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An Improved Synthesis of Dibenzofurans by a Free-Radical Cyclization[1]

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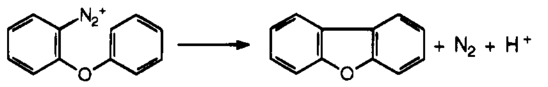
Reaction conditions for the formation of dibenzofurans from diazotized *o*-(aryloxy)anilines have been examined. Several promoters (hydroquinone, $SnCl_2$, NaI, $CuSO_4$, $FeSO_4$, etc.) have been discovered; these act as electron donors and promote a free-radical mechanism. The best of these is $FeSO_4$ which shortens the reaction time from hours to minutes and contributes to high yields (77−83%). We have been able to transform the cyclization to a reliable and convenient synthesis.

Introduction

The ring closure of 2-phenoxybenzenediazonium salt to produce dibenzofuran was first reported by Graebe and Ullmann.[2] Although their publication preceded Pschorr's work, the reaction has been designated as a Pschorr-type of ring closure.[3]



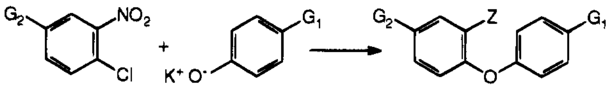
The procedure involved adding the diazonium salt of 2-aminodiphenyl ether to 50% sulfuric acid and boiling for several hours. Steam distillation of the reaction mixture produced dibenzofuran in 29% yield. Despite various modifications of reaction conditions, cyclization yields, with a single exception,[4] remained low.[3,5−11]

Herein we report that various promoters induce radical reactions and lead to excellent yields.

Results and Discussion

Previous work in this laboratory found that hydroquinone catalyzed the hydrodediazoniation of aryl diazonium salts.[12] We sought to determine whether hydroquinone would benefit the cyclization to dibenzofurans.

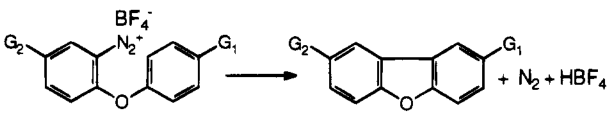
Scheme 1



a: $G_1 = CH_3$, G_2=H
b: G_1=OCH_3, G_2=H
c: G_1=CH_3, G_2=CH_3
d: G_1=H, G_2=CH_3
e: G_1=H, G_2=H
f: G_1=Cl, G_2=H

1: Z = NO_2
2: Z = NH_2
3: Z = $NH_3^+Cl^-$
4: Z = $N_2^+\,BF_4^-$

Scheme 2



4 **5**

a: $G_1 = CH_3$, G_2=H
b: G_1=OCH_3, G_2=H
c: G_1=CH_3, G_2=CH_3
d: G_1=H, G_2=CH_3
e: G_1=H, G_2=H
f: G_1=Cl, G_2=H

The required nitrodiaryl ethers **1a−f** were prepared by a standard Ullmann diaryl ether synthesis[13] in yields ranging from 35 to 60% (Scheme 1). The corresponding amines **2a−f**, initially colorless when freshly prepared, darkened rapidly in air. We found it convenient to preserve the amines as their hydrochlorides. Accordingly, the nitro compounds dissolved in anhydrous ether were reduced catalytically. After removal of the catalyst, saturation of the ether solution with HCl gas precipitated the stable amine hydrochlorides **3a−f** both in high yield (79−96%) and in high purity. The amine hydrochlorides were smoothly converted into stable diazonium tetrafluoroborates **4a−f** in good yields.

The effectiveness of various conditions to promote cyclization (Scheme 2) was assessed by the amount of product formed. Thus an aqueous suspension of diazonium salt **4a** containing an equimolar amount of sulfuric acid was added dropwise to an equimolar amount of hydroquinone dissolved in boiling water. Effervescence was immediate; 2-methyldibenzofuran (**5a**) was isolated in 70% yield from the steam distillate of the reaction mixture. Table 1 summarizes comparisons of several reaction conditions. The lowest yield of **5a** was obtained in the absence of any additive. Methods with H_2SO_4 typical of the Graebe and Ullmann procedure afforded only modest yields. The combination of hydroquinone with sodium acetate, either hot or cold, afforded no particular advantage, and the variations in yield under such conditions as a nitrogen atmosphere and use of the diazotized amine without isolation of the diazonium salt are considered equivalent within the expected experimental variation. These results clearly demonstrate that the addition of hydroquinone confers an enormous benefit in the cyclization.

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[1] (a) Ph.D. Dissertation, Ronald P. Pedemonte, University of Connecticut, 1991. (b) Presented in part at the 193rd American Chemical Society National Meeting, Denver, CO, April, 1987; Abstract ORGN 246. (c) Presented in part at the 197th American Chemical Society National Meeting, Dallas, Texas, April, 1990; Abstract ORGN 256.

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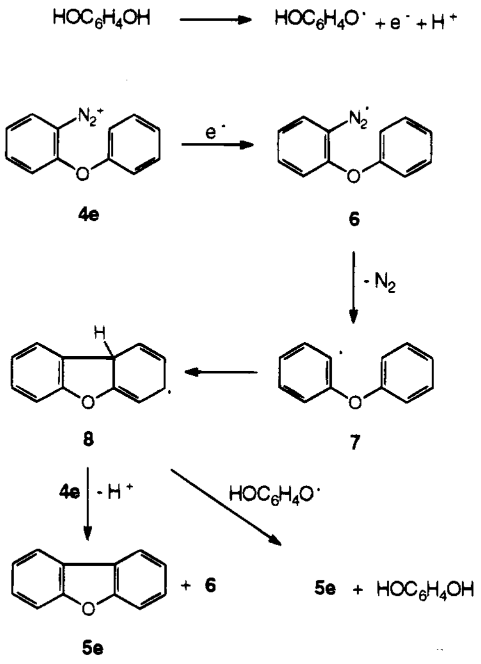
Table 1. Influence of Conditions on the Cyclization to 2-Methyldibenzofuran (5a)

conditions[a]	time[b]	% yield[c]
no additive	17 h	16
30% H_2SO_4	30 h	23
65% H_2SO_4	15 min	38
hydroquinone + NaOAc	5 min	<30
hydroquinone + NaOAc (10 °C)	<30 min	<30
hydroquinone	20 min	70
hydroquinone (under N_2 atm)	20 min	70
hydroquinone[d]	20 min	73

[a] Except where otherwise noted all cyclizations were conducted in solutions at their boiling point. [b] Measured as the time for the complete disappearance of the diazonium salt as indicated by 2-naphthol. [c] Yields of isolated products. [d] Without isolation of the diazonium salt.

Scheme 3



An ionic pathway[14–16] and a free-radical pathway[14,17,18] have both been proposed for the cyclization. In the first of these, release of nitrogen from the diazonium cation would produce an aryl cation which cyclizes. In this pathway, hydroquinone can only participate by competing for the cationic electrophile and thereby decrease the efficiency of cyclization. In the free-radical pathway, hydroquinone, by its conversion into semiquinone, can serve as an electron source (Scheme 3).[19] Acceptance of an electron by the diazonium cation leads to a diazenyl radical, and, then by loss of nitrogen, to an aryl radical which cyclizes to **8**. The intermediate **8** can either donate an electron to another molecule of the diazonium salt **4e** in continuation of a chain reaction or can release an electron and a proton to the semiquinone radical in a chain termination. Our observation of the yield enhancement caused by the hydroquinone supports only the free-radical mechanism.

Table 2. Influence of Promoters on the Cyclization to 2-Methyldibenzofuran (5a)

promoter	potential (V)[a]	half reaction	time[b]	% yield[c]
none	–	–	17 h	16
duroquinone	−0.50[d]	$C_6Me_4(OH)_2/C_6Me_4O_2$	15 min	54
hydroquinone	−0.70	$C_6H_4(OH)_2/C_6H_4O_2$	20 min	70
4,4′-biphenol	−0.95[d]	$HO(C_6H_4)_2OH/O(C_6H_4)_2O$	2 h	56
Cu_2O	−0.16	Cu^-/Cu^{2-}	15 min	45
Cu wire	−0.52	Cu/Cu^+	7 h	35
Cu powder	−0.52	Cu/Cu^+	7 h	41
$SnCl_2$	−0.15	Sn^{2-}/Sn^{4+}	15 min	75
NaI	−0.54	$2I^-/I_2$	15 min	79
$FeSO_4$	−0.77	Fe^{2+}/Fe^{3+}	15 min	80
KBr	−1.1	$2Br^-/Br_2$	14 h	35
$MnSO_4$	−1.5	Mn^{2+}/Mn^{3-}	12 h	27
$CoCl_2$	−1.8	Co^{2+}/Co^{3+}	14 h	21
$CuSO_4$	<−1.8	Cu^{2-}/Cu^{3-}	15 min	78

[a] Unless otherwise noted, values were obtained from reference 29. [b] Measured as the time for the complete disappearance of the diazonium salt as indicated by 2-naphthol. [c] Yields of isolated products. [d] Values obtained from reference 30.

The participation of hydroquinone in the free-radical mechanism can be tested by supplanting it with durohydroquinone or 4,4′-biphenol (Table 2). Like hydroquinone, both produced higher yields and fostered shorter reaction times. Duroquinone was not easily separated from the ring-closure product and made comparisons of yields less certain, but the times for complete reaction fell in the same order as the potentials.

A wider range of potentials can be screened by examination of inorganic materials as cyclization catalysts. Several trends emerged from our results and these are presented in Table 2. (1) The insoluble promoters are less effective for increasing the yields of cyclization. (2) Substances with low potentials favor faster reaction and higher yields of cyclized material. (3) Soluble promoters with potentials of −1.1 V or less have scant effect. (4) Cupric sulfate appears to be an exception to the trends of yield and potential.

Anomalies with copper(II) compounds have been noted before. What has emerged on more careful scrutiny is that under usual conditions of the Meerwein reaction, for example, copper(II) is converted into copper(I) by the solvent, and that copper(I) is in fact the promoter.[20] In the present case, we note that both the reaction time and the yield are more consistent with the potential of the Cu^-/Cu^{2-} half reaction rather than that for Cu^{2-}/Cu^{3-}. We postulate that boiling water converts some of the diazonium compound into a small amount of phenolic byproduct, that the phenol reduces copper(II) to copper(I),[21] and that copper(I) is responsible for the beneficial effects in the cyclization.

The most effective catalysts ($FeSO_4$, $SnCl_2$, NaI, and $CuSO_4$) from the screening were each examined in cyclizations affording other substituted dibenzofurans. The results of this examination are presented in Table 3. All four promoters, despite the fact that the cyclization procedure has not been optimized, afforded good yields, but reactions conducted with iron(II) sulfate or tin(II) chloride were faster than the others. Importantly, iron(II) sulfate consistently afforded the highest yields, regardless of substituent variation.

Three further modifications of the cyclization with $FeSO_4$ affording 2-methyldibenzofuran were briefly ex-

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Table 3. Influence of Soluble Promoters on the Cyclizations to Various Dibenzofurans

	promoter							
	$FeSO_4$		$SnCl_2$		NaI		$CuSO_4$	
reaction	time, min	% yield	time, min	% yield	time, min	% yield	time, min	% yield
4a → **5a**	15	80	15	75	15	79	15	78
4b → **5b**	15	82	15	73	35	79	30	80
4c → **5c**	15	80	15	68	30	48	55	45
4d → **5a**	15	77	15	67	40	56	45	64
4e → **5e**	15	83	15	82	30	81	45	79
4f → **5f**	15	79	15	81	30	75	45	73

plored. In one, it was found that when a neutral aqueous suspension of the required tetrafluoroborate was added to the catalyst in only one-fifth the volume of boiling water, there was no decrease in the 80% yield. This demonstration showed that the procedure could be simplified by the omission of the H_2SO_4 from the diazonium salt, and the procedure had the potential to be performed on five times the scale with no change in the size of the equipment. In the second modification, the amount of $FeSO_4$ was reduced to one-third of the ordinary equimolar amount. The yield of 2-methyldibenzofuran dropped from 80 to 69%. The result nevertheless showed that the additive is in fact a catalyst and that, in the mechanistic scheme, either the $FeSO_4$ is regenerated or that a chain mechanism is operational. However, for efficient synthetic work, the reduction in the amount of the inexpensive additive is inadvisable. In the last modification, the use of a freshly prepared diazonium sulfate solution replaced the tetrafluoroborate suspension and produced the product in 75% yield. Here, the reduction in yield from 80% may merely represent the efficiency of the diazotization, but, more importantly, the result shows that isolation of diazonium salts can be avoided for ordinary synthetic applications.

In summary, a number of possible promoters have been examined for the Pschorr-type of ring closure which affords dibenzofurans. Several have been discovered which both speed the reaction and foster the development of the product in high yields. The better catalysts are soluble and have potentials permitting easy electron-transfer to the diazonium salt to begin a free-radical reaction. Ferrous sulfate, an inexpensive, readily available substance of pronounced benefit, has emerged as the catalyst of choice. With its use, this method of forming dibenzofurans has become a reliable and convenient high-yield synthesis.

Experimental Section

Melting points and boiling points are uncorrected.

1-(4-Methylphenoxy)-2-nitrobenzene (1a) was prepared from 4-cresol and 2-chloronitrobenzene in 45% yield by a standard procedure;[13] yellow needles (from 95% ethanol) mp 47–49 °C (lit.[22] mp 48–48.5 °C); IR (KBr) 1510 and 1345 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.05 (m, 8 H) and 2.35 (s, 3 H).

Similarly prepared were the following:

1-(4-Methoxyphenoxy)-2-nitrobenzene (1b) from 4-methoxyphenol and 2-chloronitrobenzene in 44% yield; yellow needles (from absolute ethanol) mp 73–74.5 °C (lit.[23] mp 77 °C); IR (KBr) 1575 and 1335 cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.8 (m, 8H) and 3.5 (s, 3H).

4-Methyl-1-(4-methylphenoxy)-2-nitrobenzene (1c) from 4-methoxyphenol and 4-chloro-3-nitrotoluene in 39% yield; yellow solid (from 95% ethanol) mp 48–49 °C (lit.[24] mp 50 °C); IR (KBr) 1520 and 1330 cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.9 (m, 7H) and 2.25 (s, 6H).

4-Methyl-2-nitro-1-phenoxybenzene (1d) from phenol and 4-chloro-3-nitrotoluene in 35% yield; pale yellow oil, bp 164–166 °C (1.5 mm); IR (neat) 1510 and 1345 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.28 (m, 8H) and 2.35 (s, 3H). Anal. Calcd for $C_{13}H_{11}NO_3$: N, 6.11. Found: N, 5.91.

1-Nitro-2-phenoxybenzene (1e) from phenol and 2-chloronitrobenzene in 60% yield; pale yellow oil, bp 150–152 °C (2.2 mm)(lit.[13] bp 183–185 °C (8 mm)); IR (neat) 1520 and 1345 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.3 (m).

1-(4-Chlorophenoxy)-2-nitrobenzene (1f) from 4-chlorophenol and 2-chloronitrobenzene in 50% yield; yellow crystals (from 95% ethanol) mp 43–43.5 °C (lit.[25] mp 46 °C); IR (KBr) 1530 and 1345 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.5 (m).

2-(4-Methylphenoxy)benzenamine Hydrochloride (2a). Compound **1a** (7.00 g, 30.6 mmol) was dissolved in 90 mL of anhydrous ether; 5% palladium on charcoal (0.05 g) was added to the solution and the reduction carried out with hydrogen at an initial pressure of 34 psi. After 1 h no more hydrogen was consumed; the catalyst was filtered off and the ether solution was saturated with HCl gas from a generator. The resulting white precipitate was separated by filtration; 6.03 g (84%) mp 176–179 °C. IR (KBr) 2900–2700 cm^{-1}. Anal. Calcd for $C_{13}H_{14}ClNO$: C, 66.24; H, 5.99; Cl 15.04; N, 5.94. Found: C, 66.24; H, 6.07; Cl, 14.79; N, 5.86.

The following compounds were similarly prepared:

2-(4-Methoxyphenoxy)benzenamine hydrochloride (2b) from **1b** in 96% yield, mp 163–164 °C. IR (KBr) 2820–2760 cm^{-1}. Anal. [illegible] for $C_{13}H_{14}NO_2$: C, 62.03; H, 5.61; N, 5.56. Found: C, [illegible]; H, 5.64; N, 5.56.

4-Methyl-2-(4-methylphenoxy)benzenamine hydrochloride (2c) from **1c** in 92% yield, mp 180–182 °C (lit.[26] mp 180–184 °C), IR (KBr) 2880–2770 cm^{-1}.

2-Phenoxybenzenamine hydrochloride (2e) from **1e** in 96% yield, mp 154–155 °C (lit.[2] mp 155 °C). IR (KBr) 2900–2760 cm^{-1}.

5-Methyl-2-phenoxybenzenamine hydrochloride (2d) from **1d** in 83% yield by washing, with small amounts of cold anhydrous ether, the precipitate obtained by evaporation of the reaction solvent, mp 165–168 °C, IR (KBr) 2840–2720 cm^{-1}. Anal. Calcd for $C_{13}H_{11}ClNO$: C, 66.24; H, 5.99; Cl, 15.04; N, 5.94. Found: C, 66.24; H, 5.99; Cl, 14.78; N, 5.86.

2-(4-Chlorophenoxy)benzenamine Hydrochloride (2f). Palladium (5%) on charcoal (0.25g) was added to a solution of 5.40 g (21.6 mmol) of **1f** in 80 mL of absolute ethanol and 5 mL of concd HCl. Reduction was carried out for 45 min with hydrogen at an initial pressure of 35 psi. The catalyst was filtered off and the ethanol removed to provide a pink salt. Reprecipitation of the salt from ethanol–anhydrous ether afforded 4.35 g (79%) of a white salt, mp 181–183 °C (lit.[25] mp 181 °C). IR (KBr) 2850–2820 cm^{-1}.

2-(4-Methylphenoxy)benzenediazonium Tetrafluoroborate (3a). A solution of **2a** (5.00 g, 21.3 mmol) in 20 mL of warm water and 6.7 mL (80 mmol) of concd HCl was rapidly cooled in an ice bath with vigorous stirring. The finely divided

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hydrochloride was diazotized at 5 °C by the slow addition of $NaNO_2$ (1.66 g, 23.4 mmol) in 15 mL of H_2O. After an additional 20 min of stirring, the excess nitrous acid was destroyed by the addition of sulfamic acid and the diazonium solution filtered to remove a trace amount of solid. A solution of 4.09 g (37.3 mmol) of $NaBF_4$ in 20 mL of H_2O was added slowly to the cold diazonium solution to precipitate a light yellow solid. The solid was separated, washed with Et_2O, and dried in a vacuum desiccator overnight to afford 5.52 g (87%) of a light yellow salt, mp 152–153 °C dec. Precipitation of the diazonium salt from its filtered solution of reagent-grade acetone by the addition of ether afforded white tetrafluoroborate, IR(KBr) 2278 cm^{-1}. Anal. Calcd for $C_{13}H_{11}BF_4N_2O$: C, 52.39; H, 3.72; N, 9.40. Found: C, 52.19; H, 3.77; N, 9.24.

The following salts were prepared similarly on a comparable scale and purified by the reprecipitation method before analysis:

2-(4-Methoxyphenoxy)benzenediazonium tetrafluoroborate (3b) from **2b** in 84% yield, mp 117–118 °C dec, IR (KBr) 2270 cm^{-1}. Anal. Calcd for $C_{13}H_{11}BF_4N_2O_2$: C, 49.72; H, 3.53; N, 8.92. Found: C, 49.63; H, 3.42; N, 8.99.

5-Methyl-2-(4-methylphenoxy)benzenediazonium tetrafluoroborate (3c) from **2c** in 86% yield, mp 151–152 °C dec, IR (KBr) 2271 cm^{-1}. Anal. Calcd for $C_{14}H_{13}BF_4N_2O$: C, 53.88; H, 4.20; N, 8.98. Found: C, 53.75; H, 4.06; N, 9.12.

5-Methyl-2-phenoxybenzenediazonium tetrafluoroborate (3d) from **2d** in 85% yield, mp 154–155 °C dec, IR (KBr) 2266 cm^{-1}. Anal. Calcd for $C_{13}H_{11}BF_4N_2O$: C, 52.39; H, 3.72; N, 9.40. Found: C, 52.26; H, 3.49; N, 9.23.

2-Phenoxybenzenediazonium tetrafluoroborate (3e), from **2e** in 89% yield, mp 112–113 °C dec, IR (KBr) 2272 cm^{-1}. Anal. Calcd for $C_{12}H_9BF_4N_2O$: C, 50.75; H, 3.19; N, 9.86. Found: C, 50.51; H, 3.07; N, 9.90.

2-(4-Chlorophenoxy)benzenediazonium tetrafluoroborate (3f) was precipitated similarly from an aqueous solution of the diazonium chloride only one-tenth as concentrated, from **2f** in 74% yield, mp 148–149 °C dec, IR (KBr) 2274 cm^{-1}. Anal. Calcd for $C_{12}H_8BClF_4N_2O$: C, 45.26; H, 2.53; N, 8.80. Found: C, 45.53; H, 2.40; N, 8.92.

2-Methyldibenzofuran (4a). **3a** (1.00 g, 3.40 mmol) was suspended in 100 mL of H_2O acidified with 0.20 mL (3.40 mmol) of concd H_2SO_4. A solution of 0.37 g (3.40 mmol) of hydroquinone in H_2O (500 mL) was heated to boiling in a 1-L 3-neck flask equipped with an Eck and Krebs steam distillate collector and a mechanical stirrer. The diazonium salt suspension was added dropwise over a 30-min period. Five minutes after the addition, 2-methyldibenzofuran appeared as an oil in the distillate. Within 20 min after the completion of the addition, a 2-naphthol test showed that no diazonium salt remained. Steam distillation was continued for an additional 3 h. When the distillate was cool, the clear oil solidified. The distillate was extracted with three 30-mL portions of CH_2Cl_2 and the steam distillate collector washed with 20 mL of fresh solvent. The CH_2Cl_2 extracts and washings were combined and washed with three 10-mL portions of 5% NaOH. The CH_2Cl_2 solution was dried with $MgSO_4$. Evaporation of the solvent afforded 0.43 g (70%) of a colorless oil, which solidified upon cooling in ice; mp 40–42 °C (lit.[22] mp 44 °C). IR (KBr) 3020 and 1075 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.38 (m, 7 H) and 2.35 (s, 3 H).

Cyclization to 4a in the Absence of Oxygen. The procedure was followed exactly except that nitrogen gas was bubbled into the diazonium solution and the reaction mixture during the reaction. The reaction was complete within 20 min and the yield of **4a** was 70%.

Cyclization to 4a in the Absence of Hydroquinone. When hydroquinone was omitted, the reaction was complete within 17 h after the last addition of the diazonium salt and the yield of **4a** was 0.10 g (16%).

Cyclization to 4a in 30 and 65% H_2SO_4. The cyclization was repeated with equal volumes of 30 and 65% H_2SO_4 replacing the water. Again, hydroquinone was omitted. For the cyclization in 30% H_2SO_4, the reaction was complete within 30 h and the yield of **4a** was 23%. In contrast, the reaction in 65% H_2SO_4 was complete within 15 min and the yield of **4a** was 38%.

Cyclization to 4a Using Various Promoters. The conditions for the hydroquinone catalyzed cyclization were followed exactly except that 0.76 g of $SnCl_2{\cdot}2H_2O$, 0.48 g of Cu_2O, 0.50 g of NaI, 0.21 g of Cu powder, 0.21 g of Cu wire, 0.63 g of 4,4′-biphenol, 0.80 g of $CoCl_2{\cdot}6H_2O$, 0.57 g of $MnSO_4{\cdot}H_2O$, 0.40 g of KBr, 0.84 g of $CuSO_4{\cdot}5H_2O$, 0.94 g of $FeSO_4{\cdot}7H_2O$, or 0.56 g of durohydroquinone each separately replaced an identical molar amount (3.4 mmol) of hydroquinone. Yields of **4a** isolated by steam distillation are shown in Table 2.

In the case of duroquinone only, it was necessary to chromatograph the crude yellow oil on alumina with CCl_4 as the eluant to separate **4a** (0.32 g, 54%) from duroquinone.

Cyclization to 4a under Various Conditions with Ferrous Sulfate. The amount of solvent used to dissolve the ferrous sulfate could be reduced to one-fifth of the usual volume with no decrease in yield. In another trial, it was determined that the addition of sulfuric acid to the tetrafluoroborate was unnecessary. To test the catalytic property of ferrous sulfate, one-third the previously described amount of ferrous sulfate (0.31 g, 1.1 mmol) was used; 0.425 g (69%) of **4a** resulted. To test whether the isolation of the diazonium salt could be avoided, **2a** (1.00 g, 4.3 mmol) was diazotized by the procedure describing the preparation of **3a** except that 1.10 g (10.8 mmol) of H_2SO_4 replaced the HCl as the diazotization acid. The diazonium sulfate was added to 1.19 g (4.3 mmol) of ferrous sulfate in boiling water and the product steam distilled to afford 0.59 g (75%) of **4a**.

Cyclizations to Other Dibenzofurans 4b–f. The cyclizations of **3b–f** to **4b–f** were performed with $FeSO_4{\cdot}7H_2O$, $CuSO_4{\cdot}5H_2O$, NaI, and $SnCl_2{\cdot}2H_2O$. Yields are reported in Table 3.

2-Methoxydibenzofuran (4b), mp 43–45 °C (lit.[27] mp 45–46 °C), IR (KBr) 3060 and 1050 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.1 (m, 7H) and 3.5 (s, 3H).

2,8-Dimethyldibenzofuran (4c), mp 59–62 °C (lit.[28] mp 64 °C), IR (KBr) 1275 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.3 (m, 6H) and 2.38 (s, 6H).

Dibenzofuran (4e), mp 80–82 °C (lit.[2] mp 82–84 °C), IR (KBr) 3040 and 1090 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.45 (m).

2-Chlorodibenzofuran (4f), mp 102–103 °C (lit.[25] mp 101 °C), IR (KBr) 3040 and 1055 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.4 (m).

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