(+)-α-phenylethylammonium O-benzyl-(*R*)(−)-mandelate, 13136-59-9; O-benzyl-(*R*)(−)-mandelamide, 13136-60-2.

Acknowledgment.—We are indebted to the National Institutes of Health (Grant No. GM-06232-06) for its generous support of a portion of this study.

Solvent-Assisted Ullmann Ether Synthesis. Reactions of Dihydric Phenols

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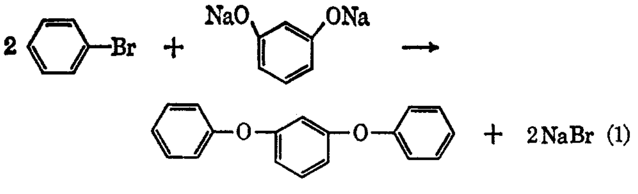
Certain organic solvents containing heteroatoms dissolve copper salts to form complexes which are catalytic in the Ullmann ether synthesis, thus allowing use of lower temperatures. When oxygen and water are excluded, salts of dihydric phenols can be allowed to react. By proper choice of solvent and conditions, the reaction can be directed toward polyphenyl ethers or phenolic ethers. Although resorcinol yields only tars under the usual melt conditions, the present system permits formation of *meta*-linked ethers in good yields. Rates of reaction of substituted bromobenzenes with disodium resorcinate in pyridine indicate nucleophilic attack by resorcinate dianion. Bromination of *m*-diphenoxybenzene under mild conditions led only to 2,4-diphenoxybromobenzene. This was condensed with various phenolic salts to synthesize a new class of nonlinear polyphenyl ethers

Although polyphenyl ethers are resistant to thermal, oxidative, and radiation damage,[1] their useful temperature range as fluids is restricted by the high melting points of the pure isomers. This problem is alleviated by employing mixtures of isomers, but liquid mixtures result only when a high proportion of the ether linkages are in the *meta* positions of the benzene rings.[2]

Low molecular weight polyphenyl ethers are usually prepared by the Ullmann ether synthesis.[3] Copper metal is the preferred catalyst and the phenate melt is exposed to air to convert the copper to an active form. When *meta*-linked ethers are sought, the synthesis of *m*-diphenoxybenzene illustrates the main problems encountered. The first choice is whether the middle ring shall be derived from *m*-dibromobenzene or from resorcinol. Pure *m*-dibromobenzene is not readily available and attempts to employ resorcinol directly in the Ullmann ether synthesis have been reported to yield only tars.[4,5] Failure to obtain polyphenyl ethers was ascribed to instability of the alkali metal salts of dihydric phenols at the temperature required for reaction.

Results and Discussion

With dry nitrogen to provide an inert atmosphere, cuprous chloride as catalyst, and pyridine as solvent, the disodium salt of resorcinol was converted to *m*-diphenoxybenzene in one step (eq 1). The yield of



recrystallized product was 70% (based on resorcinol). Details are given in experimental method A. The product is accompanied by a small yield of *m*-phenoxyphenol, which is an intermediate, as the sodium salt. The formation of *m*-phenoxyphenol and its further conversion were observed by gas chromatography during the course of the reaction. Oxygen must be rigorously excluded as it causes formation of tars at the expense of product. Phenolic salts, free of water and alcohol, are conveniently prepared from sodium methoxide. This reactant was used as described in method A for the preparation of all disalts except for those few cases where another method is specifically mentioned. An excess of base completely inhibits the reaction by destroying the copper catalyst. Reactions were therefore carried out by using only 95% of the theoretical quantity of base to make the disalt.

Solvent–Catalyst Interactions.—Successful solvents for the ether condensation must not only dissolve the reactants, but bring the copper catalyst into solution as well. Various cupric salts (chloride, bromide, sulfate, acetylacetonate) were catalytic when dissolved in solvents which brought them into solution with the formation of coordination complexes (Table I). Copper metal and cuprous oxide did not dissolve and did not promote the reaction. If copper acts as catalyst by forming a complex with the aryl bromide, it would appear that full coordination with solvent would be undesirable. Taking pyridine with cuprous chloride as

Table I

Solvents in the Preparation of *m*-Diphenoxybenzene

Solvent for reaction at 125°	Yield from disodium resorcinate in 6 hr, % *m*-Diphenoxybenzene	*m*-Phenoxyphenol
Pyridine (117°)	74	15
Pyridine + 2% water (112°)	4	22
2,4,6-Collidine	17	25
Pyridine N-oxide	18	40
Di-*n*-butylamine	32	19
1-Methyl-2-pyrrolidinone	11	46
Dimethylformamide	4	34
Hexamethylphosphoramide	5	47
Methyl sulfoxide	14	42
n-Propyl sulfone	42	33
Bis(2-methoxyethyl) ether	21	25

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[1] C. L. Mahoney, E. R. Barnum, W. W. Kerlin, K. J. Sax, and W. S. Saari, *J. Chem. Eng. Data*, **5**, 172 (1960).

[2] C. L. Mahoney and E. R. Barnum, "Synthetic Lubricants," R. C. Gunderson and A. W. Hart, Ed., Reinhold Publishing Corp., New York, N. Y., 1962, pp 402–460.

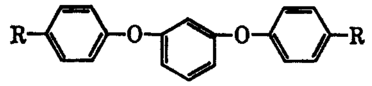
[3] F. Ullmann and P. Sponagel, *Ann.*, **350**, 83 (1906).

[4] K. J. Sax, W. S. Saari, C. L. Mahoney, and J. M. Gordon, *J. Org. Chem.*, **25**, 1590 (1960).

[5] G. P. Brown, S. A. Aftergut, and R. J. Blackington, *J. Chem. Eng. Data*, **6**, 125 (1961).

TABLE II

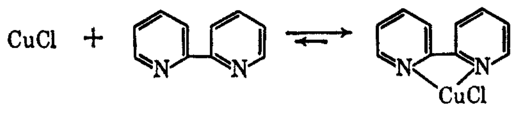
p-SUBSTITUTED DIPHENOXYBENZENES FROM RESORCINOL



R group	Registry no.	Hr at 115°	Yield, %	Mp,[a] °C	Carbon, % Calcd	Carbon, % Found	Hydrogen, % Calcd	Hydrogen, % Found
C_6H_5O	1638-12-6	8	68	84.7–85.1[b]	80.69	80.50	4.97	5.06
CH_3O	13118-91-7	10	56	83.4–83.8	74.52	74.01	5.63	5.71
CH_3CO	13118-92-8	6	60	95.8–96.3	76.29	76.03	5.24	5.22
CH_3	13131-51-6	10	61	*c*	82.73	82.41	6.25	6.23
Cl	13118-93-9	10	34	*d*	65.27	64.97	3.65	3.53
NO_2	13118-94-0	5	63	111.6–112.0	61.27	61.21	3.44	3.43
NH_2[e]	2479-46-1	..	63	114.6–115.1	74.24	74.10	5.52	5.34

[a] All melting points are corrected. [b] Lit.[4] mp 88–89°. [c] Bp 191–193 (0.5 mm). [d] Bp 172–178 (0.5 mm). [e] Prepared by quantitative hydrogenation of the *p*-nitro analog, using PtO_2 in ethanol.

an example, there should be some dissociation to partially coordinated copper. The incompletely coordinated copper might then catalyze the reaction by acting as a Lewis acid. To test for the necessity of some dissociation of the copper–solvent complex, a reaction was carried out in a mixed solvent consisting of 91% pyridine and 9% 2,2′-bipyridine (eq 2). Except for the addition of the 2,2′-bipyridine, reaction conditions were as described in method A for the ether condensation in pyridine. The greater complexing by the diamine lowered the yield of *m*-diphenoxybenzene from 70 to 31% in 9 hr. It thus appears that there is an optimum degree of complexing and that the solvent should be regarded as a cocatalyst.



(2)

Disodium resorcinate has a low solubility in most organic solvents. Even for the successful solvents shown in Table I, only a small fraction of the disodium resorcinate reactant is in solution at any instant. The reaction requires dissolved phenoxide anions and the best solvents have high dielectric constants. However, the order of effectiveness for solvents cannot be predicted from dielectric constants because of the reactions which occur between solvent and catalyst or reactant.

Acidic solvents destroy phenoxide ions. Water also interferes seriously with the ether condensation. Even 2% water in pyridine retards the desired reaction greatly. Although water can hydrolyze phenolic salts, hydrolysis would not be able to deplete the resorcinate ion concentration seriously in the presence of a large excess of pyridine. However, hydroxyl ion would be formed in this hydrolysis and by reaction between water and pyridine (eq 3). Excess base, added as sodium hydroxide or methoxide, completely inhibits the ether condensation by deactivating the catalyst. Retardation by water appears to come about in the same way.

$$H_2O + C_5H_5N \rightleftharpoons C_5H_5NH^+ + OH^- \qquad (3)$$

It is evident that solvents may fail to promote the ether condensation for various reasons, sometimes in combination. For example, *n*-decane dissolved neither disodium resorcinate nor cuprous chloride and the reaction failed. On the other hand, 1-butanol and 1-hexanol dissolved both disodium resorcinate and cupric chloride, but they allowed no formation of *m*-diphenoxybenzene and only a 3% yield of *m*-phenoxyphenol. Removal of resorcinate dianion can occur by alcoholysis, along with deactivation of the catalyst by alkoxide ion thus formed.

Other solvents were tested which probably represent classes of compounds unsuitable as catalytic solvents for the ether condensation. These include ethylene glycol, methyl *n*-decanoate, acetylacetone, heptanone-4, diphenyl ether, and bromobenzene. Neither *m*-diphenoxybenzene nor *m*-phenoxyphenol was obtained when these solvents were employed.

Substituted Diphenoxybenzenes.—Various substituted *m*-diphenoxybenzenes were prepared from resorcinol. These products were synthesized by using the appropriately substituted bromobenzenes in method A. The reactions were followed by gas chromatography and terminated when product yields ceased to increase. Yields shown in Table II are based on isolated pure products.

The chloro group is less reactive than the bromo group in the ether synthesis.[6] Here, only chloro substituents were found on the *m*-diphenoxybenzene when *p*-chlorobromobenzene was condensed with resorcinol. Acidic substituents cannot be present since they react with the sodium salt of the phenol to destroy phenoxide ions. Both *p*-bromoaniline and *p*-bromo-N,N-dimethylaniline failed to react in 6 hr. These amines remained in the worked up reaction mixture. The substituted anilines may have deactivated the catalyst. However, *m*-bis(*p*-aminophenoxy)benzene was readily prepared in quantitative yield from the corresponding nitro compound by catalytic hydrogenation.

Influence of Substituents.—The rate of ether formation depends upon the aryl bromide concentration and, at low copper levels, upon the catalyst concentration. Under our experimental conditions, the disodium resorcinate concentration is fixed by the low solubility of this salt in pyridine. The concentration of disodium resorcinate was then taken as constant during the period of rate measurements. Reactions were carried out as in method A, following the reaction rates by examination of aliquots by gas chromatography. At 1.5 g of cuprous chloride/100 ml of pyridine, the catalyst concentration is threefold above the level at which the rate is influenced by catalyst concentration.

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[6] H. Weingarten, *J. Org. Chem.*, **29**, 977 (1964).

TABLE III

AROMATIC ETHERS BY CONDENSATION OF DISODIUM SALTS OF PHENOLS WITH BROMOBENZENE

Phenolic reactant	Method	Yield,[a] %	Mp,[b] °C	Carbon, % Calcd	Carbon, % Found	Hydrogen, % Calcd	Hydrogen, % Found
Hydroquinone	B	0.3[c]	75.1–76.1[d]	...	...	...	...
Catechol	B	3[e]	90.3–91.3[f]	...	...	...	...
4,4′-Isopropylidenediphenol	A	46	58.9–60.3	85.23	84.97	6.36	6.27
2,7-Dihydroxynaphthalene	A	46[g]	103.7–104.7	84.59	83.88	5.16	5.18
Phloroglucinol	A	0.5[h]	109.7–110.1[i]	...	...	...	...

[a] All yields are based on the phenolic reactant. [b] All melting points are corrected. [c] Gas chromatography showed this to be accompanied by a 3% yield of *p*-phenoxyphenol. [d] Lit. mp 74–75°, C. Haeussermann and A. Müller, *Ber.*, **34,** 1071 (1901); lit.[3] mp 77° for *p*-diphenoxybenzene. [e] An 8.6% yield of purified *o*-phenoxyphenol was also isolated. [f] Lit.[3] mp 93° for *o*-diphenoxybenzene. [g] Only tars resulted from attempts to condense 1,5-, 1,7-, and 2,6-dihydroxynaphthalenes. [h] The trisodium salt of this trihydric phenol was used. [i] Lit.[9] mp 110° for 1,3,5-triphenoxybenzene.

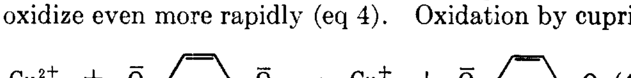
Rate of ether formation then becomes dependent upon only the aryl bromide concentration and the following equation applies.

$$k = \frac{2.303}{t} \log \frac{c_i}{c}$$

Concentration of aryl bromide (c) was chosen where the yield of substituted *m*-diphenoxybenzene was 10%, based on the aryl bromide. Thus log c_i/c is made constant and measurement of the corresponding reaction time (t) allows calculation of log k/k_0 for a Hammett σ constant plot (Figure 1). Rate enhancement by electron-withdrawing substituents is evident, the value of ρ being $+1.4$. These results indicate nucleophilic attack by resorcinate dianion.

Aryl iodides would be expected to give faster reaction rates than the corresponding bromides. However, when iodobenzene was used in place of bromobenzene under the conditions of method A, only an 11% yield of *m*-diphenoxybenzene resulted, accompanied by a 7% yield of *m*-phenoxyphenol. Iodide ion is an effective agent for converting cupric copper to cuprous iodide, which is a poor catalyst. Under the conditions of method A, cuprous iodide replacing cuprous chloride on a mole basis allowed only a 1.5% yield of *m*-diphenoxybenzene and a 4.1% yield of *m*-phenoxyphenol.

Catalysis by Copper Salts.—Salts of cuprous and cupric copper, as introduced into the reaction mixture, are about equally effective in catalyzing the condensation of aryl bromides with salts of dihydric phenols. For example, the substitution of cupric chloride for an equimolar amount of cuprous chloride in the preparation of *m*-diphenoxybenzene by method A still gave a 60% yield of that compound. The nonspecificity indicates that the active catalyst may be formed by either oxidation or reduction. For monohydric phenols, Weingarten[7] concluded that cuprous copper results from the reduction by phenoxide anion, which is thus oxidized to a semiquinone radical. Reduction of copper would proceed readily with resorcinate dianion and the dianions from catechol or hydroquinone would oxidize even more rapidly (eq 4). Oxidation by cupric ion can account for the low yields obtained from catechol, hydroquinone, 2,6-dihydroxynaphthalene, 1,5-dihydroxynaphthalene, and phloroglucinol (Table III). These reactions also gave larger yields of tars than the less readily oxidized resorcinol, 2,7-dihydroxynaphthalene, and 4,4′-isopropylidenediphenol. Analyses of reaction mixtures by gas chromatography showed that the dihydric phenols were the source of the tars. Polymerizations involving radical ions appear likely.



(4)

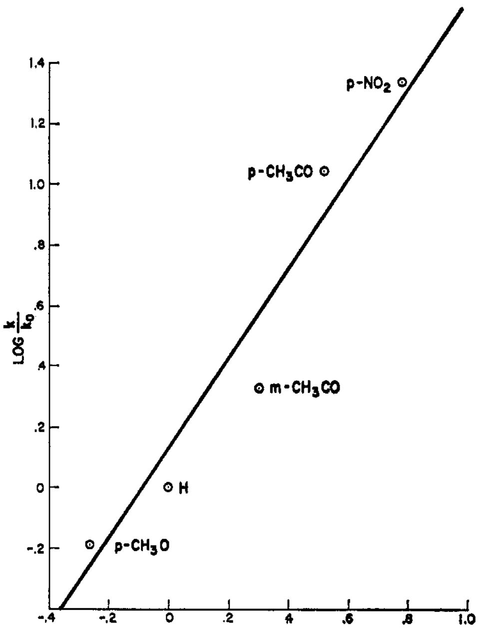


Figure 1.—Hammett plot for substituted bromobenzenes.

Under our reaction conditions, aryl bromides are in part debrominated to the corresponding hydrocarbon by cuprous chloride, the copper thus bring oxidized to the cupric level. In the case of *p*-bromophenyl phenyl ether (where the debrominated product was isolated from the reaction mixture), the conditions of method A gave a yield of diphenyl ether which was 20% of theoretical based on cuprous chloride (eq 5).

$$\mathrm{Cu^+} + p\text{-}\mathrm{BrC_6H_4OC_6H_5} + \mathrm{RH} \longrightarrow \mathrm{Cu^{2+}} + \mathrm{Br^-} + \mathrm{C_6H_5OC_6H_5} + \mathrm{R}\cdot \quad (5)$$

Bacon and Hill[8] demonstrated a similar debromination of 1-bromonaphthalene by cuprous acetate in pyridine. It thus appeared that under our reaction conditions cupric copper could not be ruled out as catalyst on the basis of its absence from the system. If copper could be held at the cupric level by the addition of an oxidizing agent to the system, the effects of cupric copper could be measured directly, but this is not feasible since the phenols are themselves easily oxidized. Maintaining copper at the cuprous level by means of a reducing agent appeared more attractive,

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(7) H. Weingarten, *J. Org. Chem.*, **29**, 3624 (1964).

(8) R. G. R. Bacon and H. A. O. Hill, *J. Chem. Soc.*, 1112 (1964).

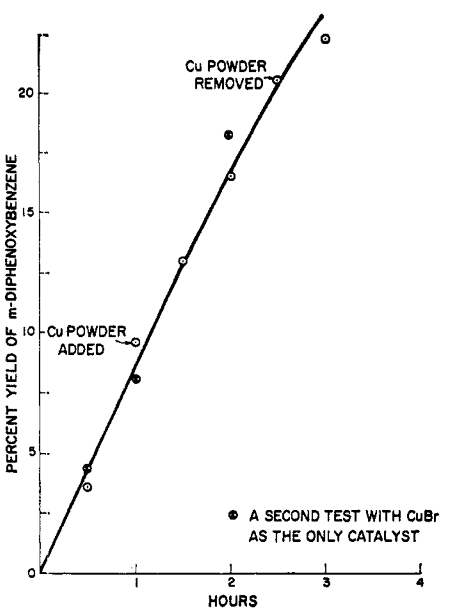


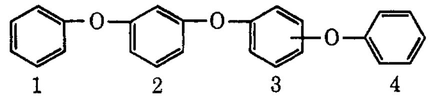
Figure 2.—Test for effect of copper powder on cuprous bromide catalyst.

but any reducing agent which may convert copper ions to copper metal or an inactive salt or complex is unsuitable.

By observing the green cupric bromide–pyridine complex change to the yellow cuprous complex, we found in a preliminary test that a suspension of precipitated copper powder (1.5 g) reduced the copper of cupric bromide (0.55 g) in 100 ml of refluxing pyridine in less than 1 min. We also found that precipitated copper powder does not itself catalyze the ether condensation. To avoid the complications of a heterogeneous reaction system, tests were made upon the sodium salt of *m*-phenoxyphenol which was completely dissolved in pyridine. Precautions described in method A were observed. The reaction employed 2.08 g (0.01 mole) of the sodium salt of *m*-phenoxyphenol in 100 ml of pyridine, 10 g (0.0636 mole) of bromobenzene, and 0.35 g of cuprous bromide catalyst. After the reaction had progressed for 1 hr, there was added 1.5 g of copper powder, freshly precipitated by zinc dust and washed with acetone. When this had been present for 1.5 hr, the copper was filtered out under nitrogen through a fine fritted-glass disk and the reaction was continued for 1 additional hr. The formation of *m*-diphenoxybenzene was followed by withdrawing aliquots at 0.5-hr intervals for analysis by gas chromatography. The presence of the suspended copper powder did not change the reaction rate relative to the initial rate (Figure 2). There was also close agreement with a control run having no added copper metal. If the reaction mixture had to oxidize the cuprous copper to the cupric level to obtain the active form of the catalyst, the reaction should be much slowed down when copper powder reduces cupric copper back to the cuprous level. Absence of a decrease in reaction rate by the reduction of cupric to cuprous copper is evidence for catalysis by cuprous copper.

Nonlinear Polyphenyl Ethers.—The numerous polyphenyl ethers known are based upon linear chains of phenoxy groups except for 1,3,5-triphenoxybenzene, which has been prepared from 1,3,5-tribromobenzene.[9] Our reaction of bromobenzene with phloroglucinol, under conditions adequate for resorcinol, gave only a trace of 1,3,5-triphenoxybenzene, but the isomeric 1,2,4-triphenoxybenzene and other nonlinear polyphenyl ethers can be prepared indirectly from *m*-diphenoxybenzene.

When *m*-diphenoxybenzene is brominated under mild conditions, 2,4-diphenoxybromobenzene can be obtained in quantitative yield by method D. To prove the structure of the product, the bromo compound was converted to a four-ring ether by reaction with sodium phenoxide in pyridine by method E. This product melted at 59.9–60.4°. The linear four-ring ethers having a *meta*-substituted benzene ring (number 2) have melting points of 40° when ring number 3 is *meta* substituted, 48° when *para* substituted, and 74° when *ortho* substituted by ring number 4.[2] Thus, the



four-ring ether product must be a triphenoxybenzene and the bromine atom must have gone onto the middle ring of *m*-diphenoxybenzene. Of the three isomers which can be written, 3,5-diphenoxybromobenzene must be excluded since the corresponding 1,3,5-triphenoxybenzene has a melting point of 110°.[9]

Selection between the two remaining bromides was made on the basis of the nuclear magnetic resonance spectrum. 2,6-Diphenoxybromobenzene has no hydrogen atoms to be shifted downfield by an *o*-bromine atom, whereas 2,4-diphenoxybromobenzene has such a hydrogen atom. The downfield shift of this hydrogen atom was observed and all three hydrogen atoms on the middle ring were accounted for. Further, the spectrum of this product could not have been generated by the symmetrical isomers, 2,6-diphenoxybromobenzene and 3,5-diphenoxybromobenzene.

Experimental Section

Melting points are all corrected. A Fisher Scientific Co. melting point block, calibrated by eight standards in the range of interest (40–140°), was used. Samples were held between cover slips while the temperature was raised 1 deg/min. Boiling points are not corrected.

Method A. *m*-**Diphenoxybenzene.**—A suspension of 10.6 g (0.196 mole) of sodium methoxide in 200 ml of benzene was prepared by stirring under a pure nitrogen stream in a 500-ml flask. The flask was also fitted with a stirrer, a dropping funnel, and a condenser arranged for distillation. All reactions in the flask were carried out under nitrogen. Then 11.0 g (0.100 mole) of resorcinol was added. Benzene and methanol were distilled off to leave a white powder of the resorcinol salt. When the salt had cooled, the condenser was arranged for reflux. Then 200 ml of pyridine was added. The stirred mixture was brought to reflux and 42 ml (0.40 mole) of bromobenzene was added rapidly through the dropping funnel. This was followed at once by the addition of 3.0 g of cuprous chloride. The reaction mixture was brought back to reflux and held at reflux for 9 hr under a blanket of nitrogen. The reaction mixture was then poured into 600 ml of water and hydrochloric acid was added until acidified. The product was extracted into four 200-ml portions of *n*-pentane and the pentane solution filtered. *n*-Pentane was removed by distillation. Distillation at 0.1 mm removed bromobenzene from the residue. The crude product crystallized on cooling. Recrystallization from 95% ethanol gave 18.4 g (70%) of *m*-diphenoxybenzene, mp 59.9–60.4° (lit.[4] mp 59.5–60.0°). Mixture with an authentic sample (mp 60.2–60.6°) from Distillation Products Industries did not depress the melting point.

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[9] F. Ullmann and P. Sponagel, *Ber.*, **38**, 2212 (1905).

Anal. Calcd for $C_{18}H_{14}O_2$: C, 82.42; H, 5.38. Found: C, 82.29; H, 5.58.

Method B. ***o*-Phenoxyphenol.**—Sodium hydride, 4.57 g (0.19 mole), was added as a *n*-pentane dispersion to 100 ml of methyl sulfoxide. The addition was carried out in a 500-ml flask under a nitrogen stream. The mixture was heated to 60° until the evolution of hydrogen ceased; then 11.0 g (0.100 mole) of catechol was added in solution in 100 ml of methyl sulfoxide. During all operations, the reaction mixture was protected by a stream of nitrogen. The temperature was brought up to 150° and *n*-pentane distilled out. The condenser was arranged for reflux and stirring was continued. Then 42 ml of bromobenzene (0.40 mole) was added in a stream through a dropping funnel. This was followed by the addition of 5.0 g of cuprous chloride. The reaction mixture was brought back to 150° and held at this temperature with stirring under a nitrogen blanket for 19 hr. It was then poured into 500 ml of water containing 10 ml of hydrochloric acid. The organic layer was extracted by two 200-ml portions of benzene. To the combined benzene extracts there was added 2 l. of *n*-pentane. The tar thus precipitated was filtered off. The pentane layer was extracted with three 100-ml portions of 5% aqueous sodium hydroxide solution. Acidification by hydrochloric acid yielded *o*-phenoxyphenol, which was extracted into *n*-pentane. Evaporation of the pentane gave 3.03 g of crude product. Recrystallization from 95% ethanol yielded 1.60 g (8.6%) of *o*-phenoxyphenol, mp 104.7–104.9° (lit.[10] mp 105–106°).

Anal. Calcd for $C_{12}H_{10}O_2$: C, 77.40; H, 5.41. Found: C, 77.06; H, 5.39.

Method C. ***m*-Phenoxyphenol.**—The reaction flask was blanketed with nitrogen and 750 ml of dry pyridine was introduced. Resorcinol, 495 g (4.5 moles), was dissolved in the pyridine with stirring. Then 162 g (3.0 moles) of sodium methoxide was added. The mixture was stirred and methanol was fractionally distilled from the mixture over a period of 0.5 hr. Bromobenzene, 1420 g (9.00 moles), was run into the reaction flask. This was followed by 22 g of cuprous chloride. The mixture was refluxed, with stirring under nitrogen for 3 hr. Pyridine was then distilled off while the pot temperature rose to 150°. The residue was poured into a solution of 500 ml of concentrated hydrochloric acid in 1100 ml of water and stirred. The organic layer was dissolved in 1 l. of benzene. This benzene solution was washed with 100 ml of hydrochloric acid in 100 ml of water. The benzene solution was then extracted by 100 g of sodium hydroxide in 1 l. of water. This was followed by a second extraction by 20 g of sodium hydroxide in 200 ml of water. The combined alkali extracts were acidified by concentrated hydrochloric acid. Liberated *m*-phenoxyphenol was extracted into 300 ml of benzene. Benzene was removed by distillation at atmospheric pressure. Distillation was continued at 0.8 mm to yield 350 g (42%) of *m*-phenoxyphenol distilling at 158–165° [lit.[4] bp 143–146° (2 mm)]. Gas chromatography indicated 99+% purity.

Anal. Calcd for $C_{12}H_{10}O_2$: C, 77.40; H, 5.41. Found: C, 77.50; H, 5.40.

Method D. **2,4-Diphenoxybromobenzene.**—A solution of 190 g (0.725 mole) of *m*-diphenoxybenzene was prepared by stirring with 400 ml of benzene at room temperature in a 2-l. flask fitted with a reflux condenser and dropping funnel. Stirring was continued and a solution of 116 g (0.725 mole) of bromine in 400 ml of benzene was dropped in slowly over a period of 3 hr. The mixture was then allowed to stand overnight (17 hr). Benzene and hydrogen bromide were distilled from the mixture. The last of the benzene was removed in a stream of nitrogen until the flask came to constant weight; the yield of 2,4-diphenoxybromobenzene was 247 g (100%); gas chromatography indicated 99% purity; the boiling point was 167–169° (0.4 mm).

Anal. Calcd for $C_{18}H_{13}BrO_2$: C, 63.36; H, 3.84; Br, 23.4. Found: C, 63.48; H, 3.98; Br, 23.1.

Method E. **1-(*m*-Phenoxyphenoxy)-2,4-diphenoxybenzene.**—A 500-ml flask was fitted with a nitrogen inlet tube, a 1-ft-long Vigreaux column, and a stirrer to prepare a solution of 55.8 g (0.300 mole) of *m*-phenoxyphenol in 200 ml of pyridine at room temperature under nitrogen. Stirring was continued while 15.6 g (0.288 mole) of sodium methoxide was added. Then 135 ml of methanol–pyridine mixture was distilled out through the column over a 1-hr period. After cooling, the column was replaced by a reflux condenser. Then 67.9 g (0.199 mole) of 2,4-diphenoxybromobenzene was added. This was followed by 2 g of cuprous chloride, washed in by 25 ml of pyridine. The mixture was refluxed with stirring for 4 hr. Pyridine was then distilled out until the pot temperature reached 160°. The reaction mixture was poured into a solution of 50 ml of hydrochloric acid in 500 ml of water and allowed to stand overnight. After decanting off the aqueous layer, the crude product was dissolved in 430 ml of benzene. This benzene solution was washed by 20 ml of hydrochloric acid in 200 ml of water and again by 10 ml of hydrochloric acid in 100 ml of water. Unreacted *m*-phenoxyphenol was extracted into 12 g of sodium hydroxide in 150 ml of water, used in two equal portions. The benzene solution was then washed with 100 ml of water. Benzene was removed by distillation. Distillation was continued at 0.5 mm to give a product collected over the range 262–268°; the yield of 1-(*m*-phenoxyphenoxy)-2,4-diphenoxybenzene was 35.8 g (40%); gas chromatography indicated 99+% purity.

Anal. Calcd for $C_{30}H_{22}O_4$: C, 80.69; H, 5.06. Found: C, 80.66; H, 4.97.

1,2,4-Triphenoxybenzene was obtained in 42% yield from 2,4-diphenoxybromobenzene reaction with sodium phenoxide by method E, mp 59.9–60.4°.

Anal. Calcd for $C_{30}H_{22}O_4$: C, 81.28; H, 5.13. Found: C, 81.25; H, 5.21.

***m*-Bis(2,4-diphenoxyphenoxy)benzene** was obtained in 12% yield from 2,4-diphenoxybromobenzene reaction with disodium resorcinate by method E, mp 109–111°.

Anal. Calcd for $C_{42}H_{30}O_6$: C, 79.99; H, 4.79. Found: C, 79.23; H, 4.61.

Materials.—Solvents were dried for at least 48 hr over Linde Molecular Sieve 4A. Phloroglucinol was dehydrated by a toluene distillation. Other materials were used as received from the suppliers. Resorcinol, hydroquinone, catechol, phloroglucinol, bromobenzene, iodobenzene, *p*-bromotoluene, *p*-bromoanisole 4′-bromoacetophenone, 1-bromo-4-chlorobenzene, sodium methoxide, methyl sulfoxide, 2,2′-bipyridine, and cuprous oxide were purchased from Matheson Coleman and Bell Division of the Matheson Co; 2,7-dihydroxynaphthalene, *p*-bromophenyl phenyl ether, and 1-bromo-4-nitrobenzene were from Distillation Products Industries; pyridine, cuprous chloride, and cupric bromide were from J. T. Baker Chemical Co.; cuprous bromide and cuprous iodide were from Fisher Scientific Co.; cupric chloride was from Baker and Adamson; sodium hydride was from K & K Laboratories; and 4,4′-isopropylidenediphenol was from Union Carbide Chemicals Co.

Registry No.—*m*-Diphenoxybenzene, 3379-38-2; *o*-phenoxyphenol, 2417-10-9; *m*-phenoxyphenol, 713-68-8; 2,4-diphenoxybromobenzene, 13118-87-1; 1-(*m*-phenoxyphenoxy)-2,4-diphenoxybenzene, 13118-88-2; 1,2,-4-triphenoxybenzene, 13118-89-3; *m*-bis(2,4-diphenoxyphenoxy)benzene, 13118-90-6.

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[10] J. F. Norris, B. G. Macintire, and W. M. Corse, *Am. Chem. J.*, **29**, 127 (1903).