryl-triphenyl-lead was used in the cleavage experiment. [d] The yield of dibenzofuran based on the phenyl-leads isolated was 50.8%.

RMgBr compounds (determined by the usual titration procedure), was 73.5% for the 2-compound and almost quantitative for 3-dibenzofurylmagnesium bromide.

The cleavage reactions with hydrogen chloride were effected in chloroform. The scission products were identified in the customary manner: triphenyl-lead chloride and dibenzofuran by the method of mixed melting points and diphenyl-lead dichloride by conversion to tetraphenyl-lead by means of phenylmagnesium bromide.

Summary

1. Indirect resolution of the supposed isomeric nitrodibenzofuran melting at about 110° has shown that some 2-nitrodibenzofuran is obtained incidental to the nitration of dibenzofuran.

2. Pyrolysis of resorcinol over heated tungstic oxide gives 3- and not 1-hydroxydibenzofuran.

3. The relative ease of nuclear substitution reactions of dibenzofuran can be correlated with the hydrogen chloride scission of the 2-, 3- and 4-dibenzofuryl-triphenyl-leads. The predominant RH product isolated from cleavage of the unsymmetrical lead compounds is dibenzofuran.

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The Magenta Series. I. The Preparation and Spectrophotometric Study of the Lower Basic Members

BY JOHN T. SCANLAN

Basic Magenta (Fuchsine) is a most important biological stain. Unfortunately, commercial samples of this dye vary widely in quality. These variations are quite troublesome in the exacting technique of biological staining. The object of this investigation is to determine the causes of the difficulties and to produce a standard product of uniform quality. Most commercial Magentas are mixtures of two or more of the lower homologs (see Table I) of the series. In their manufacture subsidiary dyes are also produced, such as the yellow diaminodiphenylacridine, known as Chrysaniline or Phosphine, and its homologs, and dyes of the Induline and Nigrosine groups. Furthermore, the products may be contaminated by the intermediates used.

The first step in this investigation was the preparation of the four lower homologs of the series for the determination of their relative merits in biological applications. In the course of this work certain anomalies were observed, and considerable further study was necessary to explain them. The spectrophotometric data necessary for the identification and evaluation of commercial samples were obtained.

Nomenclature.—Considerable confusion has resulted from the various names acquired by the members of this group, many of them relics from