Aromatic Oxygenation. Behavior of Toluene in the Organic Peroxide–Cupric Chloride System[1]

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Copper chloride catalyzed decomposition of a variety of peroxides was conducted in the presence of toluene in acetonitrile, and the resulting products were determined. With dicyclohexyl peroxydicarbonate, benzoyl peroxide, and benzoylperoxyisopropyl carbonate, aromatic oxygenation was noted. Results from the unsymmetrical peroxide indicated predominant participation of aroyloxy, rather than alkoxycarboxy, radicals. The mechanism of substitution is discussed in the light of the recently discovered aromatic substitution process in the diisopropyl peroxydicarbonate–cupric chloride–aromatic substrate system. No oxygenation was observed with *t*-butyl peresters which gave instead products characteristic of the *t*-butoxy radical. Lauroyl peroxide and perbenzoic acid were also unsuccessful in effecting nuclear substitution. Rapid fragmentation of the acyloxy radical is the rationale for the diacyl peroxide reaction. The nature of the oxygen radical required for success in the oxygenation process is discussed.

Since the discovery that copper salts drastically alter the pathway of peroxide reactions,[3] a considerable amount of work has been devoted to delineation of the mechanism.[4–7] The role of the peroxide is to provide oxygen radicals which can react with the substrate in various ways to produce the carbon radicals involved in subsequent interaction with the cupric salt. The most general means of carbon radical formation is that of hydrogen abstraction by the oxy radical from a suitable substrate, *e.g.*, alkene, aralkane, alcohol, ether, or carbonyl compound.[6] *t*-Butyl peresters, which afford the *t*-butoxy radical, have served best in this capacity,[5,6] although hydroperoxides,[8,9] and dialkyl[10,11] or diaroyl[10,12] peroxides have occasionally been used. A second route entails fragmentation as exhibited by acyloxy radicals arising from diacyl peroxides[4,7,13] and by alkoxy radicals containing appropriate alkyl groups.[14] In suitable situations a third mode of carbon radical generation can come into play, that of radical addition to olefinic compounds. For example, *t*-butoxy radicals add to conjugated dienes[4,9] and norbornadiene,[15] and benzoyloxy radicals to alkenes,[12,16] with the derived radicals then undergoing the usual oxidation by copper salt. This last method, which has been utilized less frequently, is sometimes in competition with hydrogen abstraction processes.[12]

Application of the peroxide-reducible metal salt system to aromatic substrates has received little attention. Hydroxylation, accomplished with Fenton's reagent in this manner, was shown to be facilitated by the presence of ferric ions.[17] Kochi and Gilliom,[18] who investigated intramolecular oxygenation with di-*o*-phenylbenzoyl peroxide, observed yield enhancement on addition of copper salt. Oxidation of an intermediate radical complex was postulated in the prior investigations.[17–19] Recently we reported a simple and efficient new procedure for intermolecular oxygenation using the aromatic substrate–copper salt combination. Thus, diisopropyl peroxydicarbonate was found to interact with toluene in the presence of cupric chloride to form tolylisopropyl carbonates in high yield.[20] The nature of the intermediate oxy radical is inferred to be quite vital to the success of the procedure.

The purpose of this study was to investigate the reaction behavior of various peroxides toward toluene in the presence of cupric chloride. Our primary interest was the degree of specificity required of the peroxide for aromatic oxygenation.

Results and Discussion

A. Peroxycarbonates.—Dicyclohexyl peroxydicarbonate on exposure to toluene–cupric chloride under the standard conditions (aromatic–peroxide–cupric chloride, 16.4:1:0.3; acetonitrile solvent; 60°) gave a 61% yield of tolylcyclohexyl carbonates (Table I). The analogous system with diisopropyl peroxydicarbonate is included for comparison.[20] The overall stoichiometry is represented in eq 1 ($X = Y = C_6H_{11}OCO$ or *i*-PrOCO).

$$\underset{\text{I}}{\text{XOOY}} + C_6H_5CH_3 \xrightarrow{\text{CuCl}_2} CH_3C_6H_4OX + \underset{\text{II}}{\text{YOH}} \qquad (1)$$

Similar types of products were obtained with both peroxides. The carbonate esters have been shown to arise *via* a chain mechanism[20] (eq 2–6). Thermal cleavage of the peroxide (eq 2)

$$\text{I} \longrightarrow \text{XO}\cdot + \text{YO}\cdot \qquad (2)$$

$$\text{XO}\cdot + \text{ArH} \longrightarrow \underset{\text{III}}{\text{XOArH}\cdot} \qquad (3)$$

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(1) Paper VII in the series: for a preliminary account, see P. Kovacic and M. E. Kurz, *Tetrahedron Lett.*, 2689 (1966).

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TABLE I

DIALKYL PEROXYDICARBONATE–TOLUENE–CUPRIC CHLORIDE[a]

$(ROCO_2)_2$	Products, %[b]									
	Tolylalkyl carbonates									
R =	Yield, %	o	m	p	ROH[c]	$R_2'CO$[d]	Benzyl chloride	CO_2	ΣR, %[e]	ΣCO_2, %[f]
Cyclohexyl	61	53	17	30	g	g	9	138	...	100
Isopropyl[h]	85	57	15	28	114	16	5	116	107	100

[a] Toluene–peroxide–$CuCl_2$, 16–18:1:0.3; acetonitrile solvent; 60°; 2 hr; see general procedure. [b] See Experimental Section for yield basis. [c] Cyclohexanol or isopropyl alcohol. [d] Cyclohexanone or acetone. [e] Material balance, based on alkyl groups/peroxide = 2:1. [f] Material balance, based on CO_2 groups/peroxide = 2:1. [g] Qualitative data only. [h] Ref 20.

TABLE II

BENZOYLPEROXYISOPROPYL CARBONATE–TOLUENE–CUPRIC CHLORIDE[a]

Products	Yield, %[b-d]
Tolyl benzoates[e]	33
Tolylisopropyl carbonates[f]	3
Methylbiphenyls	3
Chlorobenzene	28
Benzene	18
Isopropyl alcohol	95
Acetone	3
Benzoic acid[g]	25
Benzyl chloride	3

[a] Toluene–peroxide–$CuCl_2$, 15.6:1:0.3; acetonitrile solvent; 60°; 4–6 hr; homogeneous; see general procedure. [b] See Experimental Section for yield basis. [c] Σ(phenyl) = 107%; material balance, based on phenyl groups/peroxide = 2:1. [d] Σ(isopropyl) = 101%; material balance, based on isopropyl groups/peroxide = 2:1. [e] o/m/p = 59:17:24. [f] Isomer distribution could not be determined due to interference by methylbiphenyls. [g] Obtained by potentiometric titration; corrected for acid impurity in the peroxide.

$$\text{III} + CuCl_2 \longrightarrow XOAr + CuCl + HCl \qquad (4)$$

$$XOOY + CuCl \longrightarrow XO\cdot + \underset{\text{IV}}{CuClOY} \qquad (5)$$

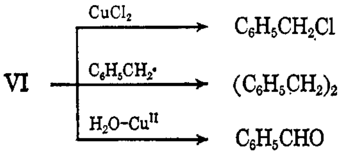
$$\text{IV} + HCl \longrightarrow \text{II} + CuCl_2 \qquad (6)$$

affords the oxy radicals needed to initiate the chain, with subsequent attack on the aromatic substrate (eq 3) and oxidation of the resulting radical adduct (III) (eq 4) leading to the aromatic product and cuprous salt. Induced decomposition of the peroxide ensues (eq 5) regenerating oxygen radicals and cupric salt. The requisite cupric halide catalyst[20] is obtained by metathesis of the mixed salt (IV) with hydrogen chloride (eq 6), thus completing the chain. Breakdown of the alkylcarbonic acid (II) would produce

$$\underset{\text{V}}{ROCO_2\cdot} \longrightarrow RO\cdot + CO_2 \qquad (7)$$

$$RO\cdot + \text{V} \longrightarrow ROH + R_2'CO + CO_2 \qquad (8)$$

$$RO\cdot + C_6H_5CH_3 \longrightarrow ROH + \underset{\text{VI}}{C_6H_5CH_2\cdot} \qquad (9)$$



$$\text{VI} \xrightarrow{CuCl_2} C_6H_5CH_2Cl \qquad (10)$$

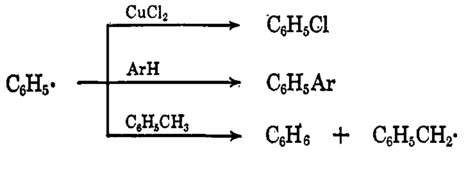
$$\text{VI} \xrightarrow{C_6H_5CH_2\cdot} (C_6H_5CH_2)_2 \qquad (11)$$

$$\text{VI} \xrightarrow{H_2O\text{-}Cu^{II}} C_6H_5CHO \qquad (12)$$

cyclohexanol and carbon dioxide. Less than quantitative yields of aryl ester accompanied by the alcohol and carbon dioxide in excess of theory were noted with both peroxides. Competing decarboxylation of the alkoxycarboxy radical is invoked as being responsible for this phenomenon and the other side products (eq 7–12). With diisopropyl peroxydicarbonate the decarboxylation route provided only minor competition at 60°, whereas with dicyclohexyl peroxydicarbonate it became more important. Indeed, the uncatalyzed rates of decomposition in toluene showed that the cyclohexyl homolog lost carbon dioxide nearly twice as fast as its diisopropyl counterpart.[21] With this background, the lower yield of tolylalkyl carbonate and greater amount of side products with the former peroxide can be rationalized. Only qualitative determinations of cyclohexanol and cyclohexanone were made. As was anticipated, the isomer distributions of the aryl esters from both peroxides were quite similar.

The mixed peroxycarbonate, benzoylperoxyisopropyl carbonate (I, X = C_6H_5CO, Y = i-PrOCO), was prepared and then allowed to fragment in contact with cupric chloride and toluene (Table II). With this unsymmetrical peroxide, two types of oxygenated product were obtained, tolyl benzoates and tolylisopropyl carbonates. The former predominated indicating that most of the peroxide underwent induced decomposition to form benzoyloxy radicals and the alkoxycarboxylate salt (eq 5; X = C_6H_5CO, Y = i-PrOCO). The benzoyloxy radicals oxygenated toluene (eq 2–6), abstracted hydrogen from toluene to generate benzoic acid and benzyl radicals (eq 9), or lost carbon dioxide to produce phenyl radicals (eq 13).[22] In sequential continuation phenyl radicals partake in a number of transformations: oxidation by cupric chloride to chlorobenzene (eq 14),[23] substitution in toluene leading to methylbiphenyls (eq 15),[22] or hydrogen abstraction from toluene to give benzene and benzyl radicals (eq 16).[22] Benzyl radicals, in turn, were oxidized to benzyl chloride by the metal halide (eq 10). Isopropyl alcohol apparently arose mainly *via* decarboxylation of i-$PrOCO_2H$ formed in eq 6. Although the isopropoxycarboxy radicals may

$$C_6H_5CO_2\cdot \longrightarrow C_6H_5\cdot + CO_2 \qquad (13)$$



$$C_6H_5\cdot \xrightarrow{CuCl_2} C_6H_5Cl \qquad (14)$$

$$C_6H_5\cdot \xrightarrow{ArH} C_6H_5Ar \qquad (15)$$

$$C_6H_5\cdot \xrightarrow{C_6H_5CH_3} C_6H_6 + C_6H_5CH_2\cdot \qquad (16)$$

have arisen by the induced decomposition occurring in part by the alternative cleavage (eq 5, X = i-PrOCO, Y = C_6H_5CO), this minor route might also result from thermal homolysis of the peroxide (eq 2). Intervention of alkoxycarboxy radicals also accounts for the acetone. Good material balance for both phenyl and isopropyl groups of the peroxide was noted.

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Thus, all the products are explicable on the basis of the mechanistic scheme with preferential involvement (greater than 90%) of the benzoyloxy radical. The isomeric composition of the tolyl benzoates ($o/m/p$ = 59:17:24) was virtually the same as from benzoyl peroxide (*vide infra*).

The behavior of still another type of peroxycarbonate, *t*-butylperoxyisopropyl carbonate (I, X = *t*-butyl, Y = *i*-PrOCO) was scrutinized in a similar fashion. Due to the greater thermal stability of this peroxide, much longer reaction times were required. Unlike most of the other peroxide systems, this mixture became heterogeneous from salt deposition as reaction progressed. Elemental analysis of the precipitate pointed to the presence of copper salts containing both halide and oxygen-containing ligands. The major organic products were isopropyl alcohol, *t*-butyl alcohol, and acetone (Table III). No nuclear substitution involving toluene was observed.

Table III

t-Butylperoxyisopropyl Carbonate–Toluene–Metal Halide Products, %[a,b]

	From $CuCl_2$	From $FeCl_3$
Isopropyl alcohol	80	84
t-Butyl alcohol	62	13
Acetone	39	80
Methyl chloride	7	17
Benzyl chloride	23	c
Benzaldehyde	4	c

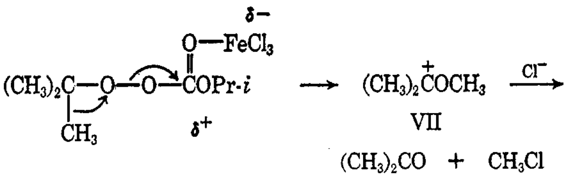
[a] Toluene/peroxide/$CuCl_2$, 18.3:1:0.3; acetonitrile solvent; 60°; 42–72 hr; heterogeneous reaction mixture; see general procedure. [b] See Experimental Section for yield basis. [c] Not determined.

The absence of oxygenation products indicated that few, if any, isopropoxycarboxy radicals were generated during scission. Acceleration of the rate with metal halides provided good evidence for induced decomposition, evidently giving rise to *t*-butoxy radicals (eq 5, X = *t*-Bu, Y = *i*-PrOCO). The alkoxy radicals behaved in their usual manner (eq 9 and 17).[24,25] Oxidation of methyl radicals resulted in the observed methyl chloride (eq 18).[26] The discussion on isopropyl alcohol in the preceding section can also be applied to this case.

$$(CH_3)_3CO\cdot \longrightarrow (CH_3)_2CO + CH_3\cdot \qquad (17)$$

$$CuCl_2 + CH_3\cdot \longrightarrow CH_3Cl + CuCl \qquad (18)$$

The use of ferric chloride instead of the copper salt increased the amount of acetone at the expense of *t*-butyl alcohol (Table III). Since *t*-butoxy radicals in a given substrate generally react in the same manner regardless of their mode of formation,[8b,27] the significant change in this case indicates that the metal salt altered the reaction course. A possible rationalization invokes complexing at the carbonyl group of the peroxide by ferric chloride[21] leading to an intramolecular ionic rearrangement (eq 19).[28] Combination of the resulting carbonium ion (VII) with chloride ion followed by subsequent collapse to acetone and methyl chloride could well account for the observed results.



$$(CH_3)_2\underset{CH_3}{C}-O-O-\overset{\overset{\delta-}{O-FeCl_3}}{C}OPr\text{-}i \longrightarrow \underset{\text{VII}}{(CH_3)_2\overset{+}{C}OCH_3} \xrightarrow{Cl^-} (CH_3)_2CO + CH_3Cl \qquad (19)$$

B. Diacyl Peroxides.—Benzoyl and lauroyl peroxides, representative of the diaroyl and diacyl types, were investigated in the presence of cupric chloride–toluene–acetonitrile. Because of the low rate of disintegration of benzoyl peroxide in this system at 60°, a small amount of cuprous chloride was added (reaction times of 19–26 hr). Tolyl benzoates were formed in 38% yield with a catalyst/peroxide ratio of 0.3 (Table IV). Increase of this ratio to 0.5 and 1 did not appreciably alter the product composition, but a decrease to 0.15 lowered the ester yield to 14%. Benzoic acid, chlorobenzene, benzene, methylbiphenyls, carbon dioxide, and benzyl chloride were produced in addition to the aryl esters. The over-all material balance for both the phenyl and carbon dioxide residues was good. In a control run (no copper salt) carried out for 144 hr, less than 1% of aryl ester resulted, and the peroxide was only 60% consumed. Benzene, methylbiphenyls, benzaldehyde, and benzoic acid were the major reaction products. When cuprous chloride was substituted for the cupric salt, incomplete peroxide decomposition afforded meager quantities of oxygenation product. Omission of the trace of cuprous chloride in the standard procedure caused a slight increase in the time necessary for reaction and some fall-off in yield of the aryl ester.

The pathways involved in the derivation of these products were discussed in connection with benzoylperoxyisopropyl carbonate as substrate. In the case of the symmetrical peroxide, the anionic half generated in the induced decomposition (eq 5, X = Y = C_6H_5CO) forms benzoic acid upon metathesis (eq 6) or work-up. Under our usual conditions, 37–45% of the benzoyloxy radicals decarboxylated to phenyl radicals (eq 13), 34–41% oxygenated toluene (eq 2–6), and the remainder (5–15%) reacted by hydrogen abstraction (eq 9). Chlorobenzene formation increased at higher catalyst concentrations.

Semiquantitative rate observations are in harmony with the more detailed studies reported for diisopropyl peroxydicarbonate–cupric chloride.[20] Both cupric and cuprous chloride catalyzed the reaction, but with the latter, the rate tapered off after the initial, rapid decomposition. Apparently the mixed copper salt (IV) is unable to regenerate cuprous ion effectively.[20,21]

The isomer distribution of the tolyl benzoates ($o/m/p$ = 56:18:26) was quite similar to the ester compositions from the dialkyl peroxydicarbonate experiments. Further evidence for a mechanistic parallel in the two cases is derived from the relative rate data ($k_{\text{toluene}}/k_{\text{benzene}} = 2.51$ for the diaroyl peroxide (Table V) and 3.77 for the peroxydicarbonate).[29]

The cupric chloride catalyzed benzoyloxylation of anisole was performed both at 60 and 80° (Table IV).

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TABLE IV

AROMATIC OXYGENATION WITH BENZOYL PEROXIDE–CUPRIC CHLORIDE[a]

Aromatic reactant	$CuCl_2$/ peroxide, M	Products, %[b]											
		Aryl benzoates[c]											
		Yield, %	*o*	*m*	*p*	Benzene	Chlorobenzene	Biphenyls[d]	Benzoic acid[e]	Benzyl chloride	CO_2	Σ(phenyl), %[f]	Σ(CO_2,) %[g]
Toluene	0[h]	1	...	...	...	24	0	12	...	0[i]	...	...	...
Toluene	0.15[j]	14	...	...	...	17	6	9	74	2	58	94	112
Toluene	0.3	38	56	18	26	14	27	4	113	5	...	96	...
Toluene	0.3[k]	25	...	...	...	18	23	4	115	6	43	97	96
Toluene	0.3[l]	6	...	...	...	24	6	7	...	2	...	...	...
Toluene	0.5	41	56	18	26	7	27	3	108	3	57	93	104
Toluene	1.0[m]	34	56	18	26	5	36	1	115	2	...	97	...
Toluene	1.0[n]	7	...	...	...	...	...	1	...	...	...	...	...
Anisole	0.3	75	68	<1	32	4	15	1	119	3[p]	32	107	113
Anisole	0[q]	0	...	...	...	77	0	27[r]	74	0	...	93	...
Anisole	0.3[s]	56	67	<1	33	10	26	3	120	3[n]	14	107	95

[a] Aromatic/peroxide, 16.3–16.8:1; acetonitrile solvent; cuprous chloride (0.02 mol % of the peroxide) was added; 60°, 19–26 hr; see general procedure. [b] See Experimental Section for yield basis. [c] Tolyl benzoates from toluene, anisyl benzoates from anisole. [d] Methylbiphenyls from toluene, methoxybiphenyls from anisole. [e] Determined by potentiometric titration. [f] Material balance, phenyl groups; based on phenyl groups/peroxide = 2:1. [g] Material balance, CO_2 residues; based on CO_2 groups/peroxide = 2:1. [h] 144 hr, unchanged peroxide, 40%. [i] Benzaldehyde, 15%. [j] Unchanged peroxide, 39%. [k] CuCl was omitted; unchanged peroxide, 4%. [l] CuCl was substituted for $CuCl_2$ in the same molar amount; unchanged peroxide, 36%. [m] Unchanged peroxide, 1%. [n] $FeCl_3$ in place of $CuCl_2$. [o] Orientation could not be determmined due to interfering products. [p] Tentatively identified as α-chloroanisole. [q] 80°; unchanged peroxide, 4%. [r] An additional product (4%) was present. [s] 80°.

TABLE V

$k_{toluene}/k_{benzene}$ WITH BENZOYL PEROXIDE–CUPRIC CHLORIDE[a]

Toluene/benzene, M	Obsd	Calcd[b]
1.34	3.72	2.77
0.57	1.29	2.25

[a] Aromatic/peroxide/cupric chloride/cuprous chloride, 85:1:0.5:0.06; acetonitrile solvent; 60°; 24–48 hr. [b] Av = 2.51.

Anisyl benzoates were obtained (56–75%) having an orientation (*o*/*m*/*p* = 67:<1:33) similar to that from diisopropyl peroxydicarbonate–anisole–cupric chloride (*o*/*m*/*p* = 63:1:36).[29] The lower yield at 80° is consistent with enhancement of decarboxylation (eq 13) at higher temperatures.[30] An uncatalyzed decomposition was carried out at 80°, conditions under which benzoyloxylation has been reported to occur in the neat substrate.[30] However, in acetonitrile, no aryl benzoates were found, the only products being benzene, methoxybiphenyls, and benzoic acid. Comparison of the anisyl benzoate isomer distribution in our system to that (*o*/*p* = 65–82:35–18) from the previous study[30] suggests that the same attacking entity (benzoyloxy radical) is operating in both cases.

With ferric chloride as the promoter, the yield of tolyl benzoates was only 7%. The orientation was not determined due to interfering products. A more extensive treatment of oxygenation in the presence of ferric chloride may be found elsewhere.[21]

Aroyloxylation has been recognized as a competing reaction of varying importance in arylations with diaroyl peroxides. Oxygenation constituted a negligible pathway in the case of less active aromatics[22,31,32a,b] whereas it occurred to an appreciable extent with the more active types,[22] such as polynuclears[32c] and aromatic ethers.[30] The yields from benzoyloxylation in our systems represent significant increases over the prior results with toluene and anisole (20%),[30] illustrating the relatively efficient conversion of intermediate complex radicals (III) into product by cupric chloride (eq 4).

Previous investigators have studied related systems containing aromatic compounds, benzoyl peroxide, and copper salts with no indications of aromatic oxygenation.[10,12] Apparently, this pathway was not followed because of the presence of alkenes or reactive substituents on the aromatic nucleus, the nature of the copper salt, and use of the catalyst in low concentrations. For example, Hey and coworkers[33] recently found that the principal influence of cupric benzoate on the decomposition of benzoyl peroxide in neat benzene or chlorobenzene was to increase the yield of biaryl product.

The diacyl peroxide, lauroyl peroxide, did not effect oxygenation under the standard conditions. The products (Table VI) can be rationalized on the basis of well-known processes.[7,26,34]

Although diacetyl peroxide was not explored, we would predict less oxygenation than for benzoyl peroxide because of the greater instability of $CH_3CO_2\cdot$ *vs.* $C_6H_5CO_2\cdot$.[35] At the same time, the acetoxy radical demonstrates a lower susceptibility to spontaneous degradation than its higher analogs.[4]

C. Peresters and Peracids.—A summary of the substances obtained upon copper halide promoted breakdown of *t*-butyl perbenzoate is given in Table VII. The products, with none from participation of oxygenation, indicated that initial cleavage occurred in the usual manner[36] so as to give *t*-butoxy radicals and benzoate anions (eq 5, X = *t*-Bu,T = C_6H_5CO).

Investigation of perbenzoic acid was performed with toluene–acetonitrile both in the presence and absence of catalyst (Table VIII). Apparently, decomposition occurred without intervention of benzoyloxy radicals since no benzoyloxylation was observed.

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Table VI

Lauroyl Peroxide–Toluene–Cupric Chloride[a]

	Products, %[b]							
Catalyst/peroxide, M	Undecyl chloride	Undecene-1	n-$C_{22}H_{46}$	Lauric acid[c]	Cupric laurate[c]	CO_2	Unchanged peroxide, %	Σ(alkyl), %[d]
0.3[e]	63	15	1	69	0[f]	. . .	34	108
0.3[g]	63	25	2	12	26[h]	54[i]	8	86
0.5[j]	83	1	1	10	44[k]	. . .	5	97

[a] Toluene/peroxide, 14.7:1; acetonitrile solvent; 60°; 2–8 hr; see general procedure. [b] See Experimental Section for yield basis. [c] By isolation. [d] Material balance, alkyl groups; based on alkyl groups/peroxide = 2:1. [e] 2 hr. [f] The salt was hydrolyzed in work-up. [g] 8 hr. [h] 87% based on the catalyst. [i] Low value due to leakage. [j] 6 hr. [k] 88% based on the catalyst.

Table VII

t-Butyl Perbenzoate–Toluene–Cupric Chloride[a]

Products	%[b-d]
t-Butyl alcohol	59
Acetone	37
Benzoic acid[e]	97
Methyl chloride	14
Benzaldehyde	4
Benzyl chloride	25

[a] Toluene/peroxide/$CuCl_2$, 16.7:1:0.3; acetonitrile solvent; 60°; 2–5 days; homogeneous reaction mixture; see general procedure. [b] See Experimental Section for yield basis; average of four runs. [c] Material balance, *t*-butyl groups, 96%; accounted for by the sum of acetone and *t*-butyl alcohol. [e] Obtained by potentiometric titration.

Table VIII

Perbenzoic Acid–Toluene–Cupric Chloride[a]

	Yield, %[b]	
Products	With $CuCl_2$[c]	Without catalyst[d]
Benzoic acid[e]	109	114
Benzyl chloride	13	. . .[f]
Benzaldehyde	3	1

[a] Toluene/peroxide, 22.1:1; acetonitrile solvent; 60°; see general procedure. [b] See Experimental Section for yield basis. [c] Catalyst/peroxide = 0.3, 3 hr. [d] 6 hr. [e] Determined by potentiometric titration. [f] Not determined.

Subjection of dialkyl peroxides to this type of study was not undertaken due to their thermal stability, and the accumulation of data indicated the absence of attack on the aromatic nucleus by *t*-butoxy radicals under our conditions.

General Considerations.—Successful oxygenations were accomplished with peroxides in which alkoxycarboxy or aroyloxy radicals were the chain-carrying species, whereas alkoxy and hydroxy, as well as the fragmentation prone acyloxy radicals, were ineffective. Therefore, oxygenation is highly dependent on the nature of the oxygen radical derived from the peroxide. Among the important considerations involved in the observed specificity are the electrophilicity and stability *i.e.*, lifetime, of the oxy radical in addition to the ease of formation.

In general, oxygen radicals are known to exhibit electrophilic character.[17,37,38] The degree should reflect the electronegative nature of the group attached to the paramagnetic oxygen. Examples of free-radical oxygenation in the literature include aroyloxylation[22,30-32] and hydroxylation.[17,39,40] On the other hand, the absence of attack by alkoxy radicals onto aromatic nuclei has been pointed out.[25,41] The interrelation of electrophilicity and oxygenation tendency is consistent with the relative rate data. In oxygenation catalyzed by copper salt, $k_{\text{toluene}}/k_{\text{benzene}}$ values for isopropoxycarboxy[29] and benzoyloxy radicals are 3.77 and 2.51, respectively.

The corollary of decrease in side-chain attack in alkylbenzenes[42] and benzotrichloride[43] with increase in electrophilicity of the radical has been demonstrated for substituted aryl radicals.[44] The analogous competition of addition *vs.* hydrogen abstraction is seen in the reaction of oxy radicals with simple olefinic substrates. Aroyloxy radicals react preferentially by addition,[12] while alkoxy radicals react by hydrogen abstraction.[5,6,36]

Radical lifetime is undoubtedly a contributing factor in the success of $ROCO_2\cdot$ and $C_6H_5CO_2\cdot$ as oxygenating species. Various lines of evidence indicate the reasonable longevity of these radicals.[22,45-48]

Based on previous literature[5,36] and our own observations, unsymmetrical peroxides are reduced by cuprous ion in such a way that the most electron-deficient member of the peroxide linkage accepts the electron. Certainly, other factors are also important, with the net result that the observed pathway becomes energetically more favorable.[5,36] Hence, mixed peroxides exhibit the following ease of oxy radical formation: $RO\cdot > HO\cdot > RCO_2\cdot > ROCO_2\cdot$.

Experimental Section[49]

Materials.—The aromatic reactants and acetonitrile, of high purity according to glpc, were used directly. Cupric chloride, cuprous chloride (about 90% pure) (Fisher), and ferric chloride (Matheson Coleman and Bell) were also employed without further purification.

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Peroxides.—Dicyclohexyl peroxydicarbonate, mp 45.5–47.5° (lit.[50] mp 46°), was prepared from cyclohexyl chloroformate in 77% yield according to a literature procedure.[50] The chloroformate precursor was obtained from phosgene and cyclohexanol in 76% yield,[50] $n^{22}\mathrm{D}$ 1.4577 (lit.[51] $n^{25}\mathrm{D}$ 1.4628). Perbenzoic acid was made (67% yield) by following a conventional literature technique.[52] Benzoylperoxyisopropyl carbonate was synthesized from perbenzoic acid and isopropyl chloroformate according to an adaptation of the method of Dodonov and Waters.[53] After the crude product in methylene chloride was washed with dilute sodium bicarbonate solution and water, solvent removal gave a crude solid, mp 54–56°, which upon two recrystallizations from petroleum ether (bp 30–60°) provided fine, white needles, mp 57–58°. The nmr spectrum was in accord with the proposed structure with aromatic protons (δ 8.2–7.7), methyl protons (doublet centered at δ 1.45), and methine proton (septet centered at δ 5.11) in the ratio 5.7:6.3:1 theory (6:6:1). The infrared spectrum (carbon disulfide solvent) was also consistent with the formulation.

Anal. Calcd for $C_{11}H_{12}O_5$: C, 58.90; H, 5.40. Found: C, 58.70; H, 5.20.

t-Butyl perbenzoate, lauroyl peroxide, and benzoyl peroxide were commercial products (Lucidol) of greater than 95% purity. Benzoyl peroxide was recrystallized from chloroform–methanol before use. We are grateful to the Pittsburgh Plate Glass Co. for generous samples of *t*-butylperoxyisopropyl carbonate.

Peroxide–Toluene–Cupric Chloride–Acetonitrile.—The general procedure is described elsewhere.[20] The indicated observations and modifications apply to specific peroxide reactions. The systems were homogeneous throughout with the exception of those containing *t*-butylperoxyisopropyl carbonate and lauroyl peroxide which deposited solid during decomposition. Those reaction mixtures involving peroxides containing the benzoyloxy function changed from an initial yellow-brown coloration to deep blue or green, characteristic of copper benzoate solutions.[12] The aliquot removed at the culmination of these reactions was used for benzoic acid determination in addition to the analysis of low-boiling products. Unless otherwise noted, product yields are based on the stoichiometry of 1 mol/mol of peroxide (equation 1), and comprise the average of two or more runs which were in satisfactory agreement. The by-products were calculated on the same basis.

Product Identification. A. Aryl Esters.—A portion of the organic solution after work-up was concentrated by removal of most of the aromatic substrate under reduced pressure. The cyclohexyl- and isopropyltolyl carbonates, tolyl benzoates, and anisylisopropyl carbonates were separated and collected by glpc, and then compared to authentic samples (infrared spectrum and glpc retention time).

B. Nonoxygenated Aromatic Products.—In a similar manner, benzaldehyde, benzyl chloride, chlorobenzene, benzene, methylbiphenyls, undecene-1, and *n*-docosane[54] were identified. Less rigorous characterization (glpc retention time without authentic samples) was employed for the methoxybiphenyls.

C. Carboxylic Acids.—The sodium carbonate washes in the general work-up procedure from the benzoyl peroxide, benzoylperoxyisopropyl carbonate, *t*-butyl perbenzoate, perbenzoic acid, and lauroyl peroxide decompositions were acidified, and the resulting solid was filtered. Additional material, obtained by ether extraction of the acidified mixture, was combined with the original portion. Benzoic acid, mp 120–122° (lit.[55] mp 121°), and lauric acid, mp 38–42° (lit.[55] mp 43°), were also characterized by infrared spectroscopy (Nujol).[54]

D. Lower Boiling Materials.—An aliquot, taken before work-up, was analyzed by glpc. Acetone, isopropyl alcohol, *t*-butyl alcohol, methyl chloride, and a contaminant, di-*t*-butyl peroxide, were determined on the basis of identity of glpc retention time with that of the authentic samples on three different columns. In addition, chemical evidence for the peroxidic entity, which occurred as an impurity in *t*-butylperoxyisopropyl carbonate,[56] was procured by subjecting to reflux for 24 hr, a portion of the worked-up reaction mixture from *t*-butylperoxyisopropyl carbonate, which also contained small portions of benzaldehyde and benzyl chloride. Analysis showed the disappearance of the peroxide peak, slight enhancement of benzaldehyde, and formation of bibenzyl (13% yield based on the amount of peroxide believed to be present). In a control run, a known concentration of di-*t*-butyl peroxide was heated at reflux in toluene under similar conditions resulting in peroxide consumption and production of bibenzyl (15%) and benzaldehyde (1%).

E. Copper Salts. 1. From Lauroyl Peroxide.—The insoluble material present at the end of reaction was filtered and dried. The blue salt gave a negative test for chloride.

Anal. Calcd for $CuC_{24}H_{46}O_4$: Cu, 13.76; C, 62.36; H, 10.03. Found: Cu, 12.52; C, 62.09; H, 10.09.

Hydrolysis of the copper salt (parallel run from Table V) by dilute hydrochloric acid produced a significant increase in the amount of lauric acid.

2. From *t*-Butylperoxyisopropyl Carbonate.—The entire reaction mixture from one of the decompositions was subjected to reduced pressure in a rotary evaporator resulting in removal of all but a small amount of oil and solid. Continuous washing with carbon tetrachloride extracted the organic oil leaving a dry, bright green, somewhat pungent solid. This salt was insoluble in organic solvents, only very slightly soluble in water, and was readily hydrolyzed by dilute hydrochloric acid. The ir spectrum (Nujol) indicated strong C–H stretching bands.

Anal. Found: Cu, 38.32; C, 19.93; H, 3.20; Cl, 9.01.

Authentic Materials.—The tolylcyclohexyl carbonates were synthesized[57] from cyclohexyl chloroformate and the corresponding cresols (Table IX). The tolyl and anisyl benzoates were prepared from the requisite phenol and benzoyl chloride (Table X). The arylisopropyl carbonates are described elsewhere.[58] All of the remaining products were commercially available.

TABLE IX

AUTHENTIC TOLYLCYCLOHEXYL CARBONATES

Isomer	Yield, %	Mp, °C Obsd	Lit.[a]
ortho[b]	72	130 (1.2 mm)[c]	148–149 (4 mm)[c]
meta[d]	87	90–91	. . .
para	43	104–105.5	103–105

[a] G. A. Razuvaev, N. A. Kartashova, and L. S. Boguslavskaya, *J. Gen. Chem. USSR*, **34**, 2108 (1964). [b] $n^{20}\mathrm{D}$ 1.4932 (lit.[a] $n^{20}\mathrm{D}$ 1.4919). [c] Boiling point. [d] *Anal.* Calcd for $C_{14}H_{18}O_4$: C, 71.77; H, 7.74. Found: C, 71.99; H, 7.86.

TABLE X

AUTHENTIC ARYLISOPROPYL BENZOATES

Aryl	Yield, %	Mp, °C Obsd	Lit.[a]
o-Tolyl	75	127–130 (0.5 mm)[b]	. .
m-Tolyl	80	51.5–53.5	54
p-Tolyl	80	69–70	70
o-Anisyl	57	58–59.5	57
p-Anisyl	31	85.5–87	87

[a] Ref 55. [b] Boiling point.

Relative Rates.—The general procedure for competitive oxygenation was utilized.[29] A 36-hr reaction time was allotted with total aromatic/peroxide/cupric chloride/cuprous chloride = 85:1:0.5:0.06. Duplicate experiments were performed at two different toluene/benzene molar concentrations (Table V).

Analytical Procedures. A. Gas Chromatography.—The instruments and glpc columns were described earlier.[20]

B. For Peroxides.—Three different iodometric methods were required for the various peroxide determinations. Dicyclohexyl peroxydicarbonate and benzoylperoxyisopropyl carbonate, analyzed by a method involving sodium iodide–acetic acid–water,[50]

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possessed purities of 94 and 91.5%, respectively. The latter peroxide contained less than 2% of benzoic acid by potentiometric titration. More vigorous conditions[28] (sodium iodide in refluxing, acidified isopropyl alcohol) were necessary in the case of the *t*-butyl peresters, perbenzoic acid, and lauroyl peroxide. *t*-Butylperoxyisopropyl carbonate, 87.5% pure by this method, was shown to contain 8% of di-*t*-butyl peroxide by iodometry and glpc. Benzoyl peroxide was analyzed with aqueous sodium iodide-carbon tetrachloride–acetic acid–ferric chloride hexahydrate.[59]

C. For Product Yields. 1. Aryl Esters.—Tolylcyclohexyl carbonates (mesitylisopropyl carbonate marker) and aryl benzoates (phenyl benzoate marker) were determined on glpc column 3 at 195°. The tolylisopropyl carbonates were analyzed as described earlier.[20]

2. Nonoxygenated Aromatic Products.—Glpc column 1 (195°) was the choice for most nonoxygenated material with trichlorobenzene as internal standard. Exceptions were benzene and chlorobenzene from the benzoyl peroxide decompositions, which were determined on glpc column 2 (mesitylene marker) at 135°. The phenylated products from the same runs were analyzed on the column described for the benzoate esters.

3. Low-Boiling Materials.—Glpc column 8 provided most of the data for the low-boiling materials (either methyl ethyl ketone or benzene as internal standard). Cyclohexanol and cyclohexanone were detected on glpc column 5 with *o*-xylene as marker.

4. Benzoic Acid.—Potentiometric titration was carried out on reaction aliquots to determine the amount of benzoic acid. Cupric ion was shown not to interfere at the concentrations employed in this study. Duplicate analyses indicated excellent precision in all cases.

5. Carbon Dioxide.—This gas was determined by a known procedure (method A).[30]

D. For Isomer Distributions.—The combination glpc–ir technique described elsewhere[20] was employed to obtain the isomeric composition of the tolylcyclohexyl carbonates and tolyl benzoates. Direct glpc analysis provided the orientation of the anisyl benzoates and the tolylisopropyl carbonates.

Registry No.—Toluene, 108-88-3; cupric chloride, 7447-39-4; I (X = Y = $C_6H_{11}OCO$), 1561-49-5; I (X = C_6H_5CO; Y = *i*-PrOCO), 16136-81-5; I (X = *t*-Bu; Y = *i*-PrOCO), 2372-21-6; benzoyl peroxide, 94-36-0.

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Cyclobutane Compounds. V.[1] Long-Range Spin Coupling in the Cyclobutyl System

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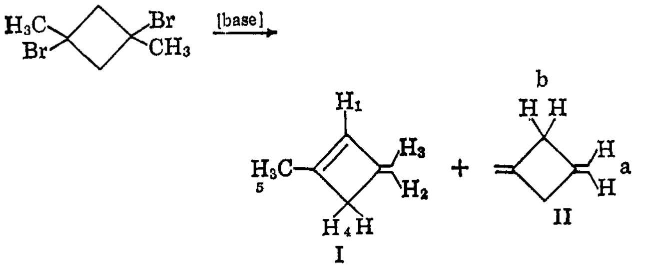
The 100-Mc nuclear magnetic resonance spectrum of 1-methyl-3-methylenecyclobutene (I) and 1,3-dimethylenecyclobutane (II) were examined. These (spectra) are novel examples of eight-spin first-order systems containing five sets of mutually coupled, nonequivalent protons. Several novel ^4J and ^6J long-range spin couplings are identified using double and triple irradiation techniques.

In connection with our interest in the chemistry and spectral characterization of four-membered carbocyclic ring systems,[2] we wish to report several novel examples of four- and six-bond (^4J, ^6J) long-range spin coupling in the cyclobutene (I) and cyclobutane (II) systems.[3] The nuclear magnetic resonance (nmr) spectra of these compounds are novel examples of eight-spin first-order systems containing five sets of nonequivalent protons in which all of the protons in each molecule are mutually coupled.

Base-catalyzed dehydrobromination of 1,3-dibromo-1,3-dimethyl-cyclobutane produces, in approximately 50% over-all yield,[4] a mixture of the isomeric olefins 1-methyl-3-methylenecyclobutene (I) and 1,3-dimethylenecyclobutane (II). The structures of these materials were established by an analysis of their characteristic nmr spectra (Figure 1) and by comparison of their physical constants with literature values.[5,6] Compound II has been previously reported to be the product of pyrolysis of (3-methylenecyclobutylcarbinyl)dimethylamino oxide[5] and a minor component in the dimerization of allene.[6] The conjugated diene (I) was previously prepared by treatment of (3-methylenecyclobutylcarbinyl)trimethylammonium hydroxide with silver oxide.[5]



The nmr spectrum of I has multiplets at 5.99 (H_1), 4.49 (H_2), 4.28 (H_3), 2.76 (H_4), and 1.86 ppm (H_5) in a ratio of 1:1:1:2:3, respectively. On expansion under conditions of high resolution (Figure 2), these multiplets may be fully resolved.[7] A clearly first-order spectrum is observed for the eight-spin system (which may be analyzed using the usual rules) even though all of the

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[1] For the previous paper in this series, see K. Griesbaum and P. E Butler, *Angew. Chem.*, **79**, 467 (1967), and *Angew. Chem. Intern. Ed. Engl.*, **6**, 444 (1967).

[2] K. Griesbaum, W. Naegele, and G. G. Wanless, *J. Amer. Chem. Soc.*, **87**, 3151 (1965).

[3] For a comprehensive review of the nmr spectra of four-membered carbocyclic ring systems, see I. Fleming and D. H. Williams, *Tetrahedron*, **23**, 2747 (1967).

[4] The synthetic details of the dehydrobromination step and the reactions of these olefins will be described elsewhere.

[5] F. F. Caserio, Jr., S. H. Parker, R. Piccolini, and J. D. Roberts, *J. Amer. Chem. Soc.*, **80**, 5507 (1958).

[6] B. Weinstein and A. H. Fenselau, *J. Chem. Soc.*, *Sect. C*, 368 (1967); Y. M. Slobodin and A. P. Khitrov, *Zh. Obschch. Khim.*, **33**, 153, 2822 (1963); **34**, 1727 (1964).

[7] Previous workers examined the nmr spectra of I and II under conditions of low resolution. Roberts, *et al.*, reported[5] the 40-Mc spectrum of I showing two groups of five component lines for the terminal olefin and allylic methylene protons, however, Weinstein, *et al.*,[6] reported a 60-Mc spectrum showing multiplets at 4.8 and 3.31 ppm for the same protons. The 40-Mc spectrum of II reported by Roberts was taken on a neat sample and showed broad absorptions with chemical shifts similar to those we report. No fine structure was observed.