

TABLE I
 PROPERTIES OF AMINES

Amine	N- <i>n</i> -Butyl- α -naphthylamine	N-Ethyl- <i>p</i> -anisidine	N- <i>n</i> -Butyl- <i>p</i> -anisidine	Benzyl- α -naphthylamine		
Yield, %	80	51	65	24		
B. p. { °C.	155-167	135-140	142-145	..		
{ Mm.	8	20	6	..		
d_{20}^{20}	1.004	1.017	0.963	..		
n_D^{20}	1.5963	1.5444	1.5207	..		
Derivative	HCl	<i>p</i> -Br-Bz-sulfonamide	HCl	Benzamide		
Deriv. m. p., °C.	151-152	113-114	187.5-188	103-104		
Anal. {	Calcd. {	C, %	71.4	48.7	61.3	N, 4.16
		H, %	7.64	4.32	8.36	
	Found {	C, %	71.4	49.3	61.5	N, 4.21
		H, %	8.07	4.50	8.60	

anhydride for one-half hour and then diluted with water. After neutralization with sodium carbonate the mixture was boiled until all the tertiary amine had distilled. Upon extraction of the oil from the filtrate with ether and evaporation of the ether the alkylations were found to have produced a 19% yield of N,N-di-*n*-butyl-*p*-toluidine and a 25% yield of N,N-di-*n*-butyl-*p*-anisidine.

Summary

The method for preparing N-alkylanilines by reducing an alcoholic solution of aniline and an aldehyde with hydrogen in the presence of Raney nickel and sodium acetate has been extended to four other aromatic primary amines from which ten N-alkylarylamines have been obtained in 24 to 88% yield.

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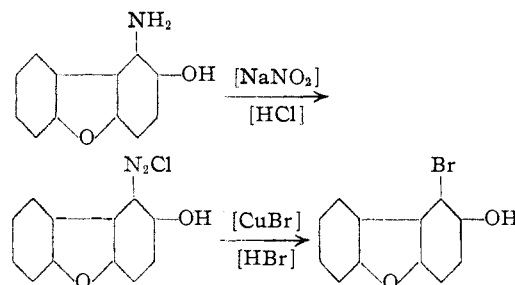
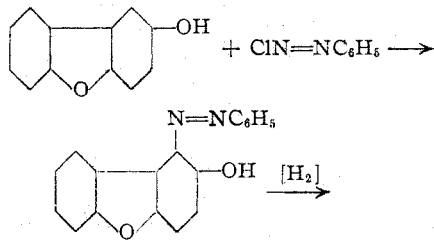
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE COLLEGE]

Dibenzofuran. XIV. Diazo Coupling of 2-, 3-, and 4-Hydroxy Compounds¹

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Introduction

The recent availability of authentic specimens of some bromohydroxydibenzofurans² has made possible the determination of structure of the benzeneazo-hydroxydibenzofurans formed by diazo coupling with the 2-, 3-, and 4-hydroxydibenzofurans. The following transformations illustrate the general procedure used for proof of structure of the coupling products.



The 3-hydroxydibenzofuran also coupled in an ortho position to give 2-benzeneazo-3-hydroxydibenzofuran; but the 4-hydroxydibenzofuran coupled in a para position to give 1-benzeneazo-4-hydroxydibenzofuran. These general directions of coupling are consistent with early observations on phenols.³ However, there are two available ortho positions for diazo coupling of the 2- and the 3-hydroxydibenzofurans. On general grounds, it might have been predicted that 3-hy-

(1) Paper XIII, Gilman, Parker, Bailie and Brown, *THIS JOURNAL*, **61**, 2836 (1939).

(2) Gilman and P. R. Van Ess, *ibid.*, **61**, 1365 (1939).

(3) Chattaway and Hill, *J. Chem. Soc.*, **121**, 2756 (1922).

droxydibenzofuran would couple predominantly in the 2-position rather than in the 4-position, because (other than by metalation) the 4- and the 6-positions are generally not susceptible to the introduction of substituents.¹

The problem of selective ortho diazo coupling is not without some interest in connection with the relative fixation of possible bond structures in dibenzofuran. It is quite likely that diazo coupling and bromination of both phenols and aliphatic enols are intimately associated, and that each involves an enolic double bond.⁴ From the experimental evidence presented at this time, it appears that there is no preferential stabilization of one of the bond structures for the isomeric hydroxydibenzofurans. If there were marked rigidity, a condition that would be unusual in the simple monosubstituted types, then the observed coupling in the 1-position of 2-hydroxydibenzofuran would indicate double bonds between the 1- and 2- and between the 3- and 4-positions. However, a fixed double bond between the 3- and 4-positions would lead one to expect that 3-hydroxydibenzofuran would couple in the 4-position, and not in the 2-position as was the case.

The solubilities of the coupling products in alkali conform with related types in the naphthalene series. The azo dyes derived from the 2- and 3-hydroxydibenzofurans were found to be insoluble in dilute alkali, even when heated, whereas the dye derived from 4-hydroxydibenzofuran was easily soluble in cold alkaline solution. 1-Hydroxy-2-benzeneazonaphthalene⁵ and 1-benzeneazo-2-hydroxynaphthalene⁶ are insoluble in alkali, and 1-hydroxy-4-benzeneazonaphthalene⁶ is readily soluble.

Experimental Part

1-Benzeneazo-2-hydroxydibenzofuran.—The general procedure for the coupling reaction was adapted from that used by Werner and Frey⁷ in preparing the benzeneazo derivative of 10-hydroxyphenanthrene. The 2-hydroxydibenzofuran, 3.68 g. (0.02 mole), was dissolved in 15 cc. of 15% potassium hydroxide solution, and subsequently diluted with 60 cc. of water, then cooled to 0° in a 200-cc. three-necked flask equipped with a stirrer, dropping funnel, and thermometer. The diazonium solution was prepared by adding 5 cc. of concd. hydrochloric acid to a mixture of 1.86 g. (0.02 mole) of aniline

and 15 g. of finely cracked ice, then adding dropwise a solution of 1.46 g. (0.021 mole) of sodium nitrite in a few cc. of water, until a slight but permanent test for nitrite ion was indicated by a test with starch-potassium iodide paper. The diazonium solution was added dropwise to the cold solution of 2-hydroxydibenzofuran through the chilled dropping funnel. The temperature was maintained at 0° by means of an ice-bath. A red precipitate formed at once. To ensure complete reaction the mixture was stirred for thirty minutes after addition was completed. The product was then removed by filtration and washed well with water. Acidification is not necessary since the desired product is insoluble in alkali. The yield was almost quantitative. The crude product melted at 161–164°, and two recrystallizations from alcohol gave red needles melting at 165.5–166°.

Anal. Calcd. for C₁₈H₁₂O₂N₂: N, 9.72. Found: N, 9.84 and 9.98.

2-Benzeneazo-3-hydroxydibenzofuran.—The 3-hydroxydibenzofuran was coupled with benzenediazonium chloride in exactly the manner described above for 2-hydroxydibenzofuran. It was found to be advantageous, however, to run the reaction at a slightly lower temperature (–5°). The mixture was filtered at the close of the reaction without previous acidification. The yield from 3.68 g. (0.02 mole) of 3-hydroxydibenzofuran was 4 g. or 73% of the theoretical. The product after twice crystallizing from alcohol, and once from ethyl acetate, and once from a mixture of ethyl acetate and alcohol melted at 177–178°. It crystallized in minute lustrous golden-brown plates.

Anal. Calcd. for C₁₈H₁₂O₂N₂: N, 9.72. Found: N, 9.70 and 9.83.

1-Benzeneazo-4-hydroxydibenzofuran.—The 4-hydroxydibenzofuran was coupled with benzenediazonium chloride by the procedure described for 2-hydroxydibenzofuran. In this case the resulting azo compound formed a salt which separated in very fine orange crystals. Direct acidification of the reaction mixture gave purplish material which turned green upon drying and was difficult to purify. In order to obtain a pure sample it was necessary either to filter out the potassium salt from the reaction mixture and then acidify, or to crystallize the purplish material obtained by acidification of the reaction mixture at once from dilute alcohol without allowing it to stand. The purified product which separated in yellow-orange needles from dilute alcohol melted at 174–175°.

Anal. Calcd. for C₁₈H₁₂O₂N₂: N, 9.72. Found: N, 9.77 and 9.99.

Conversion of 1-Benzeneazo-2-hydroxydibenzofuran to 1-Bromo-2-hydroxydibenzofuran.—The method described by Pschorr⁸ for the reduction of 9-hydroxy-10-benzeneazophenanthrene was used as a basis for the reduction of the hydroxyazodibenzofurans. One gram (0.0045 mole) of 1-benzeneazo-2-hydroxydibenzofuran was dissolved in 40 cc. of boiling glacial acetic acid, and a solution of 2.0 g. of stannous chloride hydrate in 15 cc. of concd. hydrochloric acid added gradually. The color of the solution quickly faded to yellow. The solution was then cooled, whereupon fine white needles separated out. These crystals

(4) Mills and Nixon, *J. Chem. Soc.*, 2510 (1930); Fieser and Lothrop, *THIS JOURNAL*, **58**, 2050 (1936); and Fieser in Chap. 2 of Gilman, "Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1938.

(5) McPherson, *Ber.*, **28**, 2418 (1895).

(6) Liebermann, *ibid.*, **16**, 2860 (1883).

(7) Werner and Frey, *Ann.*, **321**, 303 (1902).

(8) Pschorr, *Ber.*, **35**, 2734 (1902).

proved to be the hydrochloride of 1-amino-2-hydroxydibenzofuran. A quantitative yield was obtained. The compound had a tendency to oxidize in air, hence it was used at once to prepare the corresponding bromohydroxy compound.

The diazotization of all of the hydroxyaminodibenzofurans proved rather difficult owing to their marked sensitivity to oxidation. The procedure finally used was based on a patented process for the diazotization of *o*-aminonaphthols.⁹ The hydrochloride of 1-amino-2-hydroxydibenzofuran was suspended in ether and treated with an equivalent amount of sodium carbonate solution. The ether layer was washed with water, dried over sodium sulfate and the amine hydrobromide precipitated by passing in dry hydrogen bromide.¹⁰ The hydrobromide, 0.45 g. (0.0025 mole), was suspended in 30 cc. of water at 0° and poured gradually into a similarly cooled solution of 0.12 g. (0.0017 mole) of sodium nitrite and 0.08 g. of copper sulfate hydrate in 10 cc. of water. A light brown precipitate formed. Fifteen minutes was allowed for the completion of the diazotization, whereupon the mixture was poured into a suspension of 0.81 g. (0.0021 mole) of cuprous bromide in 20 cc. of water, and 13 cc. of 40% hydrobromic acid was added gradually. As soon as the evolution of gas ceased, the mixture was boiled for a few minutes. Some very dark precipitate was filtered from the hot solution. The filtrate on cooling deposited grayish needles, 0.015 g., melting at 115–116°. When decolorized with charcoal and crystallized from dilute alcohol, the melting point was 121.5–122° and was not depressed by mixture with an authentic sample of 1-bromo-2-hydroxydibenzofuran.

Conversion of 2-Benzeneazo-3-hydroxydibenzofuran to 2-Bromo-3-hydroxydibenzofuran.—The 2-benzeneazo-3-hydroxydibenzofuran was reduced according to the procedure described for the 1-benzeneazo-2-hydroxydibenzofuran. In the case of the 3-hydroxy derivative, the hydroxy-amine formed a complex with the tin salt and hence did not precipitate out directly as the hydrochloride upon cooling the reaction mixture. In order to break up the complex, the solution obtained after reduction was complete was cooled in an ice-bath and treated with small portions of 30% sodium hydroxide solution until the precipitated tin hydroxide had redissolved, then made barely acid with hydrochloric acid, and finally slightly basic with ammonium hydroxide. The solution was then extracted with ether, the ether layer dried over sodium sulfate, and the amine hydrobromide precipitated with dry hydrogen bromide.

The conversion of the hydrobromide to 2-bromo-3-hydroxydibenzofuran was accomplished by the method

employed for the hydrobromide of 1-amino-2-hydroxydibenzofuran. From 0.45 g. (0.0025 mole) of the hydrobromide the yield was 0.04 g. of crude product, which after decolorizing and crystallizing from dilute alcohol melted at 111–112°. A mixed melting point determination with authentic 2-bromo-3-hydroxydibenzofuran showed no depression.

Conversion of 1-Benzeneazo-4-hydroxydibenzofuran to 1-Bromo-4-hydroxydibenzofuran.—The 1-benzeneazo-4-hydroxydibenzofuran was reduced in the same manner as described for 1-benzeneazo-2-hydroxydibenzofuran. The amine hydrochloride did not form a complex with the tin salt, but separated out at once in greenish-gray crystals. The hydrochloride was converted to the hydrobromide, diazotized, and the diazonium group replaced by bromine as previously outlined for 1-amino-2-hydroxydibenzofuran. From 0.45 g. (0.0025 mole) of the hydrobromide, a crude yield of 0.015 g. of bromohydroxydibenzofuran melting at 145–146° was obtained. By decolorizing and crystallizing from dilute alcohol, white needles were produced melting at 150°. Identification of the compound as 1-bromo-4-hydroxydibenzofuran was completed by a mixed melting point determination.

Miscellany.—In some orienting experiments we have so far not succeeded in coupling dibenzofuran with benzenediazonium chloride in alcohol solution in the presence of potassium acetate, nor with the more active 2,4-dinitrobenzenediazonium chloride¹¹ in acetic acid. 2-Amino- or 2-acetaminodibenzofuran also failed to couple with benzenediazonium chloride under conditions which give quantitative yields with β -naphthylamine.¹² The principal present difficulty in this case appears to be the greater insolubility of the amine or the acetamino compound in the alcoholic reaction medium even when the reaction is run at a somewhat higher temperature.

Summary

Coupling of 2-, 3-, and 4-hydroxydibenzofurans with benzenediazonium chloride gives, respectively, 1-benzeneazo-2-hydroxydibenzofuran, 2-benzeneazo-3-hydroxydibenzofuran, and 1-benzeneazo-4-hydroxydibenzofuran. The non-isolation of any 4-benzeneazo-3-hydroxydibenzofuran from the coupling with 3-hydroxydibenzofuran indicates absence of fixed bond structures in these simple types.

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(9) German Patent 172,446 [*J. Chem. Soc.*, **90**, 908 (1906)].

(10) Hydrogen bromide gas was prepared by the method of Ruhoff, Burnett and Reid, "Organic Syntheses," Vol. XV, 35 (1935).

(11) Meyer, *Ber.*, **47**, 1747 (1914), reported that 2,4-dinitrobenzenediazonium chloride couples with mesitylene and acenaphthene under these conditions.

(12) Bamberger and Schieffelin, *ibid.*, **22**, 1376 (1889).