

## Reactions of *t*-Butylperoxy Isopropyl Carbonate with Aromatic Compounds under Friedel-Crafts Conditions<sup>1</sup>

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*t*-Butylperoxy isopropyl carbonate reacted with alkylbenzenes (toluene and *o*- and *m*-xylene) in the presence of aluminum halide to produce phenols, presumably through the intermediacy of aryl *t*-butyl ethers. Evidence (orientation, catalysis, and nature of the products) points to substitution by electrophilic oxygen. With anisole two additional modes of interaction were observed, apparently also entailing heterolytic fission of the peroxide linkage. Formation of acetone, methyl chloride, methanol and 2,2-di(*p*-methoxyphenyl) propane can be attributed to the occurrence of Criegee rearrangement. The halogenated anisole product possessed an orientation which indicated involvement of *t*-butyl hypohalite as a precursor. Resorcinol dimethyl ether resembled anisole in its behavior in this system.

Aromatic oxygenation involving cationic intermediates has been effected by various peroxide-containing systems: hydrogen peroxide in the presence of sulfuric acid<sup>3</sup> or boron trifluoride etherate,<sup>4</sup> peroxy acids alone<sup>5</sup> or with a Lewis acid promoter,<sup>6</sup> and diaryl peroxides in conjunction with a Friedel-Crafts catalyst.<sup>7</sup> More recently, alkylbenzenes<sup>8,9</sup> and aromatic ethers<sup>9,10</sup> have been converted to the corresponding phenols, quite often in good yield, by use of diisopropyl peroxydicarbonate and aluminum chloride. Various lines of evidence indicated the involvement of an electron-deficient species. Electrophilic oxygenation has also been reported for the system, toluene-dicyclohexyl peroxydicarbonate-ferrous chloride.<sup>11</sup> Esters of the type O<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>SO<sub>2</sub>OAr, formed from thermal decomposition of nitrobenzenesulfonyl peroxides in aromatic substrates are believed to arise *via* an ionic reaction scheme.<sup>12</sup> In addition, this type of transformation has been carried out with nonperoxidic reagents. Direct introduction of the acetoxy group into aromatic nuclei with lead tetraacetate<sup>13</sup> or nitric acid-acetic anhydride<sup>14</sup> appeared to involve polar intermediates.

This report concerns the behavior of a different type of peroxide, *t*-butylperoxy isopropyl carbonate, toward aromatic compounds (hydrocarbons and ethers) under Friedel-Crafts conditions.

### Results and Discussion

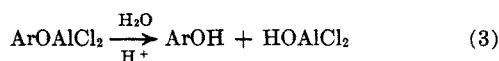
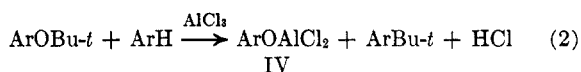
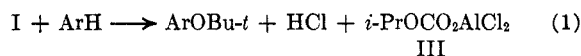
In general the reactions were carried out at 0 ± 5° with aromatic-*t*-butylperoxy isopropyl carbonate-catalyst in 15:1:2 molar ratio. Product analysis was

carried out after treatment of the reaction mixture with hydrochloric acid. This peroxide was found to react with alkylbenzenes in a manner analogous to that of diisopropyl peroxydicarbonate<sup>8,9</sup> yielding phenols and alkylated by-products. In contrast to the symmetrical peroxide, however, additional modes of reaction were available to *t*-butylperoxy isopropyl carbonate with aromatic ethers. Formation of Criegee rearrangement products and halogenated aromatics comprised the competing processes.

**Alkylbenzenes.**—Oxygenation of toluene and *o*- and *m*-xylene (Table I) provided cresols and xylenols in yields comparable with those obtained previously with diisopropyl peroxydicarbonate.<sup>8,9</sup> With the unsymmetrical peroxide two pathways leading to an electrophilic oxygenating species can be envisioned. The catalyst may initially co-ordinate with the peroxide at the carbonyl oxygen resulting in generation of *t*-BuO<sup>δ+</sup> (I), or less likely, at the peroxide linkage to



give an electrophile (II), quite similar to that obtained with a peroxydicarbonate.<sup>8,9</sup> Failure to detect aryl isopropyl carbonates with the xylenes and anisole at 0° and with toluene at -30° indicated that II was not involved, since these products were isolable from peroxydicarbonate reactions.<sup>8</sup> Hence, I denotes the probable electrophile which then attacks the aromatic substrate, presumably forming an aryl *t*-butyl ether (eq 1). Subsequent dealkylation under the reaction conditions (eq 2), followed by work-up (eq 3), afforded the free phenol.



The oxygenated product (IV) present in this case should be more susceptible to electrophilic attack than the reactant. Nevertheless, the absence of materials from further oxidation suggests inactivation of IV through precipitation or by coordination with aluminum chloride. A comparison of the isomeric cresols

(1) Paper IV, Aromatic Oxygenation, presented at the 151st National Meeting of the American Chemical Society, Pittsburgh, Pa., March 1966.

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TABLE I  
 OXYGENATION OF ALKYL BENZENES AND ANISOLE

Aromatic	Peroxide	Structure	Phenolic product	
			Orientation	% yield <sup>a</sup>
Toluene	( <i>i</i> -PrOCO <sub>2</sub> ) <sub>2</sub>	Cresols	<i>o</i> / <i>m</i> / <i>p</i> = 34/11/55 <sup>b</sup>	52 <sup>c</sup>
Toluene	<i>i</i> -PrOCO <sub>2</sub> Bu- <i>t</i>	Cresols	<i>o</i> / <i>m</i> / <i>p</i> = 30/12/58 <sup>d</sup>	37
<i>o</i> -Xylene	( <i>i</i> -PrOCO <sub>2</sub> ) <sub>2</sub>	Xylenols	3,4/2,3 = 74/26	34 <sup>c</sup>
<i>o</i> -Xylene	<i>i</i> -PrOCO <sub>2</sub> Bu- <i>t</i>	Xylenols	3,4/2,3 = 78/22	34
<i>m</i> -Xylene	( <i>i</i> -PrOCO <sub>2</sub> ) <sub>2</sub>	Xylenols	2,4/2,6 = 91/9	48 <sup>c</sup>
<i>m</i> -Xylene	<i>i</i> -PrOCO <sub>2</sub> Bu- <i>t</i>	Xylenols	2,4/2,6 = 81/19	38
Anisole	( <i>i</i> -PrOCO <sub>2</sub> ) <sub>2</sub>	Methoxyphenols	<i>o</i> / <i>p</i> = 20/80	76 <sup>c</sup>
Anisole <sup>e</sup>	<i>i</i> -PrOCO <sub>2</sub> Bu- <i>t</i>	Methoxyphenols	<i>o</i> / <i>p</i> = 37/63	37

<sup>a</sup> Based on the peroxide. See general procedure. <sup>b</sup> Reference 8,  $S_f = 1.0$ . <sup>c</sup> Reference 9. <sup>d</sup>  $S_f = 0.97$ . <sup>e</sup> Boron trichloride catalyst; insufficient phenolic product was obtained with aluminum chloride catalyst.

and xylenols obtained with *t*-butylperoxy isopropyl carbonate or diisopropyl peroxydicarbonate showed differences of a minor degree in some cases, but more pronounced in others (Table I). The cresol orientation data indicated that the electrophiles were of comparable reactivity<sup>15</sup> ( $S_f$  values of 0.97 and 1.0 for the unsymmetrical and symmetrical<sup>8</sup> peroxides, respectively). Formation of a larger amount of the more sterically hindered 2,6-xylenol from electrophile I and *m*-xylene suggested a smaller steric factor in the present case. In contrast, a higher ratio of 3,4-/2,3-xylenol from *o*-xylene resulted from this same peroxide.

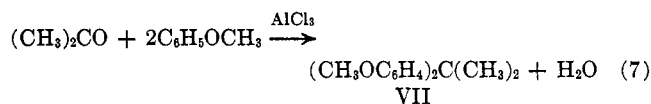
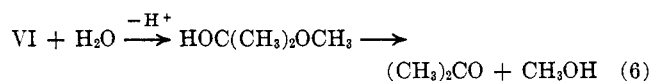
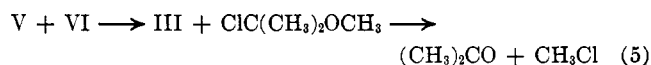
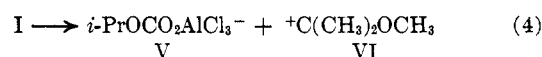
A summary of the aromatic products derived from toluene, *t*-butylperoxy isopropyl carbonate and aluminum chloride is presented in Table II. Cymenes and *t*-butyltoluenes were formed in addition to the cresols. The isomer distribution of these alkylated aromatics was quite dependent on temperature owing to facile isomerization. The hydrocarbons from *o*- and *m*-xylene, though not determined quantitatively, were similar to those obtained with diisopropyl peroxydicarbonate,<sup>9</sup> and also included *t*-butylated materials.

 TABLE II  
 TOLUENE-*t*-BUTYLPEROXY ISOPROPYL CARBONATE-  
 ALUMINUM CHLORIDE

Temp, °C	Products			% yield
	Structure	Orientation		
0	Cresols	<i>o</i> / <i>m</i> / <i>p</i> = 31/12/57		37
-30	Cresols	<i>o</i> / <i>m</i> / <i>p</i> = 29/12/59		25
0	Cymenes	<i>o</i> / <i>m</i> / <i>p</i> = 8/58/34		50
-30	Cymenes	<i>o</i> / <i>m</i> / <i>p</i> = 60/37/3		37
0	<i>t</i> -Butyltoluenes	<i>m</i> / <i>p</i> = 74/26		38
-30	<i>t</i> -Butyltoluenes	<i>m</i> / <i>p</i> = 66/34		51

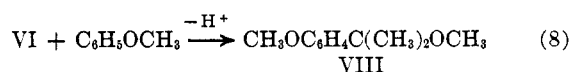
**Aromatic Ethers.**—Table III contains a list of the products resulting from anisole and the peroxide in the presence of aluminum chloride. Furthermore, the composition at various temperatures is set forth. In addition to alkylated materials and phenols, other striking products were observed. Occurrence of acetone, 2,2-di(*p*-methoxyphenyl)propane, methanol, and methyl chloride can be attributed to an intramolecular rearrangement process as outlined in eq 4–9. The first step is identical with that leading to oxygenation, *i.e.*, generation of the complex I. Methyl migration to the electron-deficient oxygen site, in concert with cleavage of the peroxidic bond, would result (eq 4) in

the carbonium ion species VI, which can collapse to acetone and methyl chloride either directly or through the transient species 2-chloro-2-methoxypropane (eq 5). On the other hand, one can visualize combination of VI with adventitious moisture in the system as a route to acetone and methanol (eq 6). It is indicative that the yields of both of these materials, particularly the ketone, were augmented by addition of water to the reaction mixture (Table III). A scheme analogous to eq 4–6 was proposed to explain origination of acetone from decomposition of *t*-butylperoxy chloroformate or *t*-butyl pertosylate in polar solvents.<sup>16</sup> Alkylation of anisole by acetone (eq 7) results in formation of the 2,2-diarylpropane. That the substitution aspect is quite dependent on temperature is evidenced in Table III. The condensate VII was present in 69 and 53% yield at 30 and 0°, respectively, but only 5% was obtained at -20°. Conversely, acetone was isolated in 76% yield at the lowest temperature, but was found in much lesser amount (17%) at 0°.



We were able to demonstrate that acetone does indeed interact when subjected to simulated reaction conditions, resulting in formation of the 2,2-diarylpropane (eq 7). The condensed product of type VII was obtained in good yield only at room temperature or above.

Alternatively, direct alkylation of anisole by VI (eq 8) may occur. This process, which is evidently highly temperature dependent, gives rise (eq 9) to the observed products, 2,2-diarylpropane and methanol, *via* intermediate VIII.



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TABLE III  
 ANISOLE-*t*-BUTYLPEROXY ISOPROPYL CARBONATE-ALUMINUM CHLORIDE

Product	Yield, % <sup>a</sup>			
	-20°	0°	+30°	0° <sup>b</sup>
2,2-Di( <i>p</i> -methoxyphenyl)propane	5	53	69	44
<i>p-t</i> -Butylanisole	38 <sup>c</sup>	36	20	..
<i>o</i> - and <i>p</i> -chloroanisoles	7	12	5	..
<i>o</i> - and <i>p</i> -methoxyphenols	5	4	4	3
<i>o</i> - and <i>p</i> -isopropylanisoles	0	2	16	..
<i>o</i> - and <i>p</i> -methylanisoles <sup>d</sup>	2	2	2	..
2-Propanol	67	65	..	63
Methanol	26	18	..	24
Acetone	76	17	..	52
Isopropyl chloride <sup>d</sup>	0	2	..	2
Carbon dioxide	..	73	..	..
Methyl chloride <sup>d</sup>	Present <sup>e</sup>	Present <sup>e</sup>	Present <sup>e</sup>	Present <sup>e</sup>

<sup>a</sup> Based on the peroxide. See general procedure. <sup>b</sup> Water added; ArH-AlCl<sub>3</sub>-peroxide-H<sub>2</sub>O = 15:2.5:1:0.5. <sup>c</sup> *o*- (8%) and *p*-*t*-butylanisole (30%). <sup>d</sup> Identification based solely on glpc retention time. <sup>e</sup> Qualitative detection only.

 TABLE IV  
 EFFECT OF CATALYST ON PRODUCT COMPOSITION FROM ANISOLE AND *t*-BUTYLPEROXY ISOPROPYL CARBONATE

Catalyst	Products, % <sup>a</sup>										
	Methyl <sup>b</sup>		Isopropyl <sup>b</sup>		XC <sub>6</sub> H <sub>4</sub> OCH <sub>3</sub> , X =		Hydroxy		Halo		2,2-Di- ( <i>p</i> -methoxy- phenyl)- propane
	<i>o</i>	<i>p</i>	<i>o</i>	<i>p</i>	<i>o</i>	<i>p</i>	<i>o</i>	<i>p</i>	<i>o</i>	<i>p</i>	
AlCl <sub>3</sub>	1	0.5	1	0.7	0	36	1	3	5	7 <sup>c</sup>	
AlBr <sub>3</sub>	2	1	2	1	0	56	1	2	9	31 <sup>d</sup>	26
BCl <sub>3</sub>	2	0.5	2	1	1	3	9	16	2	4 <sup>e</sup>	6
BF <sub>3</sub>	0	0	0	0	0	0.5	0	0	0	0	8

<sup>a</sup> Based on the peroxide. See general procedure for oxygenation. <sup>b</sup> Identification based solely on glpc retention time. <sup>c</sup> *ortho:para* = 40:60. <sup>d</sup> *ortho:para* = 23:77. <sup>e</sup> *ortho:para* = 46:54.

Evidence was obtained which supports the plausibility of this pathway. Subjection of cumyl methyl ether, a homolog of VIII, to simulated reaction conditions yielded 2-(*p*-methoxyphenyl)-2-phenylpropane in nearly quantitative yield. Methanol and methyl chloride were also formed. Although this reaction scheme nicely accounts for many of the observed products, it does not explain acetone formation. Conceivably both routes may pertain, although greater generality is associated with eq 5-7. Presumably methanol can serve as a precursor of methyl chloride as evidenced by partial conversion to the halide under conditions which approximate those prevailing during the standard procedure.

Generation of acetone from a *t*-butylperoxy substrate by an ionic process has been noted previously.<sup>16</sup> However, the aromatic alkylation step apparently represents a novel aspect of a system undergoing Criegee rearrangement. In prior cases entailing this type of rearrangement, the observed products generally arise from degradation (see eq 5 and 6)<sup>16</sup> or intramolecular interactions, *e.g.*, 1-benzoyloxy-1,6-epoxycyclodecane from 9-decalyl perbenzoate.<sup>17,18</sup> Other examples of intramolecular migration involving electron-deficient oxygen to which this reaction bears analogy are the acid-catalyzed decomposition of cumene hydroperoxide,<sup>19</sup> carboxy inversion,<sup>20</sup> Dakin reaction,<sup>21</sup> and Baeyer-Villiger oxidation.<sup>22</sup>

2-Propanol, isopropyl chloride, carbon dioxide, and isopropylanisoles probably arise from III as previously described.<sup>9</sup> The small amount of methyl-anisole could have sprung from Lewis acid catalyzed methylation by various species, most likely methyl chloride.

The occurrence of haloaromatics from the reactions of anisole with *t*-butylperoxy isopropyl carbonate and Friedel-Crafts catalysts constitutes another unusual facet of this study. Generally, halogenation by metal halides does not take place unless the inorganic reactant displays a favorable reduction potential, in addition to appreciable Lewis acid character.<sup>23</sup> Hence it is implausible to visualize the catalyst as functioning to accomplish direct halogenation.

Table IV sets forth the yields and isomer distributions for the halogenated ethers which were observed when anisole was exposed to the peroxide in the presence of aluminum chloride, aluminum bromide, or boron trichloride. A significant aspect is the high *ortho:para* ratio in contrast to the isomer distributions reported from use of molecular halogen (Table V): 40:60 (AlCl<sub>3</sub>-peroxide) and 46:54 (BCl<sub>3</sub>-peroxide) *vs.* 21:79 (Cl<sub>2</sub>),<sup>24-26</sup> and 23:77 (AlBr<sub>3</sub>-peroxide) *vs.* 2-3:97-98 (Br<sub>2</sub>).<sup>27,28</sup> Furthermore, when we carried

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TABLE VI  
 BROMINATION OF ANISOLE. ISOMER DISTRIBUTIONS

Method <sup>a</sup>	Anisole, concn <sup>b</sup>	Brominating agent <sup>c</sup>	Concn <sup>b</sup>	Acid catalyst	Concn <sup>b</sup>	-% bromoanisole-	
						<i>o</i>	<i>p</i>
1	9.0	<i>i</i> -PrOCO <sub>2</sub> Bu- <i>t</i> <sup>d</sup>	0.6	AlBr <sub>3</sub>	1.32	23	77
1	9.0	<i>i</i> -PrOCO <sub>2</sub> Bu- <i>t</i> <sup>d</sup>	0.6	AlBr <sub>3</sub>	1.2	23	77
1	9.0	<i>t</i> -BuOBr	0.3	...	...	2	98
1	9.0	<i>t</i> -BuOBr	0.36	AlBr <sub>3</sub>	1.44	4	96
1	9.0	Br <sub>2</sub>	0.3	AlBr <sub>3</sub>	1.2	4	96
2	0.10	Br <sub>2</sub>	0.010	HClO <sub>4</sub> <sup>e</sup>	0.03	3	97
2	0.10	HOBr	0.0066	...	...	11	89
2	0.10	HOBr	0.0066	HClO <sub>4</sub>	0.03	20	80 <sup>f</sup>
3	0.046	HOBr	0.0033	HClO <sub>4</sub>	0.50	26	74
3	0.046	HOBr	0.0033	H <sub>2</sub> SO <sub>4</sub>	1.00	39	61
3	0.046	<i>t</i> -BuOBr	0.005	...	...	5	95
3	0.046	<i>t</i> -BuOBr	0.005	HClO <sub>4</sub>	0.50	25	75
3	0.046	<i>t</i> -BuOBr	0.005	H <sub>2</sub> SO <sub>4</sub>	1.00	31	69
4	0.046	MeCO <sub>2</sub> Br <sup>g</sup>	0.0033	... <sup>h</sup>	...	6	94
4	0.02	MeCO <sub>2</sub> Br <sup>g</sup>	0.003	... <sup>i</sup>	...	8	92
5	0.032	MeCO <sub>2</sub> Br <sup>g</sup>	0.0056	HClO <sub>4</sub>	0.096	13	87 <sup>j</sup>

<sup>a</sup> See Experimental Section. <sup>b</sup> Normality. <sup>c</sup> Initial species present in the reaction. <sup>d</sup> Bromine is provided by the catalyst. <sup>e</sup> 70% reagent. <sup>f</sup> Higher boiling brominated material, 11%. <sup>g</sup> Probably a mixture of MeCO<sub>2</sub>Br and HOBr. <sup>h</sup> Sodium acetate, 0.50 *N*. <sup>i</sup> Sodium acetate, 0.01 *N*. <sup>j</sup> Higher boiling brominated material, 9%.

XI) makes available the requisite halogenonium ion (eq 11) for aromatic substitution (eq 12). Since the concept of catalyzed halogenation by *t*-butyl hypohalite is consonant with the orientation data, it is deemed necessary to specify rapid recombination (cage effect) of X and XI according to eq 11. Otherwise, *t*-butyl hypobromite might be expected to react rapidly with anisole without benefit of catalysis (resulting in a lower *ortho:para* ratio), as was noted with anisole-*t*-butyl hypobromite-aluminum bromide.

Nucleophilic displacement on peroxide by halide in nonaqueous systems is believed to entail formation of hypohalite in the initial step of the reaction.<sup>35</sup> Generally these species are transient intermediates reacting further with halide to produce molecular halogen. Several observations militate against the alternative premise that halide ion reacts intermolecularly with *t*-butylperoxy isopropyl carbonate in the present case: (1) in a homogeneous system consisting of lithium chloride, *t*-butylperoxy isopropyl carbonate, anisole, and acetic acid, no decomposition of the peroxide was observed even upon prolonged treatment at 60°; and (2) the peroxide is quite resistant to intermolecular attack even by strong nucleophiles such as iodide, as evidenced by the need for unusually vigorous conditions during iodometric analysis.<sup>36</sup>

Analogy to eq 10 can be drawn from several extant areas. A similar transition state may pertain in the conversion of esters<sup>37,38</sup> to alkyl chlorides by aluminum chloride. Furthermore, a resemblance is apparent to the Meerwein-Ponndorf reduction of alkyl hydroperoxides by aluminum isopropoxide.<sup>39</sup>

Other examples are recorded in the literature in which aluminum halide halogenates aromatics, apparently in an indirect manner. One may cite the formation of chlorinated *p*-polyphenyl from benzene-

aluminum chloride-manganese dioxide,<sup>40</sup> and 4,10-dichloroperylene from perylene-aluminum chloride-nitrobenzene.<sup>41</sup>

Change in temperature has little effect upon the course of the competing modes of peroxide decomposition (Table III) involving anisole-*t*-butylperoxy isopropyl carbonate-aluminum chloride. The intramolecular rearrangement process (eq 4) provides acetone and 2,2-diarylpropane, whereas oxygenation (eq 1) and hypohalite formation (eq 10) result in phenols and halogenated aromatics, respectively. A rough estimate of the extent of the competing reactions can be made by comparing the ratios of the characteristic products at the various temperatures. At -20° the ratio in terms of eq 4:10:1 is 81:7:5; at 0°, 70:12:4; and at 30°, 69:5:4. These three reaction courses account for a predominance of the total materials resulting from heterolytic fission: 93% at -20°, 86% at 0°, and 78% at 30°. The intramolecular rearrangement is favored at the various temperatures.

Table IV summarizes the products obtained from anisole and *t*-butylperoxy isopropyl carbonate in the presence of various Lewis acid catalysts. Aluminum chloride, boron trichloride and aluminum bromide were effective in promoting the three types of competing reactions. Boron trichloride favored the intermolecular oxygenation process at the expense of intramolecular rearrangement. The latter pathway was the preferred route with aluminum chloride. Aluminum bromide was by far the most effective agent in facilitating those interactions leading to nuclear halogenation, presumably owing to the greater nucleophilicity of bromide compared to chloride. Scouting experiments with aluminum iodide and boron tribromide pointed to extensive demethylation of anisole, even at low temperatures.

A brief study involving *t*-butylperoxy isopropyl carbonate and aluminum chloride was carried out with resorcinol dimethyl ether (Table VII). As with anisole, Criegee rearrangement leading ultimately to 2,2-di-(2',4'-dimethoxyphenyl)propane and hypohalite for-

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TABLE VII  
RESORCINOL DIMETHYL ETHER-*t*-BUTYLPEROXY ISOPROPYL  
CARBONATE-ALUMINUM CHLORIDE

Product	% <sup>a</sup>
2,2-Di(2',4'-dimethoxyphenyl)propane	37
4- <i>t</i> -Butylresorcinol dimethyl ether	30
4-Chlororesorcinol dimethyl ether	7
2,4-Dimethoxyphenol	5
Unidentified product <sup>b</sup>	10-23

<sup>a</sup> Based on the peroxide; see general procedure. <sup>b</sup> Very similar (glpc retention time and infrared spectrum) to 4-chlororesorcinol dimethyl ether, but shown not to be the 2- or 5-chloro isomer.

mation resulting in 4-chlororesorcinol dimethyl ether competed with the oxygenation process (production of 2,4-dimethoxyphenol).

The polar nature of the various pathways observed with the alkylbenzenes and aromatic ethers is further evidenced by the necessity of a catalyst. The peroxide remained virtually undecomposed in the aromatic substrates for prolonged periods even at room temperature.

### Experimental Section<sup>42</sup>

**Materials.**—The aromatic reactants, used as obtained, possessed purities greater than 98% according to glpc analysis. The other reagents, solvents, and some of the standards for analysis were commercial, high-purity grades. Other authentic materials used in analysis are described elsewhere.<sup>9</sup>

We are grateful to the Pittsburgh Plate Glass Co. for samples of *t*-butylperoxy isopropyl carbonate, and to the Du Pont Co. for samples of fluorotrichloromethane.

**Aromatic Oxygenation with *t*-Butylperoxy Isopropyl Carbonate. General Procedure.**—The major portion of the aromatic reactant (1.5 moles total) was cooled to 0° in a 3-neck flask equipped with stirrer, thermometer, gas-inlet tube, gas collector, and addition funnel. After the apparatus was purged with nitrogen, a slow flow was maintained. Following introduction of aluminum chloride (0.2 mole), a solution of *t*-butylperoxy isopropyl carbonate (0.1 mole) in the remainder of the aromatic reagent was added slowly during 1.5 hr at 0 ± 5° (exothermic reaction). After an additional 1.5 hr at 0 ± 5°, the reaction mixture was mixed with concentrated hydrochloric acid (100 ml) and crushed ice (500 g). The layers were separated, and a small aliquot was taken from the organic portion for glpc analysis. In some cases a small sample of the organic phase was analyzed by iodometry to ascertain the completeness of reaction. After the aqueous fraction was washed with ether, the organic solutions were combined and freed of ether by evaporation. Phenolic materials were extracted twice with 10% sodium hydroxide. The combined extract was washed with ether and then acidified with hydrochloric acid-ice. The free phenol was extracted thoroughly with ether, the extract was dried, and the ethereal solution of the crude phenol was concentrated and subjected to glpc analysis in order to obtain the composition of the phenolic product and the isomer distribution where applicable. The crude phenol was distilled under reduced pressure through a Bantamware distillation head containing a Vigreux column. In all cases there was less than 0.2 g (<7%) of distillation residue.

Yields of the phenolic products were based on the stoichiometry of one mole of oxygenated product per mole of peroxide, and were obtained by isolation. The results contained in Table I are the average of two or more runs for each aromatic substrate.

The temperature studies with anisole-aluminum chloride-peroxide were carried out in a similar manner. When catalysts other than aluminum chloride were used, the indicated modifications were made. Dissolution of aluminum bromide, aluminum iodide, or boron tribromide in cooled anisole was carried out in a drybox, and the resulting solution was transferred to a 3-neck flask. Despite cooling to -30° in the latter two cases extensive demethylation took place. Solutions of boron trifluoride or boron trichloride were made by bubbling the gas into cooled

anisole until the desired amount of catalyst was present. With the exception of aluminum iodide, the catalysts formed homogeneous solutions with anisole and resorcinol dimethyl ether. The aluminum chloride-alkylbenzene solutions were heterogeneous.<sup>9</sup>

**Product Identification. A. Phenolic Products.**—The phenolic distillates (in some cases the crude phenolic extract was used) were analyzed by gas chromatography. Isomers were separated and collected. Identification was made by comparison with authentic materials (glpc retention time and infrared spectrum).

**B. Neutral Aromatic Products.**—After extraction of the phenolic products, the remaining solution was dried and distilled. Following removal of unchanged starting material, the residue was fractionated *in vacuo*. Some components were obtained in pure form, whereas others were subsequently collected by gas chromatography of product-enriched fractions. Comparison with authentic materials was made (infrared spectrum, index of refraction, glpc retention time, and in some cases the nmr spectrum). In this manner the cymenes, *p*-*t*-butyltoluene, 5-*t*-butyl-*m*-xylene, *t*-butyl-, isopropyl-, chloro-, and bromoanisoles, 4-chloro- and 4-*t*-butylresorcinol dimethyl ether, 2,2-di(*p*-methoxyphenyl)propane, and 2,2-di(2',4'-dimethoxyphenyl)propane were characterized. Methylanisoles were identified solely by identity of glpc retention times with those of the authentic materials. Quantitative data were not obtained for the neutral materials derived from *o*- and *m*-xylene. However, with *m*-xylene the major component was 5-*t*-butyl-*m*-xylene contaminated with a compound presumed to be 4-*t*-butyl-*m*-xylene (strong infrared absorption at 12.25 μ). Other products from *m*-xylene, identified by comparison of the gas chromatograms of the organic aliquot with aliquots of corresponding reaction mixture from diisopropyl peroxydicarbonate,<sup>9</sup> were present in the indicated order of decreasing yield: 3,5- > 2,4- > 2,5-dimethylcumene. Similarly, 4-*t*-butyl-*o*-xylene is believed to be the major product from *o*-xylene with 3,4-, 2,3-, and 3,5-dimethylcumene present in the order of decreasing yield.

**C. Low-Boiling Products.**—These materials were isolated as previously described.<sup>9</sup> Separation of the low-boiling distillates was effected by gas chromatography (glpc column 1 at 55°), and the pure products were identified by comparison with authentic samples (glpc retention time and infrared spectrum). In this manner, acetone, methanol, 2-propanol, and isopropyl chloride were characterized (Table III).

**D. Methyl Chloride. From *t*-Butylperoxy Isopropyl Carbonate-Aluminum Chloride-Anisole.**—After the apparatus was purged with nitrogen, gas flow was discontinued. The peroxide (0.1 mole) in 5 ml of the aromatic was added to aluminum chloride (0.2 mole) in the remainder of the aromatic (1.5 moles) at 0° during 1.5 hr. The reaction mixture was stirred for an additional 1.5 hr. The gas outlet tube led first into a trap containing caustic (to remove hydrogen chloride and carbon dioxide) and then into a gas-collection apparatus equipped with a sampling port. After 3 hr 113 ml of gas was collected. Slow addition of a mixture of ice-hydrochloric acid to the reaction mixture during 0.5 hr resulted in further gas evolution (37 ml). The contents were swept with nitrogen (gas-dispersion tube) until the total gas in the collection apparatus amounted to 475 ml. Analysis of samples with two glpc columns (6 and 7) revealed strong peaks attributed to methyl chloride (identity of retention time with that of the authentic material).

**Carbon Dioxide Analysis.**—The experimental procedure (method B) was described previously.<sup>9</sup> During reaction the gas was collected in 15% yield, and an additional 58% evolved during hydrolysis with hydrochloric acid-ice.

**Authentic Materials. A. Alkylated Products. 1. *t*-Butylanisoles.**—*o*- and *p*-*t*-butylanisole were prepared by methylation of the corresponding phenols with dimethyl sulfate in the presence of caustic. Middle cuts taken from the fractionation of the crude ethers were shown to be 100% pure by gas chromatography.

**2. 4-*t*-Butylresorcinol Dimethyl Ether.**—To a stirred solution of resorcinol dimethyl ether (0.15 mole) in 70% perchloric acid (50 ml) at room temperature was quickly added *t*-butyl alcohol (0.05 mole). After 3 additional hr at 25°, the mixture was diluted with ice-water. The organic layer was separated, combined with an ethereal wash of the aqueous phase, dried, and distilled. After removal of unchanged starting material, a fraction boiling at 89-91° (1.5 mm) [lit.<sup>43</sup> bp 93° (2 mm)] was

(42) Elemental analyses were performed by Galbraith Laboratories, Knoxville, Tenn., and Drs. Weiler and Strauss, Oxford, England. Melting points and boiling points are uncorrected. We are grateful to Dr. S. T. Morneweck for contributing to the scouting work in this area.

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collected and shown (glpc analysis) to contain a single product in 99% purity:  $n_D^{25}$  1.5105, lit.<sup>43</sup>  $n_D^{25}$  1.5114. Nmr analysis of the pure product obtained by gas chromatography showed the presence of aromatic protons ( $\delta$  5.85–6.9), methoxyl protons (singlets of equal intensity at  $\delta$  3.22 and 3.20), and methyl protons (singlet at  $\delta$  1.01) in the ratio 3.3:6.0:8.6 (theory, 3:6:9).

**3. 4-Isopropylresorcinol Dimethyl Ether.**—The procedure for the *t*-butyl homolog was followed with 2-propanol as the alkylating agent. After removal of starting material, a fraction was collected at 83–85° (1.5 mm) which contained three products. The major component possessed an nmr spectrum which indicated the presence of aromatic protons ( $\delta$  6.1–7.0), methoxyl protons (singlets of equal intensity at  $\delta$  3.69 and 3.77), and methyl protons (a doublet centered at  $\delta$  1.11) in the ratio, 2.7:6.0:6.0 (theory, 3:6:6). Use of a dilute solution did not permit detection of the methine proton. In addition, the infrared spectrum, which was very similar to that of 4-*t*-butylresorcinol dimethyl ether, pointed to 4-isopropylresorcinol dimethyl ether.<sup>44</sup>

**B. Halogenated Products. 1. Bromoanisoles.**—*o*- and *p*-bromoanisole were prepared by methylation of the corresponding phenols with dimethyl sulfate in the presence of caustic. Middle cuts taken from fractionation of the crude ethers were shown to be 100% pure by gas chromatography.

**2. 4-Chlororesorcinol Dimethyl Ether.**—Methylation of 4-chlororesorcinol with 2 equiv of methyl sulfate and sodium hydroxide provided a pure product upon distillation, bp 90–92° (1.85 mm), lit.<sup>45</sup> bp 135–137° (17–18 mm). Nmr analysis showed the presence of aromatic protons ( $\delta$  7.2–6.3) and methoxyl protons (singlets of equal intensity at  $\delta$  4.75 and 4.67) in the ratio 2.9:6.0 (theory, 3:6).

**3. 2-Chlororesorcinol Dimethyl Ether.**—2-Chlororesorcinol was prepared by the method of Schamp.<sup>46</sup> The crude phenol was methylated with methyl sulfate and sodium hydroxide yielding a product, bp 109–111° (5.0 mm), which solidified. Two crystallizations from ethanol–water gave white crystals, mp 69–71°. Nmr analysis indicated the presence of aromatic protons ( $\delta$  7.1–6.3) and methoxyl protons (one singlet at  $\delta$  3.78) in the ratio, 3.0:6.3 (theory, 3:6).

*Anal.* Calcd for  $C_8H_9ClO_2$ : C, 55.67; H, 5.25; Cl, 20.54; O, 18.54. Found: C, 55.71; H, 5.38; Cl, 20.61; O, 18.45.

**4. 5-Chlororesorcinol Dimethyl Ether.**—3,5-Dimethoxyaniline (0.65 mole), dissolved in anhydrous ether (100 ml), was treated with hydrogen chloride gas until precipitation no longer occurred. The amine hydrochloride was filtered, washed with dry ether, and suspended in chloroform (150 ml). Slow addition of amyl nitrite (0.073 mole) to the suspension at reflux produced a vigorous reaction and bright red coloration. After a total time of 2 hr, the reaction mixture was poured onto ice–hydrochloric acid. Work-up of the organic portion provided the desired product, bp 82–83° (0.55 mm), 97% pure by glpc analysis, white needles from ethanol, mp 33–34°, lit.<sup>47</sup> mp 38°.

**C. Diarylpropane Product. 1. 2,2-Di(*p*-methoxyphenyl)propane.**—“Bisphenol A” was methylated with two equivalents each of dimethyl sulfate and sodium hydroxide. Distillation gave a fraction boiling at 167–170° (1.3 mm), lit.<sup>48</sup> bp 190° (5 mm), which was 99% pure by glpc analysis. The nmr spectrum of the pure product showed aromatic protons in an ABBA pattern centered at  $\delta$  6.76, and singlets attributable to methoxyl and methyl protons at  $\delta$  3.57 and 1.55, respectively, in the ratio, 4:3:3 (theory, 4:3:3).

**2. 2,2-Di(2',4'-dimethoxyphenyl)propane.**—A solution of acetone (0.05 mole) in resorcinol dimethyl ether (25 ml) was added to a stirred mixture of aluminum chloride (0.1 mole) in the remainder of the aromatic reactant (0.75 mole total) during 0.5 hr while hydrogen chloride was introduced intermittently through a gas-dispersion tube. After a total time of 3 hr at 0°, a small aliquot of the reaction mixture was worked up and analyzed by glpc indicating the presence of only a small amount (19% yield) of higher-boiling product. Reaction was continued for an additional 3 hr at 30°. Following work-up, distillation yielded unchanged starting material and then a fraction (92% yield) boiling at 200–208° (3 mm). The nmr spectrum was rather complicated:

a complex aromatic proton signal at  $\delta$  7.3–6.1, three singlets (one twice as large as the other two) at  $\delta$  3.62, 3.60, and 3.30 attributable to methoxyl protons, and three singlets at  $\delta$  1.63, 1.48, and 1.23 characteristic of methyl protons. Integration gave a ratio of 5.5:12.0:6.4 (theory, 6:12:6). Glpc and infrared spectroscopy were also employed in analysis.

*Anal.* Calcd for  $C_{15}H_{24}O_4$ : C, 72.13; H, 7.66. Found: C, 72.31; H, 7.80.

**Methyl Cumyl Ether.**— $\alpha,\alpha$ -Dimethyl benzyl alcohol (0.35 mole) was treated with excess sodium with heating and stirring until most of the sodium had reacted. Methyl iodide (excess) was then added cautiously, and the solution was stirred overnight at 40–50°. After filtration of sodium iodide, the oil was dried and distilled twice under reduced pressure, bp 56–57° (2.2 mm), lit.<sup>49</sup> bp 78° (20 mm). Nmr analysis revealed aromatic protons ( $\delta$  7.3–6.8), methoxyl protons (singlet at  $\delta$  2.63), and methyl protons (singlet at  $\delta$  1.12) in the ratio, 5.1:2.9:6.0 (theory, 5:3:6).

*Anal.* Calcd for  $C_{10}H_{14}O$ : C, 79.95; H, 9.39. Found: C, 79.80; H, 9.36.

**Methyl Cumyl Ether–Aluminum Chloride–Anisole–Hydrogen Chloride.**—A solution of the ether (0.03 mole) in anisole (15 ml) was added to aluminum chloride (0.06 mole) in the remainder of the aromatic (0.6 mole total) during 0.5 hr at 0°. Stirring was continued for an additional 2.5 hr while hydrogen chloride was passed into the mixture intermittently. After work-up, including two distillations, a fraction boiling at 67–92° was obtained. Identification as methanol (97% pure) was made by infrared and glpc analyses. No low-boiling product was present in the organic layer which was also shown to be free of cumyl methyl ether by glpc analysis. Distillation gave, in addition to unchanged anisole, a fraction boiling at 133–136° (1.5 mm),  $n_D^{25}$  1.5678 (64% yield based on the ether); lit.<sup>50</sup>  $n_D^{25}$  1.5698, bp 154–156° (3 mm) for 2-(*p*-methoxyphenyl)-2-phenylpropane. Gas chromatography provided a pure sample which exhibited strong bands in the infrared region at 12.96 and 14.3  $\mu$  (mono-substituted benzene) and 12.05  $\mu$  (*para* substitution). The nmr spectrum indicated aromatic protons ( $\delta$  6.9–6.4), methoxyl protons (singlet at  $\delta$  3.14), and methyl protons (singlet at  $\delta$  1.30) in the relative proportions, 8.5:2.9:6.0 (theory, 9:3:6).

*Anal.* Calcd for  $C_{16}H_{18}O$ : C, 84.91; H, 8.02. Found: C, 85.01; H, 8.20.

A duplicate run was carried out in which the gaseous products were collected and analyzed. Gas was collected by a nitrogen purge, and also by heating after addition to hydrochloric acid–ice. Methyl chloride was shown to be present.

**Methanol–Anisole–Aluminum Chloride–Hydrogen Chloride.**—A solution of methanol (0.05 mole) in anisole (20 ml) was added to aluminum chloride (0.1 mole) in the remainder of the aromatic (0.75 mole total) during 1 hr at 0°. Hydrogen chloride was periodically introduced during 3 hr. After mixing the reaction medium with hydrochloric acid–ice and separating layers, analysis for methyl chloride and low-boiling products was then carried out. Methyl chloride was found to be present along with a small amount (10%) of unreacted methanol.

**Anisole–Acetone–Aluminum Chloride–Hydrogen Chloride.**—This reaction was run in a manner similar to that described for methanol–anisole–aluminum chloride with acetone replacing methanol (3 hr at 0°). The high-boiling product from distillation was identified as 2,2-di(*p*-methoxyphenyl)propane (10% yield based on acetone).

***t*-Butyl Hypobromite.**—The method of Walling and Padwa<sup>51</sup> was used: bp 43–44° (83 mm), lit.<sup>51</sup> bp 44–45° (85 mm);  $n_D^{25}$  1.4428, lit.<sup>51</sup>  $n_D^{25}$  1.4488; 20–27% yield.

**Hypobromous Acid.**<sup>51</sup>—Bromine water was shaken with an excess of silver sulfate until the bromine color disappeared. The resulting solution was decanted from precipitated silver bromide and titrated (sodium iodide–sodium thiosulfate).

**Bromine Acetate.**<sup>52</sup>—Bromine in 75% acetic acid was shaken with an excess of silver sulfate. The resulting pale solution was decanted from precipitated silver bromide and titrated. Previous work indicated that the mixture contains bromine acetate and hypobromous acid.<sup>29, 31, 52</sup>

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TABLE VIII  
GAS-LIQUID PARTITION  
CHROMATOGRAPHIC COLUMNS

Column	Dimensions, ft, in	Temp, °C	He, ml/min	Packing
1	10, 0.25	50-170	40-60	15% Carbowax 20M on Chromosorb P, 30-60 mesh
2	10, 0.25	175-200	60-75	20% silicone fluid (SF-96) on acid-washed Chromosorb P, 30-60 mesh
3	10, 0.25	170-210	60-120	15% Apiezon L on acid-washed Chromosorb P, 30-60 mesh
4	6, 0.25	140-250	70-100	15% silicone grease (SE-52) on Chromosorb P, 30-60 mesh
5	10, 0.25	200	60	10% Apiezon N on Chromosorb G, 60-80 mesh
6	15, 0.25	28	60	7% $\alpha$ -Chloronaphthalene on Chromosorb P, 30-60 mesh
7	16, 0.25	28	100	30% Dowtherm A on Chromosorb P, 60-80 mesh
8 <sup>a</sup>	5, 0.25 2, 0.25	120	80	Terephthalic acid-Carbowax 4000, <i>m</i> -phenyl ether (five-ring), both on Chromosorb W, HMDS, 60-80 mesh

<sup>a</sup> A single column.

**Halogenating Agent-Anisole-Metal Halide. Method 1.**—The halogenating agent (0.012–0.1 mole) was added in various ways to a stirred solution of the metal halide (3–4 molar excess) in anisole (25–30 *M* excess) during 0.5–1 hr at 0°. Gaseous chlorine was bubbled in directly, bromine and *t*-butyl hypobromite were introduced dropwise, and *t*-butyl hypochlorite was added as a solution in anisole. After a total time of 1.5–3 hr, the reaction mixture was shaken with hydrochloric acid-ice. The organic phase was separated, washed with water, dried, and analyzed by glpc.

Halogenation of anisole by *t*-butyl hypobromite in the absence of catalyst was carried out by dropwise addition of the hypohalite to anisole at 0°, and then the products were analyzed. Instant decolorization was noted.

**Brominating Agent-Anisole. In Water. Method 2.**—Anisole was added all at once to a vigorously stirred solution of the brominating agent (0.00033–0.0005 mole) in water (50 ml) at 0°. After a total reaction time of 0.5 hr, the mixture was extracted with ether. The extract was washed once with 10% sodium metabisulfite solution, dried, and concentrated for glpc analysis. Identical isomer distributions were obtained from hypobromous acid with and without added silver sulfate.

The acid-catalyzed reactions were carried out in a similar manner with first the acid (perchloric, 70%, or sulfuric, 0.0015–0.05 mole) and then anisole added to the solution of brominating agent in water. This technique proved unsatisfactory since significant amounts of polybrominated material were obtained.

**Brominating Agent-Anisole. Method 3.**—After anisole (0.0092 mole) and perchloric, 70%, or sulfuric acid (0.05 mole) were stirred with water (100 ml), the mixture was cooled to 0° with vigorous agitation. Mineral acid (0.05 mole) was added to a solution of the brominating agent (0.00066–0.001 mole) in water (100 ml). Following rapid mixing, addition was made to the solution of anisole during 0.1 hr. After a total of 0.25 hr, the mixture was partially neutralized with caustic-ice, and the organic phase was extracted with ether. Work-up and analysis were carried out as in method 1.

**Bromine Acetate. Method 4.**—A mixture of anisole (0.0092 mole), sodium acetate (0.05 mole), and 75% acetic acid was made up and cooled to 0°. A solution of sodium acetate (0.05 mole) and bromine acetate (100 ml, 0.009 *N*), was quickly introduced into the anisole mixture with vigorous stirring at 0°. After a total of 0.25 hr, the reaction mixture was neutralized with caustic-ice, and the organic layer was worked up and analyzed.

**Method 5.**—Perchloric acid (70%, 0.024 mole) was added to a solution of bromine acetate (250 ml, 0.0056 *N*) at 0° with rapid stirring. Following the rapid introduction of anisole (0.008 mole), the reaction mixture was worked up and analyzed.

**Halogenation. General Comments.**—The results of the bromination reactions are summarized in Table VI. In all but two cases ( $\text{HOBr}:\text{C}_6\text{H}_5\text{OCH}_3:\text{HClO}_4 = 0.0066:0.10:0.03$ , and  $\text{BrOAc}:\text{C}_6\text{H}_5\text{OCH}_3:\text{HClO}_4 = 0.0056:0.032:0.096$ ), there was no higher-boiling product. For the exceptions, 10% of the total brominated product consisted of a higher boiling component. Instant decolorization was observed with the brominations carried out in water or acetic acid.

***t*-Butylperoxy Isopropyl Carbonate-Anisole-Lithium Chloride.**—To *t*-butylperoxy isopropyl carbonate (0.033 mole) in anisole (45 ml) at 0° was added a solution of lithium chloride (0.065 mole) in glacial acetic acid (75 ml). After 3 hr of stirring at 0°, analysis of an aliquot indicated that no peroxide decomposition had occurred. Continued agitation at room temperature for 2 hr failed to effect reaction. Heating at 60° for 15 hr did produce a slight transformation (<7% decomposition), but glpc analysis indicated the presence of only unchanged anisole.

**Analytical Procedures. A. Gas Chromatography.**—An Aerograph A-90-P gas chromatograph (columns 1–5) and a homemade unit (columns 6–8) were used: copper columns; block temperature, 250°; injector temperature, 300°; bridge current, 180 ma; sample size 5–30  $\mu\text{l}$  with the appropriate attenuations. The columns are described in Table VIII.

**B. For Peroxides.**—An iodometric method was used.<sup>36,53</sup> A weighed sample was dissolved in 50 ml of 10% acetic acid in 2-propanol, and 10 ml of a suspension of 2.5 g of sodium iodide in 2-propanol was added. The mixture was refluxed 10 min, 50 ml of water added, and the hot solution was titrated with standard thiosulfate. The peroxide exhibited a purity of 91% based on this method.

**C. For Phenolic Products.**—The isomer distributions of the cresols were determined by infrared spectroscopy (cyclohexane solvent) with a Beckman IR-8 spectrophotometer according to the previous method.<sup>8</sup>

The isomer distributions of the products from anisole, and *o*- and *m*-xylene were obtained by glpc analysis (glpc column 3 at 192°, 4 at 140°, and 2 at 175°, respectively). Known mixtures of the isomeric phenols were used as standards for analysis.

**D. For Neutral Products. 1. Product Yields.**—Solutions of pentamethylbenzene in anisole, *p*-bromoanisole in anisole, and 4,4'-dichlorobiphenyl in anisole were used as internal standards to determine yields of the various reaction products from anisole and resorcinol dimethyl ether. Chlorinated and *t*-butylated materials from anisole-aluminum chloride-peroxide were determined with the first internal standard and glpc column 3 at 210°. The same internal standard and glpc column 2 at 180° were employed for the anisole-aluminum bromide-peroxide products. All six mono-substituted anisoles from anisole-boron trichloride were separated and determined with glpc column 1 at 145° and the *p*-bromoanisole standard. In all these cases the higher-boiling diarylpropane product was determined with the 4,4'-dichlorobiphenyl internal standard and glpc column 4 at 220°. Column 2 at 200° and the pentamethylbenzene internal standard provided the quantitative data for the monosubstituted resorcinol dimethyl ethers, whereas the diarylpropane product was obtained by isolation.

A combination of isolation and glpc analysis (glpc column 3, 170°) was used to determine the toluene product yields. The alkylated xylenes were separated and qualitatively detected with glpc columns 2 and 3.

(53) We are grateful to Dr. John Crano, Pittsburgh Plate Glass Co., for this procedure.



2. **Isomer Distributions. Haloanisoles.**—The bromo- and chloroanisole isomer distributions were obtained by glpc analysis (glpc column 1 at 168°, and 8, respectively). Because of interfering products in the anisole-boron trichloride-peroxide experiment, glpc column 1 at 145° was used. Known mixtures of the various isomeric haloanisoles were prepared. A plot was made

of the peak area ratio *vs.* the concentration ratio, and the data from the various product mixtures were compared with this plot.

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## Synthesis and Properties of *p*-Polyphenyl Derivatives<sup>1</sup>

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Various derivatives of *p*-polyphenyl were prepared by chlorination (antimony pentachloride or chlorine-aluminum chloride), bromination (bromine-aluminum bromide), sulfonation (sulfuric acid), nitration (mixed acid or nitronium tetrafluoroborate), and reduction (lithium-ethylenediamine). Attempts were made to isomerize the polymer with promoted Lewis acid catalysts. Nitro-*p*-polyphenyl was converted to its amino counterpart on treatment with hydrazine-diethylene glycol or tin-hydrochloric acid. According to thermogravimetric analysis, stability of the derivatives fell in the order: chlorinated > (*p*-polyphenyl) > brominated > "isomerized" > amino > nitro. Except for the nitrated *p*-polyphenyl, none of the products exhibited appreciable solubility in boiling *o*-dichlorobenzene.

The aromatic nucleus has been shown to function as a monomer in polymerizations yielding homopolymer. For example, benzene was converted to *p*-polyphenyl in Lewis acid catalyst-oxidant systems such as, ferric chloride,<sup>2</sup> molybdenum pentachloride,<sup>3</sup> or aluminum chloride-cupric chloride.<sup>4,5</sup> As a result, appreciable quantities of this polymer can now be readily obtained by a simple procedure from inexpensive starting materials.<sup>5,6</sup>

Our principal objective in the present study was to investigate the chemical behavior of *p*-polyphenyl. More specifically, we wished to prepare a variety of derivatives and ascertain their properties. Several closely related studies have been reported involving sulfonation,<sup>7,8</sup> subsequent caustic fusion,<sup>8</sup> and finally, cross-linking of the phenolic derivative with formaldehyde.<sup>8</sup> Wherever possible in the discussion, the chemical character of *p*-polyphenyl will be compared with that of the individual, lower benzhomologs described in the prior literature.

### Results and Discussion

**Halogenation.**—Various conditions were effective for halogenation of *p*-polyphenyl. With excess antimony pentachloride at 70–115°, about 50% chlorination was achieved. Almost complete replacement of hydrogen was attained upon reaction with chlorine gas in stannic chloride with aluminum chloride as catalyst. Strong absorption maxima in the infrared spectra of the chlorinated derivatives were present at 1330 and 735 cm<sup>-1</sup>. Carbon-chlorine stretching is known<sup>9</sup> to produce bands in the 750–700-cm<sup>-1</sup> region. In addition, a weaker band was situated at 1065 cm<sup>-1</sup>. Varying degrees of halogenation were observed during preparation

of *p*-polyphenyl in Lewis acid catalyst-oxidant systems.<sup>2–5,10,11</sup> In addition, antimony pentachloride was employed in another study for introduction of chlorine (one halogen per one to six rings).<sup>12</sup> Chlorination of biphenyl has received considerable attention since before the turn of the century. The literature on monohalogenation has been summarized.<sup>13,14</sup> Complete replacement<sup>15,16</sup> can be accomplished with chlorine gas and a Lewis acid catalyst or with antimony pentachloride.

In the presence of aluminum bromide, substitution in the polymer by bromine occurred with ease to yield a product which contained an average of about three halogen atoms per monomer unit. The infrared spectrum in the 625–4000-cm<sup>-1</sup> region was quite simple, exhibiting bands of appreciable strength only at 1020, 1305, and 1330 (sh) cm<sup>-1</sup>. In the presence of a Friedel-Crafts catalyst, polybromination of biphenyl can be effected with formation of octa- and decabromobiphenyls.<sup>17</sup>

**Sulfonation.**—Treatment of *p*-polyphenyl with concentrated sulfuric acid at 264° for 20 hr produced sulfonation of about 60% of the aromatic units. The indicated absorption frequencies were noted in the infrared spectrum: 765, 820–880, 1000–1070, 1170, 1300, 1375, 1600, 1710, 3050, and 3500 cm<sup>-1</sup>. It is conceivable that the product contains some water of hydration.

Marvel and co-workers<sup>7,8</sup> found that sulfonation could be realized with chlorosulfonic acid, fuming sulfuric acid, or concentrated sulfuric acid. Depending on time and temperature, their extent of reaction varied from one sulfur per ring to one for each six rings.

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