

# Oxygenation of Toluene with Diisopropyl Peroxydicarbonate-Cupric Chloride<sup>1</sup>

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**Abstract:** The direct synthesis of tolyl isopropyl carbonates was accomplished in good yield with the system diisopropyl peroxydicarbonate-toluene-cupric chloride-acetonitrile at 60°. Isopropyl alcohol and carbon dioxide are also generated. Kinetic data and other evidence demonstrate that aromatic oxygenation is a chain process involving alkoxy-carboxy radicals and catalysis by copper halides. The ester was apparently formed from the oxy radical, aromatic substrate, and cupric chloride as precursors. A study of various reaction parameters indicated maximum involvement of oxygenation when excess toluene and more than catalytic amounts of the metal salt were used. Minor competition is afforded by decarboxylation of the isopropoxy-carboxy radical with resultant attack on active hydrogen sources by the alkoxy radical. Of a number of solvents investigated acetonitrile was found to be the most effective. This mild, efficient, and simple oxygenation procedure displays synthetic potentiality.

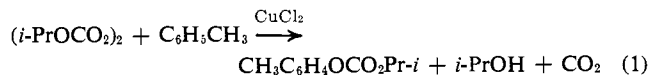
Aromatic oxygenation with peroxides is commonly effected by electrophilic attack resulting from heterolytic fission,<sup>3,4</sup> or by a radical pathway *via* homolytic cleavage.<sup>5</sup> In the polar category, conditions usually include the use of a Lewis acid catalyst. According to this technique oxygenation has been carried out with hydrogen peroxide,<sup>6</sup> peracids,<sup>7</sup> diacyl peroxides,<sup>8</sup> and peroxy-carbonates.<sup>9-11</sup> Various investigators have postulated the operation of an ionic mechanism in selected systems even in the absence of added catalyst, *e.g.*, with trifluoroperacetic acid<sup>12,13</sup> and nitrobenzenesulfonyl peroxides.<sup>14</sup> Illustrations of the radical type include hydroxylation with Fenton's reagent<sup>15</sup> and irradiated aqueous solutions,<sup>16</sup> and benzoyloxylation that in certain cases accompanies aromatic phenylation with benzoyl peroxide.<sup>5,17</sup> Significant advances have been made in the theoretical aspects of homolytic aromatic substitution,<sup>5,18</sup> although admittedly the area

has received less attention than its electrophilic counterpart. More detailed surveys of the prior literature for free-radical<sup>5,19</sup> and electrophilic<sup>3,4,9,10</sup> oxygenation can be found elsewhere.

This report<sup>20</sup> deals with a novel method of aromatic oxygenation entailing the system diisopropyl peroxydicarbonate-cupric chloride. The present study, which employs toluene as the aromatic substrate, demonstrates the synthetic potential and provides evidence for the mechanistic pathway.

## Results and Discussion

The standard procedure involved reaction for 2 hr at 60° with a toluene:diisopropyl peroxydicarbonate:cupric chloride ratio of 17.3:1:0.3 in acetonitrile as solvent. The homogeneous reaction mixture yielded tolyl isopropyl carbonates in 85% yield together with nearly theoretical amounts of isopropyl alcohol and carbon dioxide (Table I). The over-all stoichiometry of the reaction is expressed in eq 1. In addition, acetone and



benzyl chloride were formed in minor proportions from the incursion of side reactions. Substitution of cuprous chloride for cupric chloride resulted in a substantial diminution of the aryl ester yield, although the isomeric composition remained the same. In a control experiment with the peroxide and toluene in solvent, less than 1% of the nuclear oxygenation product was found. Acetone, isopropyl alcohol, and materials arising from free-radical processes involving toluene constituted the major products, as in the cuprous chloride experiment. The favorable oxygenation efficiency in the presence of cupric chloride is not surprising since alkoxy-carboxy radicals are not highly prone (less so than alkoxy radi-

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(20) For a preliminary account, see P. Kovacic and M. E. Kurz, *J. Am. Chem. Soc.*, **88**, 2068 (1966).

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- (6) D. H. Derbyshire and W. A. Waters, *Nature*, **165**, 401 (1950); J. D. McClure and P. H. Williams, *J. Org. Chem.*, **27**, 24 (1962).
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- (18) C. Rüchardt and E. Merz, *Tetrahedron Letters*, 2431 (1964);

Table I. Oxygenation of Toluene with Diisopropyl Peroxydicarbonate-Copper Chlorides<sup>a</sup>

Catalyst	Products, % <sup>b</sup>				Iso-propyl alcohol	Acetone	CO <sub>2</sub> <sup>c</sup>	Benzyl-X <sup>d</sup>	Σ <i>i</i> -Pr, % <sup>e</sup>	ΣCO <sub>2</sub> , % <sup>f</sup>
	Tolyl isopropyl carbonates									
	Yield	<i>o</i>	<i>m</i>	<i>p</i>						
CuCl <sub>2</sub>	85	57	15	28	114	16	116	6 <sup>g</sup>	107	100
CuCl <sup>h</sup>	5	58	15	27	132	55	...	20 <sup>i</sup>	96	...
None	0.7	51	13	36	120	68	180	17 <sup>j</sup>	95	91

<sup>a</sup> Toluene:peroxide:catalyst = 17.3:1:0.3, acetonitrile solvent, 60°, 2 hr; see General Procedure. <sup>b</sup> See Experimental Section for yield basis. <sup>c</sup> See Carbon Dioxide Analysis, Method A. <sup>d</sup> X = Cl, CH<sub>2</sub>C<sub>6</sub>H<sub>5</sub>, or O<sub>2</sub>COPr-*i*. <sup>e</sup> Material balance, based on isopropyl groups:peroxide = 2:1. <sup>f</sup> Material balance, based on CO<sub>2</sub> groups:peroxide = 2:1. <sup>g</sup> Benzyl chloride, 5%; bibenzyl and benzaldehyde, <1% each. <sup>h</sup> Heterogeneous reaction. <sup>i</sup> Benzyl chloride, 12%; bibenzyl, 6%; benzaldehyde, 2%. <sup>j</sup> Bibenzyl, 13%; benzaldehyde, 2%; benzyl isopropyl carbonate, 1%.

cal<sup>21,22</sup>) to participate in hydrogen transfer reactions, and oxidation by cupric salt in the analogous alkene-peroxide system is known to proceed at a high rate.<sup>23</sup>

**Reaction Kinetics.** Using gas evolution as a gauge, we investigated the initial stage of reaction in a semi-quantitative manner. Short induction periods characterized the decompositions promoted by cupric chloride, whereas significantly longer times were noted in the absence of catalyst. On the other hand, gas evolution was virtually immediate with cuprous chloride as the promoter. These observations are in keeping with findings recorded for alkenes in analogous situations.<sup>22</sup>

In order to obtain more reliable rate data, the three reactions were run at a lower temperature (50°), and the peroxide decomposition was followed both by iodometric and infrared techniques. Reproducible rates and satisfactory correlations were realized with the two methods (Figure 1). The uncatalyzed system displayed good first-order dependence<sup>2</sup> on the peroxide with a rate of  $6.45 \times 10^{-3} \text{ min}^{-1}$ , a half-life of 108 min, and an induction period of about 10 min. With cupric chloride catalysis, peroxide decomposition plotted nicely on a pseudo-first-order<sup>2</sup> basis with a rate of  $6.6 \times 10^{-2} \text{ min}^{-1}$  and a half-life of 10.4 min. Hence, the cupric chloride reaction was roughly ten times faster than that without a catalyst, possessing the earmarks of a chain process. As can be seen in Figure 1, the run with cuprous chloride was initially the fastest up to about 30% decomposition of the peroxide, but the rate subsequently fell off to a velocity quite similar to that for the thermal reaction. The experiment with peroxide and cupric chloride (no toluene) was more complex in its kinetics. Qualitatively, the initial rate was only slightly faster than that observed in the absence of metal salt, and not as rapid as the catalyzed reaction in the presence of toluene.

Our results are in accord with those of previous workers who reported first-order kinetics for the decomposition of this peroxide in selected solvents.<sup>24,25</sup> Pseudo-first-order rates have been observed for the copper-catalyzed breakdown of peresters in the presence of olefins at relatively high concentrations of copper salt.<sup>26</sup>

(21) C. Walling and P. J. Wagner, *J. Am. Chem. Soc.*, **86**, 3368 (1964); C. Walling and B. B. Jacknow, *ibid.*, **82**, 6108 (1960).

(22) J. K. Kochi and H. E. Mains, *J. Org. Chem.*, **30**, 1862 (1965).

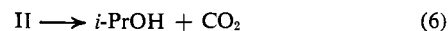
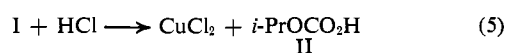
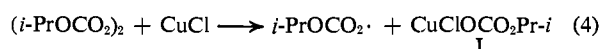
(23) J. K. Kochi and R. V. Subramanian, *J. Am. Chem. Soc.*, **87**, 4855 (1965).

(24) F. Strain, W. E. Bissinger, W. R. Dial, H. Rudoff, B. J. DeWitt, H. C. Stevens, and J. H. Langston, *ibid.*, **72**, 1254 (1950).

(25) S. G. Cohen and D. B. Sparrow, *ibid.*, **72**, 611 (1950).

(26) C. Walling and A. A. Zavitsas, *ibid.*, **85**, 2084 (1963); P. W. C. Barnard and N. C. Yang, *Chem. Ind. (London)*, 1573 (1961).

**Mechanistic Aspects.** On the basis of the experimental findings and by analogy with certain aspects of the theoretical proposals of Kochi for alkene-containing systems,<sup>22</sup> the indicated mechanism is proposed.



The induction period associated with cupric chloride was due to the necessity of thermal homolysis (eq 2) for chain initiation. Equation 3 is similar to the scheme ad-

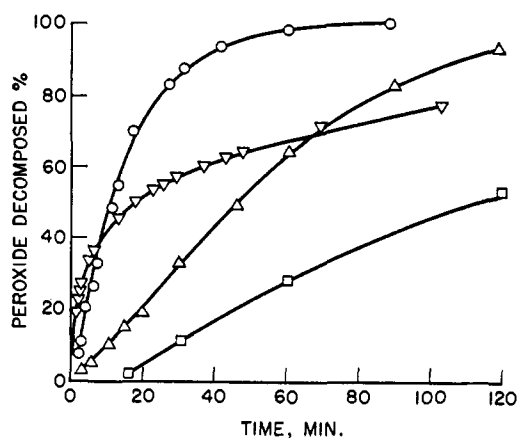


Figure 1. Catalyzed decomposition of diisopropyl peroxydicarbonate (0.02 *m*) in toluene (0.346 *m*) and acetonitrile at 50°: O, CuCl<sub>2</sub> (0.006 *m*); ∇, CuCl (0.006 *m*); □, no catalyst; Δ, CuCl<sub>2</sub> (0.006 *m*), no toluene.

vanced by Kochi and Gilliom<sup>27</sup> for intramolecular oxygenation observed in the decomposition of di-*o*-phenylbenzoyl peroxide catalyzed by cupric acetate. When cuprous chloride was the promoter it attacked the peroxide directly (eq 4). Induced decomposition of peroxides by cuprous salt is well documented.<sup>23,28,29</sup> Judging from the relative magnitudes of the catalyzed and uncatalyzed reaction rates at 50°, it is probable that the peroxide was predominantly consumed in the in-

(27) J. K. Kochi and R. D. Gilliom, *J. Am. Chem. Soc.*, **86**, 5251 (1964).

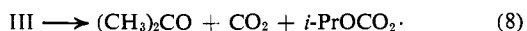
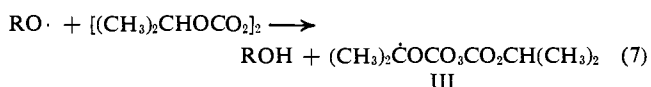
(28) G. Sosnovsky and S. O. Lawesson, *Angew. Chem. Intern. Ed. Engl.*, **3**, 269 (1964).

(29) J. K. Kochi, *Tetrahedron*, **18**, 483 (1962).

duced decomposition (eq 4) when cupric chloride was employed.

On the basis of the poor yield of ester and sudden decline in initial rate for the cuprous chloride catalyzed reaction, it appears that the mixed copper salt (I) generated in the induced decomposition<sup>30</sup> (eq 4) does not act effectively as an oxidant, and hence breaks the chain unless it can undergo metathesis to cupric chloride. With added cupric chloride, hydrogen chloride is apparently formed (eq 3) and then reacts with I (eq 5) to regenerate cupric chloride.<sup>22,29</sup> Since there is reason for believing that chloride ion forms more stable  $\text{Cu}^{\text{II}}\text{X}$  species than does acetate, methoxide, or hydroxide ion,<sup>31</sup> the exchange (eq 5) appears plausible. No such source of halide ion is available to I in the cuprous salt reaction, and thus the chain of events cannot be sustained. Indeed the reaction became heterogeneous in this case through precipitation.<sup>29,32</sup> According to the scheme isopropyl alcohol and carbon dioxide mainly arose through the intermediacy of the transient mono-alkylcarbonic acid (II) (eq 6).

The sharp decrease in the velocity of the cupric chloride catalyzed reaction in which toluene was omitted indicates that the aromatic substrate plays an important role in the redox chain process. Catalytic degradation of peroxides by copper salts cannot be maintained in the absence of carbon radicals.<sup>26,29</sup> The slight rate enhancement over the uncatalyzed reaction (with toluene) may have been due to differences in the media,<sup>33,34</sup> or to the presence of small amounts of cuprous salt in the cupric system. Induced decomposition of the type shown in eq 7 and 8 became an important pathway in



the absence of other active hydrogen compounds as evidenced by the higher order dependence on peroxide as the reaction progressed.<sup>24,25,34-36</sup> The aromatic substitution process will be discussed in more detail in a subsequent report.

**Reaction Variables.** A number of reaction variables (toluene-diisopropyl peroxydicarbonate-cupric chloride-acetonitrile system) were studied with the aim of optimizing conditions and obtaining additional information concerning the mechanism. Table II summarizes the effect of alteration in the catalyst:peroxide ratio. Below a ratio of 0.3 the amount of oxygenation decreased substantially, whereas above this level only small increases were noted. The large catalyst requirement, suggesting a sluggish chain reaction, stands in marked contrast to the system alkene-peroxide-catalyst, in which catalytic amounts of copper salt sufficed.<sup>22,28,29</sup> The greater reluctance in our case may lie in the relatively slow conversion of the

(30) J. K. Kochi, *J. Am. Chem. Soc.*, **85**, 1958 (1963).

(31) J. K. Kochi, *ibid.*, **84**, 774 (1962).

(32) In a recent study [C. H. Brubaker, Jr., and M. Wicholas, *J. Inorg. Nucl. Chem.*, **27**, 59 (1965)] cupric alkoxides and mixed halide alkoxides were found to be generally insoluble in organic solvents.

(33) K. Nozaki and P. D. Bartlett, *J. Am. Chem. Soc.*, **68**, 1686 (1946).

(34) W. A. Strong, *Ind. Eng. Chem.*, **56**, No. 12, 33 (1964); G. A. Razuvaev and L. M. Terman, *J. Gen. Chem. USSR*, **30**, 2368 (1960); G. A. Razuvaev, L. M. Terman, and G. G. Petukhov, *Dokl. Akad. Nauk SSSR*, **136**, 628 (1961); *Chem. Abstr.*, **55**, 18590 (1961).

(35) H. C. McBay and O. Tucker, *J. Org. Chem.*, **19**, 869 (1954).

(36) L. M. Terman, *Russ. Chem. Rev.*, **34**, 185 (1965).

**Table II.** Variation in Catalyst: Peroxide Ratio<sup>a</sup>

Catalyst: peroxide, M	Products, % <sup>b</sup>			Gas evolution, cc/min <sup>c</sup>
	Tolyl isopropyl carbonates	Benzyl chloride	Bibenzyl	
None	1	d	13	5
0.1 <sup>e</sup>	27	12	5	11
0.2 <sup>e</sup>	59	14	1	15
0.3	85	5	<1	14
0.5	91	5	1	12
0.95 <sup>f</sup>	87	5	<1	13
2.0 <sup>f</sup>	91	5	<1	...

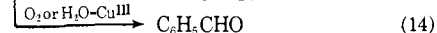
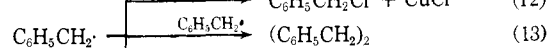
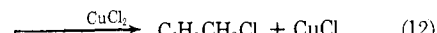
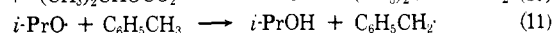
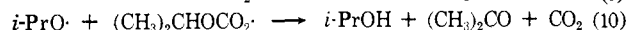
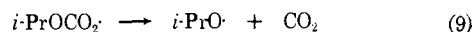
<sup>a</sup> Toluene:peroxide = 17.3:1, 60°, 2 hr, acetonitrile solvent; see General Procedure. <sup>b</sup> See Experimental Section for yield basis.

<sup>c</sup> Apparent rate; average of two runs; see Carbon Dioxide Analysis, Method B. <sup>d</sup> Benzaldehyde, 1%; benzyl isopropyl carbonate, 0.5%; and an unidentified product, 2%, were also present. <sup>e</sup> Mixture became heterogeneous. <sup>f</sup> Additional solvent was used in order to dissolve the catalyst.

mixed salt I to the requisite cupric chloride oxidant (eq 5), thus necessitating the observed minimal initial concentration of effective catalyst for optimum results. In this vein it is significant that copper salt precipitated from reaction mixtures in which a ratio less than 0.3 was used. The apparent rates of decomposition at diverse concentrations of the halide did not vary discernibly (Table II). On the basis of these findings a catalyst:peroxide ratio of 0.3 was adopted as the standard.

In Table III is presented the effect of varying the toluene:peroxide ratio. There was a marked steady decline in the extent of aromatic substitution as the molar ratio of toluene to peroxide was decreased from the 17.3 level with an accompanying increase in the acetone produced. The over-all material balance for the alkyl groups of the peroxide remained good throughout. Hence, quite a large excess of aromatic substrate was required to procure good yields of ester product.

Without appreciable amounts of catalyst and aromatic component, other pathways are favored for the isopropoxycarboxy radical. We believe that it alternatively undergoes decarboxylation to the isopropoxy radical (eq 9). The latter, which is more prone to abstract hydrogen than is an alkoxycarboxy radical,<sup>35</sup> can then react with active hydrogen sources in the system. Removal of a hydrogen atom from an isopropoxy or isopropoxycarboxy radical (eq 10) by disproportionation<sup>35,36</sup> produces acetone and isopropyl alcohol. The same products would result from similar attack on the



peroxide (eq 7 and 8), but this process is deemed important only in the absence of toluene. The excellent first-order fits of the uncatalyzed and cupric chloride catalyzed reactions with toluene connotes the absence of such radical-induced decompositions.<sup>24,25,34-36</sup> Hydrogen abstraction from the side chain of toluene gives rise to isopropyl alcohol and benzyl radical (eq 11). The latter combines with cupric chloride<sup>28,37</sup> yielding

(37) H. E. De La Mare, J. K. Kochi, and F. F. Rust, *J. Am. Chem. Soc.*, **85**, 1437 (1963).

Table III. Variation in Toluene:Peroxide Ratio<sup>a</sup>

Toluene: peroxide, <i>M</i>	Products, % <sup>b</sup>						<i>k</i> <sub>disprop</sub> / <i>k</i> <sub>abstr</sub> <sup>d</sup>
	Tolyl isopropyl carbonates	Acetone	Isopropyl alcohol	Benzyl chloride	Σ <i>i</i> -Pr, % <sup>c</sup>		
None <sup>e</sup>	...	90	99	...	95	...	
None	...	87	103	...	95	...	
1.0	18	69	110	1	99	115	
2.0	28	58	103	2	95	111	
5.0	56	38	109	4	101	103	
10.0	70	29	112	5	105	119	
17.3	85	16	114	5	107	116	
17.3 <sup>e</sup>	<1	68	120	<i>f</i>	95	87	
30.0	83	12	109	5	102	115	

<sup>a</sup> Peroxide:CuCl<sub>2</sub> = 1:0.3, 60°, 2 hr, acetonitrile solvent; see General Procedure. <sup>b</sup> See Experimental Section for yield basis. <sup>c</sup> Material balance, isopropyl groups; based on isopropyl groups:peroxide = 2:1. <sup>d</sup> Ratio of disproportionation/hydrogen abstraction from the solvent by alkoxy radical; obtained by calculating: (per cent disproportionation/per cent H abstraction) × mole ratio of toluene:peroxide. Per cent disproportionation = 2(per cent acetone)/total isopropyl accounted for. Per cent H abstraction = [2(per cent bibenzyl) + % benzyl chloride]/total isopropyl accounted for. See ref 35. <sup>e</sup> No catalyst. <sup>f</sup> Bibenzyl, 13%; benzaldehyde, 2%; and benzyl isopropyl carbonate, 1%.

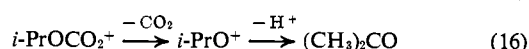
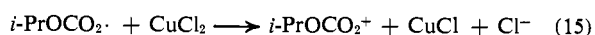
Table IV. Temperature Effect<sup>a</sup>

Temp, °C	Products, % <sup>b</sup>							
	Yield	Total isopropyl carbonates			Acetone	Isopropyl alcohol	Benzyl chloride <sup>c</sup>	Σ <i>i</i> -Pr, % <sup>d</sup>
		<i>o</i>	<i>m</i>	<i>p</i>				
35 <sup>e</sup>	95	57	12	31	6	105	3	103
50	89	57	13	30	8	102	4	100
60	85	57	15	28	16	114	5	107
80	48	58	17	25	35	114	10	99
115 <sup>f</sup>	3	...	...	...	<i>g</i>	<i>g</i>	<i>g</i>	...

<sup>a</sup> Toluene:peroxide:CuCl<sub>2</sub> = 17.3:1:0.3, 2 hr, acetonitrile solvent; see General Procedure. <sup>b</sup> See Experimental Section for yield basis. <sup>c</sup> Benzaldehyde and bibenzyl were present in less than 1% yield in all cases. <sup>d</sup> Material balance, isopropyl groups; based on isopropyl groups:peroxide = 2:1. <sup>e</sup> 8 hr. <sup>f</sup> *n*-Butyronitrile solvent. <sup>g</sup> Not determined.

benzyl chloride (eq 12), dimerizes to bibenzyl (eq 13), or reacts with oxygen or adventitious water in the presence of cupric salt to give benzaldehyde (eq 14).

A competition exists for the hydrogen-abstracting species between the two types of active hydrogen in the system. If acetone is taken as a measure of the extent of disproportionation (eq 10), and the sum of the various products derived from benzyl radical as the amount of abstraction from the toluene side chain (eq 11), a relatively constant ratio of disproportionation to benzyl hydrogen abstraction is observed after correction for concentration changes (Table III).<sup>35</sup> This fairly constant selectivity holds not only over a wide range of toluene:peroxide concentrations, but also for cases in which cupric chloride is both present and absent. On this basis, the isopropoxy radical as the hydrogen abstractor best explains the facts. Indeed the by-products are typical of the chain-transfer reactions of isopropoxy radicals.<sup>24,36,38</sup> This coupled with the rate data in the absence of toluene and the dependence of the catalyzed oxygenation on high concentrations of toluene would tend to rule out oxidation of the isopropoxycarboxy radical (eq 15 and 16). Furthermore, there are no indications from prior studies that oxy radicals undergo oxidation by cupric salts.<sup>22,37</sup>



(38) W. A. Pryor, D. M. Huston, T. R. Fiske, T. L. Pickering, and E. Ciuffarin, *J. Am. Chem. Soc.*, **86**, 4237 (1964).

The effect of temperature is summarized in Table IV. The yield of tolyl isopropyl carbonates is highest at 35° and decreases steadily as the temperature is increased. Decarboxylation of the isopropoxycarboxy radical (eq 8) becomes a more serious competing reaction at the higher temperatures,<sup>36</sup> as evidenced by the decrease in oxygenation and increase in products due to the isopropoxy radical. Elevation in temperature would be expected to diminish selectivity in aromatic substitution, a trend indicated by the increase in *meta* isomer at the expense of *para* as the temperature is raised.

The influence of various additives on the oxygenation pathway is shown in Table V. Small amounts of water did not seriously alter the yield or isomer distribution of the carbonate esters. Running the reaction under an oxygen atmosphere caused no real change in yield. Use of the mixed acetonitrile-acetic acid solvent also did not alter the yield, but did increase the amount of *meta* isomer somewhat. Nitrobenzene exerted a moderate adverse effect, with the isomer distribution remaining essentially the same. Quite strikingly, on addition of pyridine, immediate precipitation of a copper salt occurred with concomitant, virtual elimination of aromatic substitution. Both iodine and sodium iodide caused substantial diminution in the amount of carbonate ester formed.

The results of a more extensive study of other solvents are contained in Table VI, from which the relative effectiveness is rated as indicated: acetonitrile > *t*-butyl alcohol, tetramethylene sulfone, phenylacetonitrile >

Table V. Effect of Additives<sup>a</sup>

Additive	%	Products, % <sup>b</sup>								
		Tolyl isopropyl carbonates			Acetone	Iso-propyl alcohol	Benzaldehyde	Benzyl chloride	Σ <i>i</i> -Pr, % <sup>d</sup>	
Yield	<i>o</i>	<i>m</i>	<i>p</i>							
None	...	85	57	15	28	16	114	<1	5	107
Oxygen	<i>e</i>	89	58	15	27	12	99	3	2	100
Water	0.5	79	60	15	25	19	108	2	5	103
Pyridine	0.5 <sup>f</sup>	4	54	18	28	51	131	2	1	93
Acetic acid	42	87	58	18	24	<i>g</i>	<i>g</i>	1	7	...
Nitrobenzene	13	66	59	15	26	20	123	<1	6	104
Iodine	<i>h</i>	6	49	25	26	7	181	<1 <sup>i</sup>	<1	97
Sodium iodide	<i>j</i>	18	48	31	21	56	124	<1 <sup>i</sup>	12	99

<sup>a</sup> Toluene:peroxide:CuCl<sub>2</sub> = 17.3:1:0.3, 60°, 2 hr, acetonitrile solvent; see General Procedure. <sup>b</sup> See Experimental Section for yield basis. <sup>c</sup> Per cent by volume of the total solvent. <sup>d</sup> Material balance, isopropyl groups; based on isopropyl groups:peroxide = 2:1. <sup>e</sup> Solution continuously saturated with oxygen at 60°. <sup>f</sup> Pyridine:peroxide = 1:1; addition of pyridine caused precipitation of copper salt; reaction was run heterogeneously. <sup>g</sup> Not determined. <sup>h</sup> Iodine:peroxide = 1.5:1. <sup>i</sup> Also iodotoluenes, 3%. <sup>j</sup> NaI:peroxide = 0.3:1; initially homogeneous, subsequently heterogeneous.

Table VI. Solvent Study<sup>a</sup>

Solvent	Products, % <sup>b</sup>					
	Yield	Tolyl isopropyl carbonates			Benzyl chloride	Other
		<i>o</i>	<i>m</i>	<i>p</i>		
Acetonitrile	85	57	15	28	5	1 <sup>c</sup>
<i>n</i> -Butyronitrile <sup>d</sup>	55	59	16	25	...	...
Isobutyronitrile <sup>e</sup>	22	55	15	30 <sup>f</sup>	...	...
Phenylacetone <sup>g</sup>	65	...	...	...	...	...
Ethyl cyanoacetate <sup>d</sup>	14	59	15	26	...	...
Nitromethane <sup>e</sup>	14	58	16	26	...	...
Pyridine <sup>h</sup>	0	...	...	...	1	1 <sup>c</sup>
Dimethylformamide	1	...	...	...	1	1 <sup>c,i</sup>
Dimethyl sulfoxide <sup>j</sup>	0	...	...	...	0	0
Tetramethylene sulfone <sup>e</sup>	66	56	17	27	11	1 <sup>c</sup>
Ethyl acetate <sup>e</sup>	7	63	16	21	...	...
Acetone	44	60	16	24	12	0
Methanol	13	66	19	15	2	3 <sup>k</sup>
Ethanol	15	65	18	17	<1	1 <sup>k</sup>
Isopropyl alcohol	14	63	17	20	0	1 <sup>k</sup>
<i>t</i> -Butyl alcohol <sup>h</sup>	70	68	17	15	6	6 <sup>k</sup>
Acetic acid <sup>d</sup>	7	59	18	23	15	15 <sup>l</sup>

<sup>a</sup> Toluene:peroxide:CuCl<sub>2</sub> = 17.3:1:0.3, 60°, 2 hr; see General Procedure. <sup>b</sup> See Experimental Section for yield basis; acetone and isopropyl alcohol were not determined. <sup>c</sup> Benzaldehyde and bibenzyl. <sup>d</sup> Slightly heterogeneous initially, but homogeneous at end of the reaction. <sup>e</sup> Heterogeneous throughout. <sup>f</sup> Poor agreement in triplicate runs, approximate values only. <sup>g</sup> Solvent interfered with isomer analysis. <sup>h</sup> Initially homogeneous, but heterogeneous at end. <sup>i</sup> Acetone, 20%; isopropyl alcohol, 173%. <sup>j</sup> Very exothermic reaction between the peroxide and solvent. <sup>k</sup> Unidentified, but seemingly formed from reaction of benzyl radicals with solvent. <sup>l</sup> Bibenzyl, 7%; benzyl acetate, 7%; and benzaldehyde, 1%.

*n*-butyronitrile > acetone >> others. Owing to the slight solubility of cupric chloride in many of these solvents, care should be exercised in drawing conclusions from the findings. Nevertheless, a careful gleaning of the data presents some interesting correlations.

One of the implications from the mechanism presented earlier is that there is interconversion of Cu<sup>II</sup> and Cu<sup>I</sup> during reaction. In solvents, e.g., water,<sup>39,40</sup> in which Cu<sup>I</sup> is unstable with respect to Cu<sup>II</sup>, it is expected that oxygenation would not proceed smoothly, whereas those which are characterized<sup>41</sup> by a relatively

high solvation energy for the cuprous ion and/or low solvation energy for the cupric ion should sustain the chain reaction (eq 3-5). Polarographic studies<sup>40,41</sup> indicate that Cu<sup>I</sup> undergoes reversible conversion to Cu<sup>II</sup> in acetonitrile, isopropyl alcohol, acetone, and nitromethane. In fact in acetonitrile the Cu<sup>II</sup>-Cu<sup>I</sup> couple provides a comparatively powerful oxidant.<sup>40</sup> These factors, in addition to the solubility of cupric chloride in acetonitrile, may explain why this solvent is particularly effective. In ethanol and methanol, on the other hand, reduction of Cu<sup>II</sup> to Cu<sup>0</sup> takes place without intervention of Cu<sup>I</sup>.<sup>41</sup> On this basis the moderate yield with acetone and the poor results with ethanol and methanol can be partially rationalized. However, isopropyl alcohol and nitromethane did not prove to be beneficial solvents as might be predicted, indicating that other factors are also important (note the poor solubility of the metal halide in nitromethane, and see the subsequent discussion on isopropyl alcohol). Additional polarographic studies<sup>42</sup> showed that the oxidation potential of cupric ion in nitrile solvents decreases in the order: benzonitrile > phenylacetone > propionitrile > acetonitrile. Thus the predicted ability of cupric chloride to function as oxidant in our system might be expected to follow the above order. Unfortunately, solubility problems with nitriles, other than acetonitrile, render impossible any meaningful correlations.<sup>43</sup>

In addition to the desirable solubility characteristics and solvation effects, the solvent must possess a certain degree of inertness. With several of the media in which oxygenation was not favored, rapid destruction of the peroxide occurred. Addition of the peroxydicarbonate to dimethyl sulfoxide was vigorously exothermic with resultant immediate consumption of the oxidant, in keeping with its known susceptibility to attack by peroxides.<sup>44</sup> On the other hand, tetramethylene sulfone proved to be a good oxygenation solvent. Isopropyl alcohol, with a readily abstractable hydrogen,<sup>36,45</sup>

*Chem.*, 22, 279 (1961); I. V. Nelson and R. T. Iwamoto, *Inorg. Chem.*, 1, 151 (1962).

(42) R. C. Larson and R. T. Iwamoto, *J. Am. Chem. Soc.*, 82, 3526 (1960).

(43) Reaction was not attempted in benzonitrile because of the extreme insolubility.

(44) W. O. Raney and D. C. Nelson in "Organic Sulfur Compounds," Vol. 1, N. Kharasch, Ed., Pergamon Press Inc., New York, N. Y., 1961, p 170; R. Curci and G. Modena, *Tetrahedron*, 22, 1227 (1966).

(39) W. M. Latimer, "Oxidation Potentials," Prentice-Hall, Inc., New York, N. Y., 1952, p 185.

(40) I. M. Kolthoff and J. F. Coetzee, *J. Am. Chem. Soc.*, 79, 1852 (1957).

(41) I. V. Nelson, R. C. Larson, and R. T. Iwamoto, *J. Inorg. Nucl.*

Table VII. Studies with Acetonitrile-Water Solvent<sup>a</sup>

—Solvent, % by vol.—		Products, % <sup>b</sup>							
CH <sub>3</sub> CN	H <sub>2</sub> O	Tolyl isopropyl carbonates				Acetone	Iso-propyl alcohol	Benzyl chloride	Σ <i>i</i> -Pr, % <sup>c</sup>
		Yield	<i>o</i>	<i>m</i>	<i>p</i>				
100	0	85	57	15	28	16	114	5	107
99	1	79	60	15	25	19	108	5	103
95	5 <sup>d</sup>	76	58	17	25	30	114	8	110
90	10 <sup>d</sup>	76	59	17	24	25	116	14	108
85	15 <sup>d</sup>	46	65	16	19	46	135	25	113

<sup>a</sup> Toluene:peroxide:CuCl<sub>2</sub> = 17.3:1:0.3, 60°, 2 hr; see General Procedure. <sup>b</sup> See Experimental Section for yield basis. <sup>c</sup> Material balance, isopropyl groups; based on isopropyl groups:peroxide = 2:1. <sup>d</sup> The initially homogeneous reaction mixture became heterogeneous subsequently.

Table VIII. Studies with Acetic Acid-Water Solvent<sup>a</sup>

—Solvent, % by vol.—		Products, % <sup>b</sup>							
HOAc	H <sub>2</sub> O	Tolyl isopropyl carbonates				Benzaldehyde	Benzyl chloride	Benzyl acetate	Unknown <sup>c</sup>
		Yield	<i>o</i>	<i>m</i>	<i>p</i>				
100 <sup>d</sup>	0	7	59	18	23	1	15	7	<1 <sup>e</sup>
98	2	51	63	19	18	<1	15	3	3
95	5	36	65	18	17	2	17	6	4
90	10	17	66	17	17	1	23	5	4
85	15	11	63	17	20	2	28	5	3

<sup>a</sup> Toluene:peroxide:CuCl<sub>2</sub> = 17.3:1:0.3, 60°, 3 hr; see General Procedure. <sup>b</sup> See Experimental Section for yield basis; acetone and isopropyl alcohol not determined. <sup>c</sup> Glpc retention time fell between those for benzyl chloride and benzyl acetate. <sup>d</sup> Initially heterogeneous; all the rest were homogeneous throughout. <sup>e</sup> Also bibenzyl, 7%.

probably interacted with the isopropoxycarboxy moiety yielding much acetone, accompanied by a paucity of aromatic ester. The analogous process would be expected to a lesser extent with ethanol and methanol. *t*-Butyl alcohol, as anticipated, proved to be more satisfactory, reflecting its relative inertness. Another medium prone to interact with the initially formed radicals was dimethylformamide, as evidenced by the unusually high amount of isopropyl alcohol and low quantity of acetone. Pyridine bases form complexes with cupric ion which are reported to be less potent oxidants than simple cupric salts.<sup>23,46</sup> This loss in oxidation power plus the removal of copper by precipitation explain pyridine's failure to function as a solvent for oxygenation. Solubility constituted the main problem with ethyl acetate.

It is interesting to note the similarity of the ester isomer distribution for the various nitrile solvents, nitromethane, acetic acid, acetone, and tetramethylene sulfone. With the alcohols, slightly higher *ortho:para* ratios were obtained. No clear-cut pattern relating isomer distribution to dielectric constant emerged. Looking at the over-all picture, one can conclude that the effect of solvent on orientation is relatively small. A similar insensitivity to solvent was observed in the composition of octenyl acetates formed from peroxide-copper salt-octene-1.<sup>22</sup>

The acetonitrile-water combination was also explored (Table VII). As the water content in the mixture increased the yield of ester declined. The decrease was small below 10% by volume of water and the changes in isomer distribution were also minor. However, at the 15% level (near the maximum amount of water for

which a single liquid phase could be retained), the oxygenation process seriously suffered, and analysis showed an increase in *ortho* isomer at the expense of *para*. Addition of water appears to have two effects. First, although all the reactions were initially homogeneous, those in which 5% or more of water was present became heterogeneous subsequently. Precipitation of cuprous salts by water is presumably an important factor, thus reducing the concentration of copper necessary to maintain the chain reaction (eq 3-5). A second aspect is the decrease in oxidation potential of the metal ion in the presence of water. Kolthoff and Coetzee found that the half-wave potentials of the cupric-cuprous couple in acetonitrile decreased upon addition of water, while reversibility was maintained.<sup>40</sup>

The oxygenation reaction was also investigated in the acetic acid-water solvent mixture (Table VIII). With glacial acetic acid, only a small amount of oxygenation occurred due to the very low solubility of cupric chloride. Introduction of just enough water to effect homogeneity produced a very substantial increase in the amount of ester formed. Further addition of water caused the yield to diminish sharply. These data, together with the pertinent information from Table V, demonstrate that acetic acid is inherently a favorable medium, but that the difficulty arises from a solubility problem. Once homogeneity is attained, this system is much more sensitive in an adverse manner to incremental additions of water than is the one with acetonitrile.

Finally, a brief comment concerning synthetic utility is in order. Although a variety of procedures are available for introduction of oxygen into the aromatic nucleus, in most cases several steps are required.<sup>47</sup> The peroxydicarbonate-cupric chloride combination

(45) P. Gray and A. Williams, *Chem. Rev.*, **59**, 239 (1959); E. S. Huyser and C. J. Bredeweg, *J. Am. Chem. Soc.*, **86**, 2401 (1964); L. M. Terman, G. A. Razuvaev, and G. G. Petukhov, *Dokl. Akad. Nauk SSSR*, **136**, 1349 (1961); *Chem. Abstr.*, **55**, 18579 (1961).

(46) J. K. Kochi, *J. Am. Chem. Soc.*, **84**, 3271 (1962).

(47) R. B. Wagner and H. D. Zook, "Synthetic Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1953, p 167.

provides a simple, one-step method for preparation of the oxygenated aromatic derivative in high yield. Evidence points to less interference from competing side reactions in comparison with prior processes involving peroxides. Therefore, we anticipate that an investigation of reaction scope will demonstrate the synthetic usefulness of this novel technique.

## Experimental Section<sup>48</sup>

**Materials.** Toluene (Matheson Coleman and Bell Spectral Grade), acetonitrile (Mallinckrodt Nanograde), and the other solvents (high-grade materials) were checked for purity by glpc and generally were used directly. Cupric chloride and cuprous chloride (about 90% pure) (Fisher) were also used without further purification. We are grateful to the Pittsburgh Plate Glass Co. for generous samples of diisopropyl peroxydicarbonate.

**Aromatic Oxygenation with Diisopropyl Peroxydicarbonate. General Procedure.** The metal salt (0.003 mole) was dissolved in the solvent (150 ml) with heating and stirring. The solution (in some cases a suspension) was transferred to a three-necked flask equipped with stirrer, thermometer, gas-inlet tube, addition funnel, and condenser. The flask was immersed in a constant temperature bath at 60°, and a solution (20 ml) of diisopropyl peroxydicarbonate (0.50 *N*) in toluene was pipetted into the pressure-equalizing addition funnel. After the entire system was purged with nitrogen for a few minutes, gas flow was discontinued. The peroxide solution was added rapidly, causing a momentary temperature drop to 55°. In some cases the time from addition of the peroxide to initial evolution of carbon dioxide was noted. Generally the mixture remained homogeneous throughout the reaction, and in most cases peroxide decomposition was complete within 2 hr. At this point, an aliquot was removed for analysis of the low-boiling products, and the remainder of the mixture was stirred with hydrochloric acid (50 ml) and crushed ice (250 g). The organic layer was separated, washed first with a 50% saturated solution of sodium carbonate (three 100-ml portions), then with water, and next dried over sodium sulfate. Iodometric analysis was carried out in some experiments in order to determine the completeness of peroxide decomposition. Qualitative and quantitative analysis of the toluene solution was performed by glpc. When the solvent could not be removed by aqueous extraction, the reaction mixture was investigated directly. Unless otherwise noted, product yields are based on the stoichiometry of 1 mole/mole of peroxide (eq 1), and comprise the average of two or more runs which were in satisfactory agreement. Side products were calculated on this same basis.

**Work-Up Procedure. A. Product Stability and Recovery.** A small amount of *p*-tolyl isopropyl carbonate was dissolved in toluene (10 ml). An aliquot was removed, diluted 1:1 with a marker solution, and shown by glpc to contain 0.00177 mole of ester. Acetonitrile (100 ml) was added to the bulk of the solution, and the mixture was subjected to the standard work-up procedure. After solvent removal, a sample of the remaining toluene solution was diluted 1:1 with the same marker and shown by glpc analysis to contain 0.00176 mole (99% recovery) of *p*-tolyl isopropyl carbonate. Also, in some cases direct analysis for carbonate ester yield and isomer distribution was made on the mixture immediately after reaction, with the results checking to within 3% of the data obtained from the worked-up mixture.

**B. Peroxide Stability.** A toluene solution (10 ml) of diisopropyl peroxydicarbonate (0.50 *N*) was mixed with acetonitrile (75 ml). Following the regular work-up procedure, the dried organic layer was found to be 0.49 *N* by iodometry (less than 2% loss).

**Product Identification.** A portion of the organic solution after work-up was concentrated by removal of most of the aromatic substrate under reduced pressure. The various products were then separated and collected by glpc. Comparison with authentic samples was made (infrared spectrum and glpc retention time). In this manner the isopropyl carbonate esters, benzaldehyde, benzyl chloride, benzyl acetate, iodotoluenes, and bibenzyl were characterized. The more volatile products, acetone and isopropyl alcohol, were identified on the basis of glpc retention time on three different columns with an aliquot from the reaction mixture before work-up.

**Carbon Dioxide Analysis. Method A.** The indicated modifications were applied to the general procedure. A slow flow of nitrogen was maintained throughout the reaction. Exit gases from the condenser were passed through a tube containing Drierite and a preweighed vessel filled with Ascarite. The difference in weight of the vessel plus contents before and after reaction gave the amount of carbon dioxide evolved. Total material balance for carbon dioxide residues by this method fell in the range of 87–100%.

**Method B.** The general procedure was employed with some modification. Immediately after nitrogen flow was discontinued, the exit port was connected to a tube leading into an inverted graduated cylinder filled with a 75% saturated solution of sodium sulfate, and the volume of gas evolved during reaction was determined directly by the amount of solution displaced. According to this method, the total material balance for carbon dioxide residues amounted to 92–111% from runs in which no solvent was used. With acetonitrile solvent the accuracy was such that the method could only be used in a semiquantitative manner. In a control run, a suspension of sodium bicarbonate (0.02 mole) in toluene (20 ml) and acetonitrile (150 ml) was decomposed by addition of excess, dilute hydrochloric acid (35 ml). Carbon dioxide evolution amounted to 260 ml, 0.0116 mole, 58%. This method was used for the determination of induction periods with the same solvent system.

**Authentic Materials.** All of the products with the exception of the carbonate esters were commercially available. Two of the carbonate esters were prepared by a literature procedure:<sup>49</sup> *m*-anisyl isopropyl carbonate, bp 115° (0.9 mm) (*Anal.* Calcd for C<sub>11</sub>H<sub>14</sub>O<sub>4</sub>: C, 62.85; H, 6.71. Found: C, 63.00; H, 6.80), and benzyl isopropyl carbonate, bp 99° (3 mm) (*Anal.* Calcd for C<sub>11</sub>H<sub>14</sub>O<sub>3</sub>: C, 68.02; H, 7.26. Found: C, 67.92; H, 7.40). The remaining carbonate esters are described elsewhere.<sup>10</sup>

**Kinetic Studies. General Procedure.** A few modifications were made of the general procedure for oxygenation. The quantities of the reactants, catalyst, and solvent were doubled, a positive nitrogen flow was maintained throughout reaction, and the temperature was regulated at 50°. The peroxide solution in toluene was added all at once in the usual manner. Aliquots (10 ml) were pipetted at the desired intervals and quickly mixed with ice-hydrochloric acid. After work-up in the usual manner, iodometric analysis was accomplished with 0.01 *N* sodium thiosulfate. Many of the samples were also subjected to infrared analysis (toluene in the reference cell) by measuring the intensity of the band at 11.05 μ characteristic of the peroxide. Comparison with a plot of known concentrations of standard solutions vs. their intensities yielded the concentrations of the unknown solution. It was ascertained that the various products formed in the reaction did not interfere with the absorption frequency used to measure the peroxide concentration. Good agreement was noted between the iodometric and infrared methods of analysis. In addition, excellent checks were obtained for the various rates in duplicate reactions. The results are summarized in Figure 1.

**Analytical Procedures. A. Gas Chromatography.** An Aerograph A-90-P (columns 1–4), a home-made unit (column 5), or an Aerograph Hy-Fi 600C (columns 6–9) gas chromatograph was used: copper column, block temperature, 250°, injector temperature, 300°, bridge current, 195 ma, sample size, 5–30 μl, with the appropriate attenuations for the A-90-P unit; and block temperature, 200°, hydrogen flow, 25 cc/min, sample size 0.4–4 μl, with the appropriate attenuations for the Hy-Fi unit. The columns are described in Table IX.

**B. For Peroxides.** An iodometric method was taken from the literature.<sup>24</sup>

**C. For Product Yields. 1. Carbonate Esters.** Solutions of either trichlorobenzene or phenyl isopropyl carbonate in the aromatic substrates were used as internal standards to determine the yields of the carbonate esters and aromatic by-products. Glpc column 1 at 195° was selected for analysis of the worked up reaction mixtures, and glpc column 7 for direct product analyses on reaction aliquots. The latter procedure also served for oxygenations carried out in tetramethylene sulfone, nitromethane, ethyl acetate, and the nitrite solvents other than acetonitrile. Mesityl isopropyl carbonate in toluene comprised the internal standard in these cases.

**2. Low-Boiling Products.** Glpc column 8 provided the majority of the acetone-isopropyl alcohol analyses, with methyl ethyl ketone in toluene as the internal standard. Some of the yields for the low-

(48) Elemental analyses were performed by Galbraith Laboratories, Knoxville, Tenn. Boiling points are uncorrected.

(49) D. S. Tarbell and E. J. Longosz, *J. Org. Chem.*, **24**, 774 (1959).

Table IX. Glpc Columns

Column	ft	Dimensions in.	Temp, °C	He or N <sub>2</sub> , cc/min	Packing
1	10	0.25	195, 155	75	20% silicone fluid (SF-96) on acid-washed Chromosorb P (30-60 mesh)
2	10	0.25	135	85	20% silicone fluid (SF-96) on acid-washed Chromosorb P (30-60 mesh)
3	6	0.25	190-215	80-100	15% silicone grease (SE-52) on Chromosorb P (30-60 mesh)
4	10	0.25	165	75	15% Apiezon L on acid-washed Chromosorb P (30-60 mesh)
5	10	0.25	45, 120	75-100	20% Carbowax 20M on Chromosorb P (30-60 mesh) (5% NaOH)
6	10	0.13	145	20	5% Carbowax 6000 on Chromosorb W (60-80 mesh)
7	10	0.13	107	20	5% Carbowax 4000 on Aeropak-30 (80-100 mesh)
8	15	0.13	94	15	15% Carbowax 1540 on Chromosorb P (60-80 mesh) (5% KOH)
9	6	0.13	150	12	Poropak Q (80-100 mesh)

boiling products were determined on glpc column 5 (methyl ethyl ketone in acetonitrile as internal standard).

**D. For Isomer Distributions. 1. Carbonate Esters.** Glpc column 6 at 145° was used for the tolyl isopropyl carbonates in most cases. Known mixtures of the various carbonate esters were prepared, plots were made of the peak area ratio *vs.* the concentration ratio, and the data for the product mixtures were compared with these plots. In addition, a combination of the infrared and glpc techniques was used for some of the determinations. The ratio of *ortho*:(*meta* + *para*) tolyl isopropyl carbonates was ascertained by means of glpc column 1. The *meta* and *para* mixture was then carefully collected by gas chromatography (glpc column 2, 195°), and subjected to infrared analysis with carbon disulfide as the solvent. Characteristic bands at 12.2 (*para*) and 14.65 (*meta*)  $\mu$  constituted the basis of the analysis. Known mixtures of the two carbonate esters were prepared, and a plot of the relative intensities of the characteristic infrared bands *vs.* the relative concentrations was procured. Data for the product mixtures were compared to this plot, revealing a deviation of about 1% for the results from the two methods.

**2. Cresols.** When diisopropyl peroxydicarbonate was decomposed thermally in toluene, benzyl isopropyl carbonate and a small amount of unknown product interfered with the usual methods of analysis. The combination infrared-glpc technique described in part 1 above was used. In this case benzyl isopropyl carbonate was also present in the *meta-para* glpc peak. Infrared analysis served satisfactorily for this mixture (a characteristic band at 14.35  $\mu$  was used for the benzyl isomer). In order to check the accuracy of the method, half of the reaction mixture from a large-scale run was hydrolyzed with alcoholic potassium hydroxide after removal of acetonitrile, and the isomeric cresols were determined by infrared spectroscopy according to the previous method.<sup>9</sup> The isomer distributions obtained by the two procedures were in agreement to within 3%.

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