TABLE I

REDUCTION OF 9.1 G. (0.05 MOLE) OF AZOBENZENE AT 45 LB. PRESSURE

Expt.	Purpose of experiment	Catalyst	Grams	95% alcohol,[a] cc.	Concd. H_2SO_4, cc.	Temp., °C.	H_2 absorbed, mole	Time, min.	Yield, grams Benzidine	Yield, grams Aniline	Yield, grams Azobenzene	Total
1	To reduce to aniline	Pt	0.2	150	None	22–27	0.101	25	0.99[b]	0.35[c] 6.85	None	8.19
2	Attempt to stop at hydrazo stage by discontinuing when the H_2 absorbed is one-half that above	Pt	.2	150	None	22–27	.050	8	4.92[b]	2.36	0.89	8.17
3	Effect of lower temperature	Pt	.2	200	None	5–8	.069	14	6.14[b]	2.22	.25	8.61
4	Attempt to stop at hydrazo stage by introducing H_2SO_4 and converting to insol. benzidine sulfate	Pt	.3[d]	200	10	22–27	.068	120[e]	5.35	3.09	None	8.44
5	Effect of lower temperature	Pt	.2	200	10	8	.072	20[e]	7.45	1.05	None	8.50
6	Effect of higher temperature	Pt	.3[d]	100	10	99	.089	180[e]	3.79	5.16	None	8.95
7	Stopped before H_2 absorption complete in attempt to increase yield of hydrazobenzene	Pt	.3[d]	150	10	22–27	.050	57	2.82	2.29	2.73	7.84
8	Lower temperature to increase yield of hydrazobenzene	Pt	.2	200	10	5–8	.056	10	7.33	0.97	None	8.30
9	To reduce to aniline	Ni	1	100	None	99	.101	120	None	8.70	None	8.70
10	Attempt to obtain hydrazobenzene by stopping when one-half reduced	Ni	1	150	None	99	.052	32	2.88	3.16	2.1	8.14
11	Effect of lower temperature	Ni	1	150	None	55	.058	120	1.19	5.93	None	7.12

[a] The amount of solvent used was varied as the solubility of azobenzene decreased with decrease in temperature. [b] The hydrazobenzene was determined as benzidine. [c] This 0.35 g. of amine remained as residue after the aniline had distilled off. It could not be distilled without decomposition. [d] The reaction started with 0.2 g. of $PtO_2 \cdot H_2O$ but the catalyst became inactive in a few minutes. Upon addition of 0.1 g. of catalyst reduction continued. [e] The velocity of the reaction was less at high temperatures than at 8°, requiring greater time to absorb an equivalent amount of hydrogen.

mole of hydrogen per mole of azobenzene is allowed to be absorbed, hydrazobenzene, aniline and unchanged azobenzene are found to be present. If the temperature is lowered to 55°, the hydrogen absorption takes place much more slowly with an increase in the amount of aniline and decrease in the amount of hydrazobenzene formed. Nickel does not appear to be as satisfactory as platinum catalyst for this type of reduction.

(B) Catalytic Reduction of *p*-Aminoazobenzene.—A solution of 9.85 g. (0.05 mole) of *p*-aminoazobenzene in 100 cc. of 95% alcohol was shaken with hydrogen under pressure of 45 lb. per sq. in. in the presence of 0.1 g. of platinum oxide for twenty minutes, at which point absorption of hydrogen ceased. Separation and analysis of reduction products gave 5.12 g. of *p*-phenylenediamine and 2.92 g. of aniline.

Summary

1. The catalytic reduction of azobenzene to hydrazobenzene and to aniline using platinum and nickel catalysts has been studied.

2. *p*-Aminoazobenzene has been hydrogenated to give *p*-phenylenediamine and aniline using platinum as catalyst.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE COLLEGE]

Dibenzofuran. I. Sulfonation

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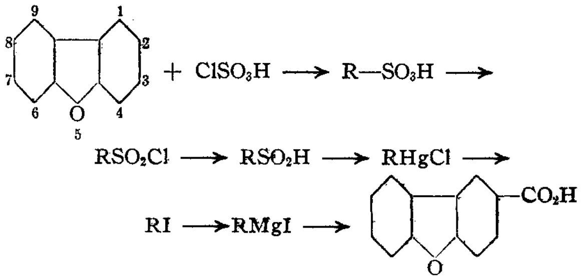
Introduction

In connection with studies on the physiological properties of dibenzofuran derivatives it was necessary to determine the positions assumed by nuclear substituents. It has been found that sulfonation takes place with great ease and gives excellent yields. The following sequence of reactions was used to prove that the sulfonic grouping entered the 2-position.[1]



Additional evidence for the 2-position was obtained by converting the dibenzofurylmercuric chloride to the known 2-bromodibenzofuran. However, there is a possibility that the 2-bromo-

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[1] The system of numbering is the International Rules for Numbering of Organic Ring Systems. See Patterson, THIS JOURNAL, **47**, 543 (1925). *Chemical Abstracts* uses these Rules in numbering all new ring systems, and beginning with Vol. 31 will number all systems according to the Rules.

dibenzofuran might have formed as a consequence of initial cleavage of the mercurial by hydrogen bromide to give dibenzofuran which is known to undergo bromination in the 2-position. This possible difficulty was circumvented by starting with known 2-bromodibenzofuran, and converting it successively to the Grignard reagent and then to 2-dibenzofurylmercuric chloride, which was shown to be identical with the mercurial obtained via the sulfonic acid.

A related series of transformations was used to demonstrate that the disulfonic acid had the two sulfonic acid groups in the 2,8-positions. In this case the di-mercurial, obtained from the disulfinic acid, was converted to the known 2,8-dibromodibenzofuran.

It is interesting to recall that mono-nitration involves predominatingly the 3-position; and that halogenation, as well as acylation by the Friedel–Crafts reaction, appears to give monosubstituents exclusively in the 2-position. The marked effect of the nature of the entering group is strikingly illustrated in the following paper wherein it has been shown that mercuration takes place in the 4-position. This combination of results would in all probability not have been predicted on the basis of current knowledge of orientation influences.

In this connection it is significant to consider the effect of a substituent already present on the position assumed by a like second substituent. Di-halogenation,(2) di-acetylation by the Friedel–Crafts reaction, and, as already mentioned, disulfonation take place in the 2,8-positions. Dinitration, however, gives the 3,8-dinitrodibenzofuran. Of greater significance is the extreme difficulty, at this time, of correlating both mono- and di-substitution of dibenzofuran with the formally related dibenzothiophene (biphenylene sulfide) and dibenzopyrrole (carbazole), as well as with fluorene and fluorenone. The several problems, which will be reviewed elsewhere, are not without some interest on electronic theories of orientation.

The positions of sulfonic acid groups were not established in any of the previous studies although replacement reactions were attempted without success. Hoffmeister(3) obtained a disulfonic acid whose barium salt was analyzed. Zehenter(4) prepared a monosulfonic acid by the action of fuming sulfuric acid on 2,2′-dihydroxybiphenyl, and assigned the sulfonic group to either the 2- or the 4-position. This monosulfonic acid was sulfonated to give a disulfonic acid. Borsche and Schacke(5) sulfonated 3-nitrodibenzofuran to a 3-nitrodibenzofuransulfonic acid. Mailhe's(6) hexanitrodibenzofurandisulfonic acid was subsequently withdrawn by him.

Experimental Part

2-Dibenzofuransulfonic Acid.—In a typical preparation, 24.5 g. (0.21 mole) of chlorosulfonic acid was added dropwise over a fifteen-minute period to a solution of 33.6 g. (0.2 mole) of dibenzofuran in 100 cc. of dry carbon tetrachloride contained in a flask provided with a mechanical stirrer. The reaction mixture was kept at about 25° and significant variations from this temperature markedly affect the yield. After stirring for an additional forty-five minutes, the solution was poured upon cracked ice and then diluted to one liter. Subsequent to removal of the carbon tetrachloride layer, the aqueous solution was extracted once with ether; neutralized with a slight excess of 10% sodium carbonate, and the resulting white precipitate filtered and then dried at 110° to give an 89% yield of sodium 2-dibenzofuransulfonate.

The free acid was obtained as white glistening plates (decomposing above 300°) upon acidifying and then cooling a hot saturated solution of the sodium salt.

The barium salt was recrystallized several times from water prior to analysis.

Anal. Calcd. for $(C_{12}H_7O_4S)_2Ba$: Ba, 21.75. Found: Ba, 21.92 and 21.77.

2-Dibenzofuransulfonyl Chloride.—One hundred and thirty-five g. (0.5 mole) of dry, powdered sodium 2-dibenzofuransulfonate and 92 g. (0.6 mole) of phosphorus oxychloride were heated for six hours at 165–180°. The product was shaken on to cracked ice, filtered, dried in the air and crystallized from toluene to give an 85.2% yield of the sulfonyl chloride which melts at 140°.

Anal. Calcd. for $C_{12}H_7O_3SCl$: Cl, 13.30; S, 12.03 Found: Cl, 13.39 and 13.05; S, 12.33.

2-Dibenzofuransulfinic Acid.—To 39.3 g. (0.6 atom) of zinc dust in 500 cc. of water heated to 80° was added, in small portions over a fifteen-minute period, 53.4 g. (0.2 mole) of finely powdered 2-dibenzofuransulfonyl chloride. The temperature of the well stirred solution was raised to 90° during the addition, and then after an additional stirring for fifteen minutes at 90°, 25 cc. of 10% sodium hydroxide was first added, followed by sufficient powdered sodium carbonate to give a definitely basic solution. The solution was filtered hot and this filtrate was combined with that obtained after digesting the precipitate with 200 cc. of hot water to give, upon cooling, a 67% yield of sodium 2-dibenzofuransulfinate. The salt was recrystallized several times from water prior to analysis.

Anal. Calcd. for $C_{12}H_7O_3SNa$: S, 12.61. Found: S, 12.59 and 12.15.

2-Chloromercuridibenzofuran.—A hot solution of 12.7 g. (0.05 mole) of sodium 2-dibenzofuransulfinate in 150 cc.

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(2) The experiments on di-chlorination and di-iodination will be described in a forthcoming paper by George E. Brown.

(3) Hoffmeister, *Ann.*, **159**, 191 (1871).

(4) Zehenter, *J. prakt. Chem.*, **131**, 331 (1931).

(5) Borsche and Schacke, *Ber.*, **56**, 2498 (1923).

(6) Mailhe, *Compt. rend.*, **154**, 1515 (1912), and *Bull. soc. chim.*, **11**, 1011 (1912).

of water was added rapidly with stirring to 27.2 g. (0.1 mole) of mercuric chloride in 200 cc. of boiling water to yield 82% of the chloromercuri compound which melted at 236.5–237° after crystallization from acetone.

Anal. Calcd. for $C_{12}H_7OClHg$: Hg, 49.76. Found: Hg, 49.05 and 49.14.

2-Dibenzofurylmagnesium bromide prepared in a toluene–ether solution from authentic 2-bromodibenzofuran, was treated in the customary manner with an equivalent of mercuric chloride in ether to give 2-chloromercuridibenzofuran. This compound was shown to be identical with the mercurial obtained from the sulfinic acid.

Conversion of 2-Chloromercuridibenzofuran to 2-Bromo- and 2-Iododibenzofuran.—A glacial acetic acid solution of bromine was added in small portions to 4 g. (0.01 mole) of the mercurial suspended in 75 cc. of acetic acid until the bromine color persisted after shaking for ten seconds. The solution was then diluted; the excess bromine removed by sodium thiosulfate; and the precipitate obtained after filtration boiled vigorously with 500 cc. of water for fifteen minutes and filtered hot. The dried precipitate was extracted with hot toluene, and, on removal of the toluene and crystallization from alcohol, there was obtained an 80% yield of 2-bromodibenzofuran (mixed m. p.).[7]

In order to determine the effect of hydrogen bromide on the mercurial, a suspension of 0.5 g. of 2-chloromercuridibenzofuran in glacial acetic acid was treated with 5 cc. of an aqueous hydrobromic acid solution, and the mixture allowed to stand overnight at room temperature. The crude yield of dibenzofuran was 20%. From this it is apparent that the replacement of the –HgCl group by bromine is reliable under the experimental conditions previously described.

The chloromercuri group was replaced by iodine in the customary manner[8] to give a 53.7% yield of 2-iododibenzofuran melting at 109–109.5° and identical with that previously prepared by George E. Brown by the iodination of dibenzofuran by iodine and nitric acid. It is interesting to note that the ready replacement of halogen by nitro (using nitrous acid or its equivalent) in the furan series is less applicable in the dibenzofuran series.

Dibenzofuran-2,8-disulfonic Acid.—Dibenzofuran was sulfonated with hot concentrated sulfuric acid in accordance with the directions of Hoffmeister[3] to give a quantitative yield of sodium dibenzofuran-2,8-disulfonate. The same compound was obtained by sulfonation of 2-dibenzofuransulfonic acid by means of concentrated sulfuric acid, and its identity was established by conversion to dibenzofuran-2,8-disulfonyl chloride.

Dibenzofuran-2,8-disulfonyl Chloride.—A 54.3% yield of the disulfonyl chloride was obtained by heating a mixture of 97.5 g. (0.26 mole) of dry sodium dibenzofuran-2,8-disulfonate and 104 g. (0.5 mole) of phosphorus pentachloride for four hours at 160–175°. The compound melted at 219° after recrystallization from toluene.

Anal. Calcd. for $C_{12}H_6O_5S_2Cl_2$: S, 17.56. Found: S, 17.89 and 17.75.

Dibenzofuran-2,8-disulfinic Acid.—The reduction of 55 g. (0.15 mole) of dibenzofuran-2,8-disulfonyl chloride with 49 g. (0.75 atom) of zinc was effected in the manner previously described for the monosulfonyl chloride to give an 85% yield of sodium dibenzofuran-2,8-disulfinate. The relatively high solubility in water of the sodium disulfinate makes it desirable to concentrate by evaporation to the formation of a crust.

Anal. Calcd. for $C_{12}H_6O_5S_2Na_2$: S, 18.85. Found: S, 19.05 and 19.08.

2,8-Dichloromercuridibenzofuran.—A quantitative yield of the di-mercurial was obtained in a 0.1 mole run in essential accordance with the procedure described for the preparation of the mono-mercurial, the excess of mercuric chloride being 50% instead of 100%. The slightly cream colored mercurial has no melting point and is not appreciably soluble in any common solvent. It was made ready for analysis by successive protracted extractions in a Soxhlet with benzene, acetone, water and methanol.

Anal. Calcd. for $C_{12}H_6OCl_2Hg_2$: Hg, 62.86. Found: Hg, 63.89 and 63.51.

Conversion of 2,8-Dichloromercuridibenzofuran to 2,8-Dibromo- and 2,8-Di-iododibenzofuran.—A 20% yield of 2,8-dibromodibenzofuran (mixed m. p.) was obtained by the slow addition of bromine in acetic acid to 12.8 g. (0.02 mole) of the dichloromercurial in acetic acid. The 2,8-di-iododibenzofuran, obtained in the usual manner from the dimercurial and iodine, melted at 171–172° and was shown to be identical with the di-iodo compound prepared by G. E. Brown by the di-iodination of dibenzofuran.

Summary

Sulfonation of dibenzofuran involves positions unlike those noted in nitration. Mono-sulfonation gives dibenzofuran-2-sulfonic acid and disulfonation gives dibenzofuran-2,8-disulfonic acid.

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(7) For the 2-bromo- and the 2,8-dibromodibenzofuran see Ref. 3; Mayer and Krieger, *Ber.*, **55**, 1659 (1922); Cullinane, *J. Chem. Soc.*, 2367 (1932); and McCombie, Macmillan and Scarborough, *ibid.*, 524 (1931).

(8) Gilman and Wright, THIS JOURNAL, **55**, 3302 (1933).