

Aromatic Oxygenation with Benzoyl Peroxide-Iodine¹PETER KOVACIC,² C. GLENN REID,³ AND MATTHIAS J. BRITTAIN⁴*Department of Chemistry, University of Wisconsin—Milwaukee, Milwaukee, Wisconsin 53201, and Department of Chemistry, Case Western Reserve University, Cleveland, Ohio 44106*

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A study was made of the direct synthesis of aryl benzoates from benzoyl peroxide-aromatic-iodine at 90°. After investigation of several reaction parameters, a standard procedure was adopted with toluene as substrate. Quantitative data were obtained for toluene, chlorobenzene, and anisole. The orientations and relative rates indicate that the substitution mechanism is similar to that previously established for the peroxide-cupric chloride reaction. Rates of peroxide disappearance were determined under various conditions. A chain sequence seems to be operative with halogen but not with benzoyl peroxide. The method appears to possess synthetic capability.

The literature describes various approaches to investigation of the peroxide-iodine system. In 1945, Perret and Perrot⁵ reported the formation of aryl benzoates from reaction of benzoyl peroxide with aromatic substrates in the presence of iodine. For example, toluene afforded tolyl benzoates in 64% yield, accompanied by small quantities of *o*- and *p*-iodotoluene. In a similar manner, benzoyloxylation of several arenes was subsequently effected by other investigators.⁶⁻⁸ With only the two reactants, benzoyl peroxide and iodine in carbon tetrachloride, Hammond and Soffer⁹ were able to isolate iodobenzene in high yield. The preparative value of this technique¹⁰ was subsequently improved,¹¹ extended^{12a} to other aryl iodides, and enlarged in relation to the peroxide component.^{12b} Alkyl iodides have been prepared^{11,13} in an analogous fashion, *e.g.*, 1-iodooctane from pelargonyl peroxide. An investigation¹¹ of the benzoyl peroxide-iodine reaction in a variety of solvents revealed that aromatic compounds exerted a deleterious effect on iodobenzene production. Thus, benzoate esters were generated in a competing process when anisole, benzene, and chlorobenzene served as the media. The lack of requisite quantitative information in the existing literature for aromatic oxygenation with the peroxide-iodine combination precluded any meaningful mechanistic interpretation.^{13a}

Previous reports¹⁴⁻¹⁹ from this laboratory have

presented a method for the oxygenation of aromatic compounds involving an appropriate peroxide and cupric chloride. With diisopropyl peroxydicarbonate, toluene afforded tolyl isopropyl carbonates in 85% yield,¹⁵ and benzoyl peroxide gave tolyl benzoates in 40% yield.¹⁶ A study¹⁹ of the effect of variation in the catalyst demonstrated that iodine was relatively ineffective in the toluene-diisopropyl peroxydicarbonate-acetonitrile system.

Our main concern was to elucidate the mechanism of aromatic oxygenation with benzoyl peroxide-iodine. Investigation of a number of reaction variables was carried out, including several aromatic substrates. Quantitative data were obtained for the orientations and relative rates. Attention was also given to the synthetic utility.

Results and Discussion

After exploration of several reaction variables,³ a standard procedure was adopted entailing benzoyloxylation for 20 hr at 90° with a toluene:peroxide:iodine ratio of 12.6:1:0.21, the same relative concentrations employed by Perret and Perrot.⁵ Under these homogeneous conditions, tolyl benzoates were formed in 60% yield (based on peroxide), 50:20:30 *ortho:meta:para*; benzoic acid was formed in 78% yield and carbon dioxide in 37% yield; small amounts of benzene, bibenzyl, biphenyl, methylbiphenyl, phenyl benzoate, iodobenzene, *o*- and *p*-iodotoluenes, and benzyl iodide were also formed. The material balance based on carbon dioxide units was 175%, and the amount of iodine consumed was 62%. The earlier workers⁵ reported no specific orientation data.

The findings from alteration in the catalyst:peroxide ratio are set forth in Table I. The yield of ester declined⁵ when the ratio was less than 0.21 and, at higher values, remained essentially constant or perhaps passed through a maximum. Low ratios favored products derived from breakdown of benzoyloxy radicals, indicating that iodine exerts the net effect of countering decarboxylation. The figure 0.13 represents 62% of the iodine employed in the standard procedure, which is the amount consumed in the reaction. It is obvious that this level of iodine must be augmented for maximum efficiency in oxygenation. Hammond⁸ noted in a similar study that the quantity of ester passed through a maximum during decomposition of the peroxide in benzene containing iodine.

Variation in the toluene:peroxide ratio (Table II)

- (1) Paper XII of a series on aromatic oxygenation.
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TABLE I
 VARIATION IN THE CATALYST:PEROXIDE RATIO^a

Catalyst: peroxide, <i>M</i>	Products, % ^b						
	Tolyl benzoates				Ben- zoic acid	By- products ^c	CO ₂
Yield	<i>o</i>	<i>m</i>	<i>p</i>				
1.00 ^d	57	49	11	40	89	1	13
0.525	63	46	18	36	89	2	10
0.210	60	50	20	30	78	5	37
0.130	35	53	19	28	76	12	46
0.084	16	54	16	30	78	21	100
0.040 ^e	6	58	15	27	90	28	

^a Toluene:peroxide = 12.6:1, 90 ± 2°, 20 hr. ^b See Experimental Section for yield basis. ^c Biphenyl, bibenzyl, and methylbiphenyl. ^d Heterogeneous. ^e Iodine color disappeared after 1 hr.

 TABLE II
 VARIATION IN THE TOLUENE:PEROXIDE RATIO^a

Toluene: peroxide, <i>M</i>	Products, % ^b					
	Yield	Tolyl benzoates			Benzoic acid	By- prod- ucts ^c
<i>o</i>		<i>m</i>	<i>p</i>			
25.5	62	52	17	31	96	7
19.1	63	50	19	31	91	6
12.6	60	50	20	30	78	5
9.55	62	46	22	32	96	1

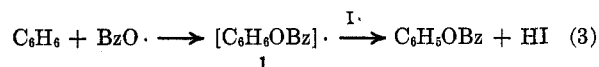
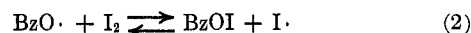
^a Peroxide:iodine = 1:0.21, 90 ± 2°, 20 hr. ^b See Experimental Section for yield basis. ^c Biphenyl, bibenzyl, and methylbiphenyl.

elicited little change in yield of the ester product. With large quantities of toluene reactant, a slight increase was observed in hydrocarbon by-products. The ratio could not be lowered below 9.55 owing to insolubility of the peroxide. Unfortunately, the presence of solvents such as acetonitrile, *o*-dichlorobenzene, or nitromethane, produced a dramatic decrease in yield.⁸

Quite significant information was obtained from a study of the rate of peroxide disappearance at 85° with and without iodine. In the presence of iodine, peroxide decomposition displayed good first-order dependence³ with a rate of $1.6 \times 10^{-3} \text{ min}^{-1}$. First-order dependence, with a rate of $1.7 \times 10^{-3} \text{ min}^{-1}$, also pertained when the halogen was omitted. Hence, little or no difference in rate under the two sets of conditions was detected. These values compare favorably with that ($k = 1.55 \times 10^{-3} \text{ min}^{-1}$ at 79°) previously reported for breakdown of the peroxide in benzene both in the presence and absence of iodine.⁸ Iodine is reported to produce a slight decrease in rate (carbon dioxide evolution) for the decomposition of acetyl peroxide in carbon tetrachloride.²⁰ The use of iodine as a radical trap, *e.g.*, in preventing the induced decomposition of peroxides, has been well documented.^{9,21}

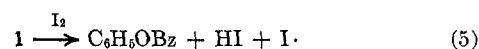
The organic chemistry of iodine is complicated by its versatility—the ready involvement in radical reactions, the variety of oxidation states, its ability to form complexes, and the behavior of possible by-products, such as hydrogen iodide. In light of the present findings, and by analogy with related systems, the salient

features of a plausible mechanism are presented (eq 1–4).



Thermal homolysis of benzoyl peroxide (eq 1) is followed by combination of benzoyloxy radicals with iodine (eq 2) to produce benzoyl hypoiodite and iodine atoms, in accord with the observations of Hammond and Soffer.⁹ One might expect this to be a reversible process,⁵ considering that iodine atoms abstract iodine from alkyl iodides.^{22a} Furthermore, other acyl derivatives of iodine have been reported, such as $\text{I}(\text{OCOR})_3$,¹⁸ and may be present. Equation 3 illustrates aromatic attack entailing the benzoyloxy radicals with subsequent rearomatization by iodine atoms to afford the aryl ester and hydrogen iodide. This pathway is analogous in some respects to that proposed for the peroxide-cupric chloride reactions;^{14–19} the basic similarity in the substitution process is supported by an essentially identical orientation from toluene (*ortho:meta:para* = 56:18:26 with cupric chloride).¹⁶ Although abstraction of alkane hydrogen by iodine atoms is not a facile process,^{22a} the favorable energetics of rearomatization should be taken into account. It is noteworthy that hydrogen transfer between benzyloxy radicals and iodine appears to be exothermic.²³ During oxygenation, iodine could be regenerated subsequently by radical recombination^{22b} or by metathesis of benzoyl hypoiodite and hydrogen iodide²⁴ (eq 4), similar to the interaction of benzoyl hypochlorite with hydrogen chloride.^{25,26} A reviewer suggested that hydrogen iodide might combine with benzoyl peroxide. Whereas a chain process nicely accounts for the tenfold rate increase in peroxide disappearance with copper salt catalysis,¹⁴ it is clear from the decomposition kinetics that such a sequence involving benzoyl peroxide is not occurring in the present case. At the same time, since a relatively small amount of iodine will suffice, a chain reaction with halogen as a link appears to be operative.

Several alternatives for removal of hydrogen from the cyclohexadienyl radical deserve consideration. It is possible that abstraction is effected by molecular iodine (or benzoyl hypoiodite) as illustrated in eq 5. This



possibility resembles the peroxide-cupric chloride process wherein oxidative rearomatization produces esters, hydrogen chloride, and cuprous chloride.¹⁴ Unlike the copper-catalyzed system, however, iodine atoms are ineffective in inducing peroxide decomposition. Since evidence exists that benzoyloxy radicals transform the σ complex in the last step of aromatic

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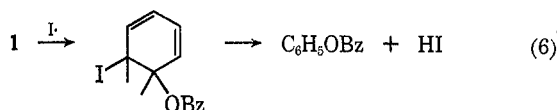
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substitution by phenyl radicals,²⁷ the same pathway may be involved to a minor extent in oxygenation. Also, atomic iodine may add to 1 with subsequent loss of hydrogen iodide (eq 6) in an overall scheme which



amounts to substitution by addition-elimination.²⁸ Addition of benzoyl hypoiodite to the alkene functionality has been recorded.⁵ In any event, a catalyst characterized by efficient oxidizing power is evidently present since this type of component appears to be necessary for smooth operation.^{14,17,19}

The by-products are typical of processes arising from decomposition of benzoyl peroxide.^{27,29} Decarboxylation of benzoyloxy radicals gives phenyl radicals which may dimerize to give biphenyl, or react with toluene by substitution or hydrogen abstraction. Benzyl radicals produced by the latter process account for benzyl iodide and bibenzyl. The small extent of side-chain participation is not surprising since benzoyloxy radicals are known to display a much lower propensity for hydrogen abstraction than do *t*-butoxy radicals.³⁰ Phenyl benzoate is believed to be the result of a cage effect.³¹

Benzoyl hypoiodite presumably serves as the precursor^{9,32} of iodobenzene in a manner similar to the formation of chlorobenzene from the corresponding hypochlorite.²⁵ By analogy with the orientation observed in aromatic halogenation²⁴ by benzoyl peroxide-lithium chloride and by the Hunsdiecker reagent,³² we believe that the *o*- and *p*-iodotoluenes arise via a pathway involving an electrophile^{12b} derived from benzoyl hypoiodite. Perhaps a Lewis acid, *e.g.*, I₂ or HI, is exerting a catalytic effect.^{12b} In a control experiment in the absence of peroxide, aryl iodides were not produced.

Relative rate data for a few of the aromatic substrates are presented in Table III. The minor amounts of phenyl benzoate formed from the peroxide in a side reaction have a negligible effect on the validity of the results. The figure for $k_{\text{toluene}}/k_{\text{benzene}}$, 3.3, is very close to the values recorded for the cupric chloride promoted

TABLE III
RELATIVE RATES WITH BENZOYL PEROXIDE-IODINE^{a,b}

ArH	ArH: C ₆ H ₅ , <i>M</i>	Temp, °C	[ArO ₂ CC ₆ H ₅]: [C ₆ H ₅ O ₂ - CC ₆ H ₅]		Rel rate ^c
Toluene	0.836	88	2.46		2.94 ± 0.01 ^d
Toluene	0.250	84	0.935		3.74 ± 0.15 ^d
Anisole	0.820	89	5.07		6.19 ± 0.05 ^e
Anisole	0.250	87	3.64		14.5 ± 0.10 ^e

^a Relative to benzene. ^b Total aromatic:peroxide:iodine = 51-28:1:0.21, 20 hr; see Experimental Section. ^c Each value is the average of two or more runs in close agreement. ^d Average for all toluene runs, 3.34 ± 0.4. ^e Average for all anisole runs, 10.3 ± 4.

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reactions (2.5 for benzoyl peroxide¹⁶ and 3.8 for peroxydicarbonate¹⁷), which emphasizes the mechanistic parallel.

With diisopropyl peroxydicarbonate-toluene in acetonitrile, iodine was found to be an inefficient catalyst for oxygenation.¹⁹ Table IV summarizes the results

TABLE IV
OXYGENATION OF TOLUENE
WITH DIISOPROPYL PEROXYDICARBONATE^a

ArH, mol	I ₂ , mol	Tolyl isopropyl carbonates			
		Yield, %	<i>o</i>	<i>m</i>	<i>p</i>
17.3	0.3	7 ^b	48	30	22
17.7	0.21	36	58	17	25
12.6	0.21	36	58	17	25

^a Peroxide, 1 mol, 60°. ^b Acetonitrile solvent, 150 ml; see ref 19.

from further investigations of oxygenation with this system, which were obtained at 60° because of thermal instability of the peroxide. Under neat conditions, ester production was increased to 36% with essentially the same orientation as observed for cupric chloride (*ortho:meta:para* = 57:15:28).¹⁴ However, the yield is appreciably greater with benzoyl peroxide, presumably owing to the relative rates of decarboxylation of the isopropoxycarboxy and benzoyloxy radicals under these conditions. It is mechanistically pertinent that the orientations resulting from the two peroxides are similar. At 60° in the presence of iodine, the rate of decomposition of the peroxydicarbonate in toluene⁸ was $5.73 \times 10^{-8} \text{ min}^{-1}$ compared¹⁴ with $6.45 \times 10^{-8} \text{ min}^{-1}$ for the uncatalyzed case at 50° and $6.6 \times 10^{-2} \text{ min}^{-1}$ in the presence of cupric chloride.

A number of other aromatic substrates possessing a range of activities were scrutinized with benzoyl peroxide (Table V). Benzene afforded phenyl benzoate in

TABLE V
OXYGENATION OF AROMATIC COMPOUNDS
WITH BENZOYL PEROXIDE-IODINE^a

Aromatic	Yield	Products, % ^b			Benzoic acid
		<i>o</i>	<i>m</i>	<i>p</i>	
Benzene	62				115
Chlorobenzene	25	47	21	32	49
Anisole	87	47	<1	53	95
<i>m</i> -Dimethoxybenzene	54 ^{c,d}		2,4		122

^a Aromatic:peroxide:iodine = 12.6:1:0.21, 90 ± 2°, 20 hr. ^b See Experimental Section for yield basis. ^c 2,4-Dimethoxyphenol; the nmr spectrum was in accord with this structure. ^d 72% of the unchanged *m*-dimethoxybenzene was recovered by distillation.

62% yield while chlorobenzene produced only modest amounts of an isomeric mixture of esters (for comparison, *ortho:meta:para* = 54:13:33 from peroxydicarbonate-cupric chloride¹⁵ and, for benzoyl peroxide-cupric chloride³³ at 60°, 52:16:32). The indicated yield order, from the present work and earlier studies,⁵ anisole > toluene > chlorobenzene > nitrobenzene, correlates nicely with the electrophilic character of carboxy radicals.¹⁶ We observed the same type of relationship in the studies with diisopropyl peroxydicarbonate-cupric chloride.¹⁵ Thus, further support is

(33) M. E. Kurz and M. Pellegrini, unpublished work; we are grateful to Dr. Kurz for making available these data.

provided for the proposed reaction scheme. Observations concerning the preparation of iodobenzene from benzoyl peroxide-iodine in various solvents are relevant.¹¹ There was essentially an inverse relationship between iodobenzene formation and susceptibility of the aromatic solvent to electrophilic attack (oxygenation was observed as a competing reaction). For example, in chlorobenzene the competing process was claimed to provide 2- and 4-chlorophenyl benzoates in equal amounts. Oldham and Ubbelohde also commented that solvents such as toluene or xylene appear to react with iodine acyls.¹³

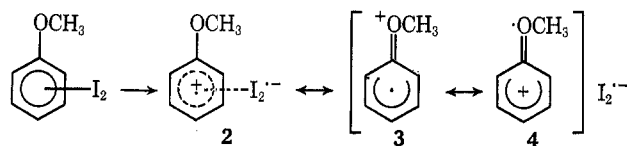
With anisole-benzoyl peroxide-cupric chloride,¹⁶ it was found that the yield of anisyl benzoates decreased from 75 to 56% with an increase in temperature from 60 to 80°, which was attributed to an increased rate of decarboxylation of the benzoyloxy radical at the higher temperature. However, iodine as catalyst at 90° produced anisyl benzoates in 87% yield, in part because of the effect of the halogen in reducing the extent of decarboxylation. In addition to the favorable reactivity of the aromatic substrate, the high yield may also reflect stabilization of benzoyloxy radicals by complexing with the ether oxygen (*cf.* the interaction proposed with bromobenzene³⁴).

The orientations present an even more vivid comparison. Oxygenation both in the neat system (*ortho:para* = 65-82:35-18)³⁵ and in the presence of cupric chloride (*ortho:meta:para* = 68:<1:32)¹⁶ affords high *ortho:para* ratios, just as in the case of diisopropyl peroxydicarbonate-cupric chloride (*ortho:meta:para* = 63:<1:36).¹⁷ The *ortho:para* ratio from benzoyl peroxide-iodine, however, was found to be considerably smaller, *i.e.*, slightly less than one (Table V). In independent work entailing a similar system, equal amounts of the *ortho* and *para* isomers were reported.¹¹ The relative rate data (6-15) for anisole *vs.* benzene (Table III) are close to that (10.4, *cf.*³³ 10.3) observed with copper salt catalysis (compare with 24.9 for peroxydicarbonate-cupric chloride).¹⁴ The decomposition of benzoyl peroxide at 87° in anisole with iodine present displayed good first-order dependence,³ rate of $2.3 \times 10^{-3} \text{ min}^{-1}$, which is negligibly different from the value of $4.98 \times 10^{-3} \text{ min}^{-1}$ for decomposition at 80° in the absence of catalyst.³⁶ In addition there is good correspondence to the data obtained in toluene.

Several interpretations of the anomalous isomer distribution can be advanced. Within the framework of the working hypothesis, it is possible to visualize participation of a bulky attacking species, thus making for reduced entry at the *ortho* position. Since anisole is quite prone to substitution, a somewhat less active radical moiety, such as $\text{C}_6\text{H}_5\text{C}(=\text{O})-\text{O}^\delta\text{---I}^\delta$ or $\text{C}_6\text{H}_5\text{CO}_2\text{---I}_2$, but with an enhanced steric factor, might be able to effect oxygenation. One should bear in mind that appreciable variation in isomer distributions for radical oxygenation can result from changes^{14,19} in catalyst, solvent, time-temperature, or concentration.

Alternatively, a charge-transfer phenomenon might be involved. Studies^{36,37} of iodine-aromatic complexes

indicate that the stability increases with increasing electron donation by the substituent. Also, findings concerning the influence of solvents led to the conclusion that 2 contributes to stabilization of the complex.³⁸



However, substituent effects³⁶ suggest that resonance participation is not pronounced. The canonical form 3 which should be favored over 4 energetically, might possibly interact with a benzoyloxy radical followed by loss of a proton.

One other aromatic ether, *m*-dimethoxybenzene, was explored. The crude ester, which was not isolated, provided 2,4-dimethoxyphenol³⁹ (54% overall yield) on hydrolysis.

A number of the prior investigators who observed aromatic oxygenation under related conditions commented on the mechanistic aspects. By analogy to the behavior of olefins, Perret and Perrot⁵ proposed initial addition of benzoyl hypoiodite to the aromatic nucleus. Rearomatization was then accomplished by liberation of hydrogen iodide. Hammond⁸ hypothesized that the ester is derived from benzoyl hypoiodite and aromatic substrate in an iodine-catalyzed reaction which is nonradical in nature. In benzoyloxylation of chlorobenzene by silver bromide dibenzoate, an electrophilic pathway involving $\text{C}_6\text{H}_5\text{CO}_2 + [\text{Ag}(\text{O}_2\text{CC}_6\text{H}_5)\text{Br}]^-$ was suggested.⁴⁰ However, it is evident from the $k_{\text{chlorobenzene}}/k_{\text{benzene}}$ data (0.34 for the Bryce-Smith and Clarke reagent⁴⁰) that the process is decidedly more akin to free-radical oxygenation¹⁵ (0.46) than to nitration (0.03). Hence, a "complexed" $\text{C}_6\text{H}_5\text{CO}_2\cdot$ species appears to be a more likely participant.

Finally, a brief discussion of synthetic utility^{14,15} would be appropriate. In general, the peroxydicarbonate-cupric chloride combination affords somewhat higher yields of oxygenated product. However, the present procedure, which represents an improvement over the earlier method,⁵ employs the more readily available benzoyl peroxide.

Experimental Section⁴¹

Materials.—Benzoyl peroxide (98%, Eastman) and iodine (Fisher, resublimed) were used as obtained. The solvents and aromatic reagents, of high purity by glpc analysis, were used directly. We are grateful to the Pittsburgh Plate Glass Co. for generous samples of diisopropyl peroxydicarbonate.

Aromatic Oxygenation. General Procedure.—The aromatic reactant (0.942 mol) was placed in a three-neck flask equipped with a stirrer, thermometer-gas inlet, and condenser. The flask was immersed in a constant-temperature bath and allowed to equilibrate at 90° (60° for diisopropyl peroxydicarbonate). Iodine (4 g, 0.0157 mol) was added, followed by benzoyl peroxide (17.92 g, 0.074 mol), causing a momentary temperature drop to 85°. After 20 hr, the mixture was quenched by pouring over ice (200 g), and the layers were separated. As noted in certain cases, the amount of iodine remaining was determined by removal of an aliquot from the reaction mixture. The organic layer from the reaction mixture was washed with sodium thiosulfate solu-

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(41) Boiling points and melting points are uncorrected.

tion (150 ml), saturated sodium carbonate (two 150-ml portions), and water and then dried over sodium sulfate.

A portion of the reaction mixture was concentrated by removal of most of the aromatic substrate under reduced pressure. After the products were separated and collected by glpc, the retention times and infrared spectra were compared with those of authentic samples. In this manner, the benzoate esters, biphenyl, benzyl, methylbiphenyl, iodotoluene, and the chlorobiphenyls were identified. The more volatile products, benzene, iodobenzene, and benzyl iodide, were characterized on the basis of the glpc retention time and peak enhancement with authentic material.

The combined aqueous extract, excluding the sodium thiosulfate wash, was acidified with concentrated hydrochloric acid (75 ml)-ice (50 g). The crude benzoic acid was collected, washed with cold water, and air-dried. Extraction of the filtrate with ether, followed by solvent removal, afforded additional crude benzoic acid which was combined with the first crop. In general, the acid was not further purified.

In the case of *m*-dimethoxybenzene, the reaction mixture was refluxed with 5% ethanolic potassium hydroxide (150 ml) under nitrogen for 2 hr. After removal of most of the ethanol *in vacuo*, the remaining semisolid material was washed with water (150 ml), and the layers were then separated. The organic portion was washed again with 10% sodium hydroxide (150 ml), and the combined aqueous extract was acidified with concentrated hydrochloric acid-ice. The mixture was then extracted with ether (two 150-ml portions), and the ethereal solution was washed with 10% sodium bicarbonate (two 100-ml portions). After removal of most of the ether *in vacuo*, distillation of the residue afforded 5.2 g (54%) of the phenolic product (pure by glpc, column 2), bp 86–90° (1.2 mm), along with 0.33 g (4%) of residue. The *p*-nitrobenzoate derivative melted at 127–128° (lit.⁴² mp 129°). Acidification of the basic extracts of the original reaction mixture yielded 9.21 g (122%) of crude benzoic acid. In a similar manner, 1.2 g of benzoic acid was obtained after hydrolysis of the ester by acidification of the bicarbonate extracts.

Where noted, the additives were introduced into the standard reaction mixture before the iodine and benzoyl peroxide.

Authentic Materials.—Most of the products were commercially available. The benzoate esters were prepared by adaptation of a technique described for aryl isopropyl carbonate esters.⁴³

Competitive Oxygenation.—After the aromatic reactants were equilibrated in the constant temperature bath, iodine and benzoyl peroxide were added as in the general procedure. The molar ratio of total aromatic:peroxide:iodine was 51–28:1:0.21, with a reaction time of 20 hr following peroxide addition. Duplicate runs were performed in each competition with excellent agreement.

Kinetic Studies. General Procedure.—A few modifications of the general procedure for oxygenation were made. The quantities of the reactants were doubled, and the temperature

was maintained at 85°. Aliquots (10 ml) were removed at intervals and quenched with ice. After the usual work-up procedure, iodometric analyses were performed with 0.1 *N* sodium thiosulfate. Control experiments indicated that the peroxide was unaffected by the standard work-up procedure.

Analytical Procedures. A. Gas Chromatography.—A home-made unit and a Varian Model 1800 gas chromatograph were employed: block temperature, 250°; injector temperature, 280°; bridge current, 195 mA; sample size, 5–30 μ l, with the appropriate attenuations for the home-made unit; the block temperature, 250°; injector temperature, 270°; bridge current, 150 mA; sample size, 5–20 μ l, with the appropriate attenuations for the Varian unit. Two columns were used: (1) 6 ft \times 0.25 in., 15% silicone grease (SE-52) on acid-washed Chromosorb P (30–60 mesh), He flow 60 ml/min; and (2) 10 ft by 0.25 in., 5% Apiezon L on acid-washed Chromosorb P (30–60 mesh), He flow 60 ml/min.

B. For Product Yields.—The benzoate esters and aromatic by-products were analyzed as previously described¹⁶ by the method of internal standards, *m*-di(isopropoxycarboxy)benzene except for anisole, in which case α -naphthyl isopropyl carbonate was employed. Glpc column 1 at 150–200° was used for all of the analyses. The yields are based on 1 mol/mol of peroxide.

C. For Isomer Distributions.—A portion of the reaction mixture was concentrated by removal of the residual aromatic substrate under reduced pressure. The *meta*-*para* glpc peak was then collected and subjected to infrared analysis (Beckman IR-8). The molar ratio of the isomers was ascertained by comparing the respective intensity ratios with plots of intensity *vs.* mole ratio for known mixtures of the two isomers.

D. For Carbon Dioxide.—The indicated modifications were applied to the general procedure. A slow flow of nitrogen was maintained throughout the reaction, and the exit gases were passed through a preweighed Ascarite trap. In some cases, where gas evolution was exceptionally vigorous, a cold trap (Dry Ice-acetone) was inserted between the condenser exit and the Ascarite. The difference in weight of the vessel plus contents before and after reaction gave the amount of carbon dioxide evolved.

E. For Competitive Oxygenation.—Glpc column 1 was used in all of the experiments.

F. For Peroxides.—Iodometric methods were taken from the literature.^{44,45}

Registry No.—Benzoyl peroxide, 94-36-0; iodine, 7553-56-2; toluene, 108-88-3; chlorobenzene, 108-90-7; anisole, 100-66-3.

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