a solution of *o*-bromofluorobenzene (8.8 g, 0.05 mole) in THF (15 ml). Addition of a crystal of iodine and warming started the reaction. A solution of 1,2,3,4-tetramethyl-1,4-dihydro-1,4-(N-*n*-butylimino)naphthalene (12.8 g, 0.05 mole) in THF (15 ml) was added, and the mixture was heated to 65–70°. At this temperature the remaining *o*-bromofluorobenzene solution was added during 1.5 hr, and the solution was refluxed 3 hr more. Upon cooling, it was extracted with 150 ml of saturated aqueous ammonium chloride, the THF layer was dried over potassium carbonate, and the solvent was removed under reduced pressure. The remaining solid (16 g) was dissolved in hexane, and the solution was extracted several times with a total of 2 l. of 0.1 *N* hydrochloric acid to remove any unreacted imine (3.4 g of imine was recovered on neutralizing the acid). The hexane solution was washed free of acid, dried, evaporated to about 20 ml, and refrigerated several days. After filtering off the crystalline product, further concentration of the liquors gave additional product, for a total of 4.30 g, mp 83.5–84.5°. The final liquors were chromatographed on alumina to give an additional 4.0 g, mp 68–75°. Two recrystallizations from methanol gave an analytical sample, mp 84.5–85.3°.

Anal. Calcd for $C_{24}H_{29}N$ (331.5): N, 4.23. Found: N, 4.44.

Its nmr spectrum showed signals of a multiplet centered at δ 0.55 (terminal methyl), 1.16 and 1.19 (tertiary methyls), 1.64 and 2.00 (Ar methyls), a triplet at δ 2.80 (N–CH_2), and several at δ 6.27–7.56 (Ar–H), with proper proton count. The ultraviolet spectrum had λ_{max}^{MeOH}, mμ (log ϵ), 220 sh (4.48), 226 sh (4.34), 257 (4.42), and 310 sh (3.45).

11-Cyclohexyl-6a,11a-dihydro-5,6,6a,11a-tetramethyl-11H-benzo[*a*]carbazole (1b).—Using the imine, 1,2,3,4-tetramethyl-1,4-dihydro-1,4-(N-cyclohexylimino)naphthalene, **1b** was prepared as in the procedure just described: 5.6 g (31.4%), mp 109–110°. Recrystallization from methanol–benzene gave rhombs: mp 110.8–111.3°; λ_{max}^{MeOH}, mμ (log ϵ), 220 (4.39), 228 sh (4.26), 262 (4.33), and 310 sh (3.34). The nmr spectrum showed signals at 1.11 and 1.40 (tertiary methyls), 1.53 and 1.96 (Ar methyls), 2.73 (N–CH), and several at δ 6.44 to 7.61 (Ar–H), with proper proton distribution.

Anal. Calcd for $C_{26}H_{31}N$ (357.5): N, 3.92. Found, 4.13.

11-Methyl-6a,11a-dihydro-5,6,6a,11a-tetramethyl-11H-benzo[*a*]carbazole (1c).—Unlike the preceding benzocarbazoles, this one was not prepared deliberatedly from benzyne and the imine, since the latter had not been isolated. Instead, it appeared as one of the products of the reaction of benzyne with pentamethylpyrrole (0.1 mole) by the procedure described above for the preparation of the imines. The hexane solution of the reaction products was not extracted with acid, but was concentrated and cooled to give 1 g of crystals, which were recrystallized from methanol to give mp 147–147.5°; λ_{max}^{MeOH}, mμ (log ϵ), 227 (4.40), 255 (4.41), and 272 sh (4.12). Its nmr spectrum showed signals at δ 1.15, 1.23, 1.67, 2.01, and 2.39 (five kinds of methyl groups), and several at 6.28–7.53 (Ar–H).

Anal. Calcd for $C_{21}H_{23}N$ (289.4): C, 87.2; H, 8.01; N, 4.84. Found: 87.43; H, 8.11; N, 4.71.

Reaction of the Imines with Aqueous Acid at Room Temperature.—The imine (1 g) was dissolved in 0.11 *N* hydrochloric acid (100 ml). Within about 1 hr the solution became turbid, and, on standing, increasing amounts of crystals appeared, which were filtered and recrystallized from methanol to give thin rods, mp 177–177.5°, identified as 1-(hydroxymethyl)-2,3,4-trimethylnaphthalene: λ_{max}^{MeOH}, mμ (log ϵ), 228 sh (4.15), 233 (5.12), 272 sh (3.61), 283 sh (3.78), 291 (3.84), and 300 sh (3.72). Its infrared spectrum showed strong hydroxyl absorption at 3300 cm^{-1}, which disappeared on acetylation. Its nmr spectrum showed signals at δ 2.42, 2.52, and 2.63 (three aryl methyl groups), 5.18 (CH_2O), and a multiplet centered at about δ 7.37 (Ar–H).

Anal. Calcd for $C_{14}H_{16}O$ (200.3): C, 83.9; H, 8.05. Found: C, 83.2; H, 8.29.

Its acetyl derivative had mp 72–73°; the compound was found to be identical with that formed by the reaction 1-(chloromethyl)-2,3,4-trimethylnaphthalene[3] with silver acetate.

Reaction of the Imines with Boiling Aqueous Acid.—A solution of the imine (0.5 g) in 2 *N* hydrochloric acid was refluxed 3 hr, cooled, and filtered; the crystals were washed with dilute acid and dried. The product, mp 172–183°, was recrystallized from methanol to give mp 189.5–190°, identified by mixture melting point and infrared spectrum to be bis[2,3,4-trimethylnaphthyl-(1)-methyl] ether.[3] The same product was obtained by boiling a mixture of the alcohol (above) and 2.8 *N* hydrochloric acid for 7 hr. The yields were 75–80% of theoretical.

Reaction of the Imines with Methanolic Hydrochloric Acid.—A solution of the imine (about 0.5 g) in methanol (5 ml) was treated with 5 drops of concentrated hydrochloric acid, and then refluxed 4 hr after which it was poured into 100 ml of water containing 4 g of sodium carbonate. The precipitate was extracted with hexane, the solution was extracted several times with dilute acid to remove unreacted imine (usually only a trace), and the hexane was removed to leave the product, mp 76.5–77° (methanol crystallization). Mixture melting point and infrared spectrum showed it to be 1-(methoxymethyl)-2,3,4-trimethylnaphthalene.[3]

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Friedel–Crafts Oxygenation of Aromatic Ethers, Biphenyl, and Naphthalene with Diisopropyl Peroxydicarbonate[1,2]

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Direct electrophilic oxygenation has been effected with various types of peroxides.[3] Particularly with the simpler aromatic substrates, low yields of monohydric phenols resulted because of continued oxidation. Recently, we found that use of diisopropyl peroxydicarbonate under Friedel–Crafts conditions produced controlled monooxygenation with essentially no undesirable side reactions.[4,5] The best yields of phenolic product were observed with the highly active aromatic reactants, such as, anisole and pentamethylbenzene.[5] The present study is concerned with extension of the diisopropyl peroxydicarbonate oxygenation to other types of aromatic compounds, *e.g.*, naphthalene, biphenyl, and chlorobenzenes. Primary attention was devoted to a more extensive investigation of the aromatic ethers.

In general, the reactions were carried out in *o*-dichlorobenzene solvent at 0–5° with a catalyst to peroxide ratio of 2. The results from the aromatic ethers are summarized in Table I, and the data for the other types of aromatic substrates are set forth in Table II. The oxygenated products from the aromatic ethers and naphthalene were present in the reaction mixture in the form of the corresponding aryl isopropyl carbonate esters, as was noted previously in the case of anisole.[5] However, with biphenyl and the halobenzenes, the oxygenated material appeared to be of the type, $ArOCO_2AlCl_2$, presumably derived from cleavage of the initially formed ester. Facile ester degradation during reaction is also characteristic of the toluene system.[4] In all cases the oxygenated materials were converted to the phenolic stage by hydrolysis. Some of the identification data for the phenols is summarized in Table III.

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(1) Paper III of the series, Aromatic Oxygenation.

(2) From the forthcoming Ph.D. Thesis of M. E. Kurz.

(3) See ref 4 and 5 for literature surveys.

(4) P. Kovacic and S. T. Morneweck, *J. Am. Chem. Soc.*, **87**, 1566 (1965).

(5) P. Kovacic and M. E. Kurz, *ibid.*, **87**, 4811 (1965).

TABLE I

OXYGENATION OF PHENYL ETHERS[a]

	Phenolic end products	
Aromatic reactant	Yield, %	Isomer distribution (%)
Anisole[b,c]	76	*o*- (20) and *p*-methoxyphenol (80)
Diphenyl Ether	39	*o*- (43) and *p*-phenoxyphenol (57)
o-Dimethoxybenzene	65	2,3- (52) and 3,4-dimethoxyphenol (48)
m-Dimethoxybenzene[b]	77	2,4-Dimethoxyphenol
m-Dimethoxybenzene	38	2,4-Dimethoxyphenol
p-Dimethoxybenzene[d]	31	2,5-Dimethoxyphenol
1,3,5-Trimethoxybenzene[d]	62	2,4,6-Trimethoxyphenol
1,3,5-Trimethoxybenzene[e]	78	2,4,6-Trimethoxyphenol

[a] See the general procedure, ref 5. [b] No solvent; aromatic reactant:aluminum chloride:peroxide = 15:2:1. [c] See ref 5. [d] *o*-Dichlorobenzene:aromatic reactant:aluminum chloride:peroxide = 20:5:2:1. [e] *o*-Dichlorobenzene:aromatic reactant:aluminum chloride:peroxide = 20:5:3:1.

TABLE II

OXYGENATION OF BIPHENYL, NAPHTHALENE, AND CHLOROBENZENES[a]

	Phenolic end products	
Aromatic reactant	Yield, %	Structure
Biphenyl[b]	20	*o*- (38%) and *p*-phenylphenol (62%)
Naphthalene[b]	18	α- and β-naphthol
Chlorobenzene[c]	2[d]	*o*-, *m*-, and *p*-chlorophenol
o-Dichlorobenzene[c]	3	2,3- and 3,4-dichlorophenol

[a] See the general procedure, ref 5. [b] *o*-Dichlorobenzene:aromatic reactant:aluminum chloride:peroxide = 25:5:2:1. [c] No solvent; aromatic:aluminum chloride:peroxide = 15:2:1. [d] Unidentified higher boiling phenols, 5%.

This represents an improved method for preparation of certain polymethoxyphenols, particularly 2,4-dimethoxy- and 2,4,6-trimethoxyphenol. Yields greater than 60% were the usual result with the aromatic ethers. In many cases isomeric mixtures were formed, as with diphenyl ether, *o*-dimethoxybenzene, biphenyl, and naphthalene. Nevertheless, the phenolic mixture from *o*-dimethoxybenzene could be readily separated by simple fractional distillation. A competing process, discussed later, constituted a serious problem in the *p*-dimethoxybenzene reaction. Extremely low yields were observed in studies involving chlorobenzene and *o*-dichlorobenzene.

There are prior reports concerning oxygenation of aromatic ethers and polynuclear hydrocarbons by peroxides, which apparently occur *via* an electrophilic pathway.[6,7] The previous studies were usually characterized by low to modest yields of monosubstitution product, quite often the result of over-oxidation.[6,8,9] Additional complications have been encountered in the form of dealkoxylation reactions with the aromatic ethers.[8,9] Oxygenation of aromatic ethers[10] and naphthalene[11] has been carried out under conditions which favor radical intermediates.

Comparison with nonoxygenation routes leading to these phenols will be limited to the two compounds of principal synthetic interest in the present study. 2,4-Dimethoxyphenol can be obtained from the corresponding aldehyde by treatment with peroxide[12] or from the corresponding ketone by exposure to peracid.[13] The yields from these three-step procedures are in the range of 50–75% based on 1,3-dimethoxybenzene, contrasted with the 77% yield from our two-step transformation. 2,4,6-Trimethoxyphenol has been synthesized previously from 1,2,3,5-tetramethoxybenzene by selective demethylation with the Grignard reagent.[14] In comparison with our two-step procedure (78% yield from 1,3,5-trimethoxybenzene), the earlier method constitutes a four-step sequence based on 1,2,3-trimethoxybenzene as precursor, with an over-all yield of 24%.[14,15]

Although in most cases oxygenation proceeded cleanly, two exceptions were noted. From the *p*-dimethoxybenzene reaction mixture, a neutral product was isolated in 30% yield, which was identified as 2,2′,5,5′-tetramethoxybiphenyl. Similar coupling of activated aromatic compounds has been shown to occur in various peroxide-containing systems.[7,9,11,16] However, in a control experiment we detected no coupled product in the absence of aluminum chloride. This then suggests that the dehydrogenative condensation might fall in the category of the Scholl reaction.[17] In our case, *p*-dimethoxybenzene remained unchanged in the presence of aluminum chloride when the peroxide was omitted. Thus, if a Scholl transformation is involved, apparently the peroxide plays a crucial role as the oxidant. Alternatively, reaction may proceed through intermediacy of a radical cation.[18]

In addition to the expected oxygenation product, *o*-dimethoxybenzene yielded a solid containing carbon, hydrogen, chlorine, aluminum, and presumably oxygen, which was degraded to aluminum oxide on prolonged treatment with ethanolic potassium hydroxide. When peroxide was omitted from the system, the unknown substance was not formed. Characterization work was abandoned when scouting experiments uncovered no promising leads.

Experimental Section[19]

Materials.—The aromatic reactants, used as obtained, possessed purities greater than 98% according to glpc analysis. *o*-Dichlorobenzene was fractionally distilled from calcium hydride. We are grateful to the Pittsburgh Plate Glass Co. for generous samples of diisopropyl peroxydicarbonate. 1,3,5-Trimethoxybenzene, mp 49–51.5°, was obtained from phloroglucinol in 47% yield by the method of Clark-Lewis.[20]

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TABLE III

IDENTIFICATION OF PHENOLIC PRODUCTS

Substituents in the phenol	Mp, °C		Derivatives	
	Obsd	Lit	Trimethoxybenzene from methylation	Others
o-Phenyl	58–59	58[a]		
p-Phenyl	162–164	163[b]		
o-Phenoxy	104–105	103–104[c]		
p-Phenoxy	81–82	82–83[c]		
2,3-Dimethoxy[d]			1,2,3	
2,4-Dimethoxy			1,2,4	*p*-Nitrobenzoate, mp 124–127°, lit.[e] mp 129°
2,5-Dimethoxy[f,g]			1,2,4	*p*-Nitrobenzoate, mp 133–135°, lit.[e] mp 135°
3,4-Dimethoxy	82.5–83.5	81.5[h]	1,2,4	
2,4,6-Trimethoxy[i]	62–63	61.9–63.5[j]		Acetate, mp 96–97.5°, lit.[k] mp 99–100.6° Chloroacetate, mp 150–152°, lit.[j] mp 152–153.1°

[a] W. Hückel and O. Neunhoeffer, *Ann.*, **477**, 106 (1930). [b] L. C. Raiford and J. C. Colbert, *J. Am. Chem. Soc.*, **47**, 1454 (1925). [c] See ref 6. [d] *Anal.* Calcd for $C_8H_{10}O_3$: C, 62.32; H, 6.54. Found: C, 62.15; H, 6.71. [e] K. R. Hargreaves, A. McGookin, and A. Robertson, *J. Appl. Chem.* (London), **8,** 273 (1958). [f] *Anal.* Calcd for $C_8H_{10}O_3$: C, 62.32; H, 6.54. Found: C, 62.27; H, 6.54. $n^{25}D$ 1.5445, lit.[g] $n^{25}D$ 1.5434. [g] C. A. Bartram, D. A. Battye, and C. R. Worthing, *J. Chem. Soc.*, 4691 (1963). [h] J. Böeseken and J. Greup, *Rev. Trav. Chim.* **58,** 528 (1939). [i] *Anal.* Calcd for $C_9H_{12}O_4$: C, 58.69; H, 6.57. Found: C, 58.91; H, 6.70. [j] See ref 14. [k] W. J. Horton and M. G. Stout, *J. Org. Chem.*, **27,** 830 (1962).

High purity commercial phenols and trimethoxybenzenes were used directly as standards in the infrared analyses and glpc analyses.

Aromatic Oxygenation with Diisopropyl Peroxydicarbonate.—The general procedure is described elsewhere.[5] Unless otherwise noted, the aromatic ethers were oxygenated in *o*-dichlorobenzene solvent with the ratio, solvent: aromatic: aluminum chloride: peroxide = 15:5:2:1. Owing to the lower solubility of naphthalene and biphenyl, a larger amount of solvent was used, solvent: aromatic: aluminum chloride: peroxide = 25:5:2:1. The haloaromatic reactions were carried out neat, aromatic: aluminum chloride: peroxide = 15:2:1. A small aliquot of the reaction mixture was removed immediately after addition to hydrochloric acid–ice and subjected to glpc analysis (glpc col 1). Hydrolysis of the ester products and isolation of the phenols were carried out as previously described.[5] Distillation of the phenols gave <10% residue from the aromatic ethers, 18–28% from chlorobenzene, and 67% from *o*-dichlorobenzene. The naphthols, phenylphenols, and phenoxyphenols were isolated by crystallization.

Yields in all cases were calculated from the isolated products, and comprise the average of at least two runs. The stoichiometry is based on 1 mole of oxygenated product per mole of peroxide. Isomer distribution data on the phenols was obtained by glpc analysis of the crude phenolic products.

Product Identification. A. Phenolic Products.—The phenolic distillates (in some cases the crude phenolic extract was used) were analyzed by gas chromatography (glpc col 1 and 2). Isomers were separated and pure products were collected. Identification of the phenylphenols, naphthols, 2,3-dimethoxyphenol, and chloro- and dichlorophenols was made by comparison with authentic materials (glpc retention time and infrared spectrum). Other characterization data are contained in Table III.

In addition, the nmr spectra of 2,4-dimethoxy- and 2,4,6-trimethoxyphenol showed methoxyl, aromatic, and hydroxyl protons present in amounts consistent with the corresponding molecular structures.

B. Carbonate Esters.—The carbonate esters formed in the oxygenations were isolated by gas chromatographic separation and collection with the small aliquot of the reaction mixture removed before alkaline hydrolysis. The infrared spectra exhibited characteristic strong absorption[21] at 5.6–5.75 (C=O) and at 7.8–8.0 μ (C—O). The esters were not characterized rigorously.

C. Nonoxygenated Products. 1. From *p*-Dimethoxybenzene. 2,2′,5,5′-Tetramethoxybiphenyl.—Gas chromatographic analysis of the reaction mixture from *p*-dimethoxybenzene indicated the presence of a higher-boiling material in addition to the oxygenated product. After hydrolysis of the carbonate ester and extraction of the resulting phenol, the organic layer was dried and distilled. Removal of the solvent and unreacted aromatic ether left 10 g of material which was recrystallized from ethanol yielding a white crystalline powder, mp 104–105°. This compound was identified as 2,2′,5,5′-tetramethoxybiphenyl by means of its melting point, lit.[22] mp 104°, nmr spectrum, and elemental analysis. The nmr spectrum showed the presence of two closely spaced singlets at δ 3.65 and 3.75 (relative to tetramethylsilane) corresponding to the two nonequivalent sets of methoxyl protons and an aromatic singlet at δ 6.74. The integrated ratio of methoxyl to aromatic protons was 1.94: 1.0, in good agreement with the theoretical ratio of 2:1. This product was obtained in 31 and 29% yields in duplicate runs.

Anal. Calcd for $C_{16}H_{18}O_4$: C, 70.06; H, 6.61. Found: C, 69.90; H, 6.81.

2. From *o*-Dimethoxybenzene.—Upon stirring the reaction mixture from *o*-dimethoxybenzene with hydrochloric acid–ice, a purple substance separated which was isolated by filtration. The dry powdery material was insoluble in aqueous systems, virtually insoluble in lower-boiling organic solvents, such as, ethyl ether, carbon disulfide, carbon tetrachloride, and acetone, and sparingly soluble in higher-boiling solvents, such as, dimethylformamide, *o*-dichlorobenzene, and α-chloronaphthalene at the reflux temperature. The infrared spectrum (potassium bromide pellet), though quite complex, indicated the presence of a benzenoid system and carbon–oxygen bonds and the absence of characteristic absorptions due to hydroxyl or carbonyl groups. The crude solid did not melt below 300°, and left a residue upon combustion.

Anal. Found: C, 55.13; H, 4.79; Al, 9.58; Cl, 9.02.

Analytical Procedures. A. Gas Chromatography.—An Aerograph A-90-P gas chromatograph was used: copper column; block temperature, 250°; injector temperature, 300°; bridge current, 180 ma; sample size, 5–30 μl. with the appropriate attenuations. Column 1 was 6 ft by 0.25 in., 10% silicone grease (SE-52) on Chromosorb P (30–60 mesh), 150–250°, 60–90 ml of He/min. Column 2 was 10 ft by 0.25 in., 15% Apiezon L on acid-washed Chromosorb P (30–60 mesh), 175–245°, 85 ml of He/min.

B. For Peroxides.—The iodometric method is described elsewhere.[4]

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