

money order for \$3.00 for photocopy or \$2.00 for microfiche, referring to code number JOC-74-3327.

### References and Notes

- (1) A. Schoenberg, I. Bartoletti, and R. F. Heck, *J. Org. Chem.*, **39**, 3318 (1974).  
 (2) F. Weigert, *J. Org. Chem.*, **38**, 1316 (1973).  
 (3) E. W. Stern and M. L. Spector, *J. Org. Chem.*, **31**, 596 (1966).  
 (4) F. Straus, *Ann.*, **343**, 190 (1905).  
 (5) M. Hidai, M. Kokura, and Y. Uchida, *J. Organometal. Chem.*, **52**, 431 (1973).  
 (6) P. Canbere, *Bull. Soc. Chim. Fr.*, 144 (1964).  
 (7) L. C. Raiford, R. Taft and H. P. Lankelma, *J. Amer. Chem. Soc.*, **46**, 2051 (1924).

## Ceric Ammonium Nitrate Promoted Aromatic Substitution with Peroxydicarbonates<sup>1</sup>

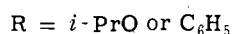
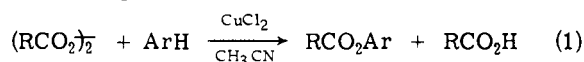
Michael E. Kurz,\* Edward M. Steele, and Robert L. Vecchio

Department of Chemistry, Illinois State University, Normal, Illinois 61761

Received February 26, 1974

The decomposition of dialkyl peroxydicarbonates in the presence of a two-molar excess of ceric ammonium nitrate (CAN) in toluene led to tolyl alkyl carbonates in yields of 75–90% based on two carbonate moieties from each peroxide molecule. Unlike the previously reported catalytic effect of cupric chloride, where the chain-induced peroxide breakdown by cuprous limited the aryl ester yield to 1 mol/mol of peroxide, the CAN involvement was stoichiometric as both halves of the peroxide substituted onto the aromatic. No peroxide-cerous ion interaction seemed to occur; indeed the overall peroxide decomposition rate was actually retarded relative to that in the absence of metal salts and all the cerium was recovered as cerous nitrate. Based on isomer distributions and relative rates the substituting entity possessed more selectivity than the free carbonate radicals. No polymer production was noted in reactions performed with acrylonitrile, suggesting low oxy radical concentrations. The importance of the hexanitrate cerium(IV) complex as an oxidant in the overall aromatic substitution process was established by studying a variety of other ceric and cerous salts in this reaction.

The decomposition of peroxydicarbonates and diacyl peroxides in the presence of toluene can be modified by the inclusion of suitable redox agents (e.g., CuCl<sub>2</sub>,<sup>2</sup> FeCl<sub>3</sub>,<sup>3</sup> I<sub>2</sub>,<sup>4</sup> O<sub>2</sub>,<sup>5</sup> and various other metal salts<sup>3,6</sup>) which oxidize oxy radical-aromatic adducts to form aryl esters. With most of the metal salts a lower valence inorganic species is produced which then reduces the peroxide, leading to a chain reaction.<sup>2,3</sup> The net stoichiometry is indicated in eq 1 for cupric chloride, which proved to be the most effective metal salt,



forming nearly 1 mol of aryl ester/mol of peroxide.<sup>2</sup> With molecular oxygen as a promoter the reaction went by a nonchain mechanism and aryl ester yields somewhat in excess of 1 mol/mol of peroxide were realized.<sup>5</sup> In the absence of added oxidant less than 1% nuclear oxygenation resulted, as the oxy radicals reacted by other pathways.

Recently we found that use of sufficient quantities of ceric ammonium nitrate (CAN) with the same peroxides and toluene led to nearly doubled aromatic oxygenation yields, and we wish to report on the details of this reaction.

### Results and Discussion

**Reaction Products.** The optimum general procedure involved adding a solution of known concentration of diisopropyl peroxydicarbonate (IPP) in toluene to a 2.25 molar excess of CAN, and a 25- to 50-fold molar excess of toluene in acetonitrile at 60°, and allowing the reaction to go for 24 hr. Table I summarizes the organic reaction products.

Apparently, both oxy fragments formed from peroxide homolysis were capable of reacting with the aromatic, as 1.6 mol of oxygenation products (tolyl isopropyl carbonates) were formed from 1 mol of peroxide. This meant that 80% of the potential alkoxy-carboxy moieties (2 mol/mol of peroxide) added to the ring, while the remaining 20% decomposed to form carbon dioxide, acetone, and isopropyl

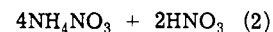
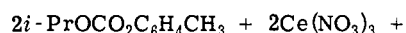
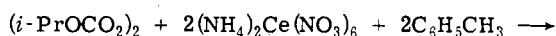
**Table I**  
Organic Reaction Products from Diisopropyl Peroxydicarbonate-Toluene-Ceric Ammonium Nitrate System<sup>a</sup>

Product	Yield, <sup>b</sup> %
Tolyl isopropyl carbonates <sup>c</sup>	160
Isopropyl alcohol	26
Acetone	16
Carbon dioxide	47
Benzaldehyde	4
Benzyl alcohol	2
Nitrotoluenes	1
$\sum(\text{CO}_2)^d$	103
$\sum(i\text{-Pr})^e$	101

<sup>a</sup> Toluene:CAN:peroxide = 25:2.25:1, acetonitrile solvent, 60°, 24 hr (see general procedure). <sup>b</sup> Based on 1 mol of product/mol of peroxide. <sup>c</sup> Isomer distribution, ortho:meta:para = 56.2:11.8:32.0. <sup>d</sup> Material balance based on two CO<sub>2</sub> groups/mol of peroxide. <sup>e</sup> Material balance based on two isopropyl groups/mol of peroxide.

alcohol. The material balance based on starting peroxide was excellent in all cases.

As the reaction proceeded, crystals of cerous nitrate gradually precipitated from the reaction mixture. This and all the other inorganic reaction products were isolated and quantitatively determined (Table II) utilizing total acid, ammonium ion, nitrate ion, and cerium analyses. On the basis of these product studies (Tables I and II), the following stoichiometry was proposed for the reaction (eq 2).



Normally, cerous nitrate is soluble in acetonitrile, but apparently it is salted out by ammonium nitrate and nitric

**Table II**  
**Inorganic Products from Diisopropyl Peroxydicarbonate-Toluene-Ceric Ammonium Nitrate System<sup>a</sup>**

Product	Yield, mol <sup>b</sup>		Yield, %
	Exptl	Theor	
HNO <sub>3</sub> <sup>c</sup>	2.10	2.00	105
Ce(III) <sup>d</sup>	2.09	2.00	104
NO <sub>3</sub> <sup>-</sup> (nonvolatile) <sup>e</sup>	9.60	10.00	96.0
NO <sub>3</sub> <sup>-</sup> (total) <sup>f</sup>	11.8	12.00	98.3
NH <sub>4</sub> <sup>+</sup> <sup>g</sup>	3.44	4.00	85.8

<sup>a</sup> Toluene:CAN:peroxide = 25:2:1, acetonitrile solvent, 60°, 24 hr; see Experimental Section. <sup>b</sup> Based on the stoichiometry indicated in eq 6. <sup>c</sup> Determined by potentiometric titration. <sup>d</sup> Determined by ultraviolet spectrophotometry. <sup>e</sup> Determined by phenol-disulfonic acid method.<sup>9</sup> <sup>f</sup> Calculated from HNO<sub>3</sub> and NO<sub>3</sub><sup>-</sup> (nonvolatile). <sup>g</sup> Distilled as NH<sub>3</sub> and determined by titration. The low yield is probably the result of sublimation of some ammonium nitrate during vacuum drying of isolated salts.

acid.<sup>7</sup> We were able to verify this common ion effect by adding ammonium nitrate and nitric acid to solutions of cerous nitrate in acetonitrile in the relative quantities present in eq 2, and observing precipitation.

Further checks on the proposed stoichiometry were derived from pH measurements and the analysis of salts from aqueous extracts of the reaction mixture. Aqueous extracts possessed a pH of 1.8, suggesting the presence of a strong acid, and this value agreed closely with the pH 1.7 calculated from the expected yield for nitric acid. The salt yields from duplicate experiments were 100.50 and 99.14% of the value calculated on the basis of the stoichiometry given in eq 2. Failure of this salt to liberate iodine from potassium iodide solution<sup>10</sup> was taken as evidence for the absence of ceric ion in the final mixture. All of these findings lend support to the stoichiometry proposed in eq 2.

The theoretical production of 2 mol of product/mol of peroxide (eq 2) affords a distinct advantage for synthetic purposes over the copper-catalyzed reaction (eq 1), where the theoretical yield is just 1 mol of aryl ester/mol of peroxide.

**Reaction Variables.** To maximize the efficiency of the CAN-controlled oxygenation reaction and to learn more about the mechanism, a number of reaction variables were studied. Table III summarizes the effect of modifying the catalyst:peroxide ratio on the oxygenation yield for reactions containing toluene:peroxide ratios of 50:1. Unlike the cupric chloride catalyzed system,<sup>2</sup> for which a maximum yield of nuclear oxygenation was obtained using a catalyst:peroxide ratio of just 0.3:1, the amount of ester formed closely paralleled the molar amount of CAN used (Table

III). This lends further support to the proposed stoichiometry (eq 2). Although the oxygenation yield leveled off once the stoichiometric amount of CAN was present, a slight improvement in yield was realized when a small excess of the stoichiometric requirement of CAN was used, perhaps because some of the CAN is consumed in side reactions (*e.g.*, benzyl alcohol oxidation<sup>11</sup>).

Under experimental conditions favoring optimum yield, 20–25% of the peroxide was degraded to isopropyl alcohol, acetone, and carbon dioxide. At lower CAN:peroxide ratios, the lesser oxygenation yields were accompanied by correspondingly increased amounts of these by-products, which are the usual products from the thermolytic decomposition of the isopropoxycarboxy radical.<sup>2,12</sup> In like manner benzaldehyde, benzyl alcohol, and bibenzyl, resulting from side-chain abstraction by an alkoxy radical,<sup>2</sup> were found.

Small amounts of nitrotoluenes were also formed in the CAN-promoted systems (Table III), and the yield of these by-products decreased as the concentration of CAN was increased to the stoichiometric amount (eq 2). It is surprising that the greatest nitrotoluene formation occurred with a CAN:peroxide ratio of only 0.5 (Table III), because of those systems containing CAN this one would be expected to contain the lowest concentration of nitric acid (eq 2). It is noteworthy that qualitatively, the meta isomer was the major nitrotoluene product, whereas for straightforward electrophilic substitution by nitric acid, the meta proportion is normally quite small (4%).<sup>13</sup>

With insufficient CAN, considerable intact peroxide would remain to decompose after all of the limited CAN had been consumed in product formation (eq 2). Under these conditions, nitric acid can promote concurrent nitration-oxygenation which results in this unusual isomeric nitrotoluene product pattern.<sup>14</sup> With sufficient CAN present to promote oxygenation little involvement of HNO<sub>3</sub> with the peroxide is noted.

Further evidence for nitric acid involvement can be gleaned from Table III. As the CAN:peroxide ratio was lowered the percentage of *p*-tolyl isopropyl carbonate systematically became larger at the expense of the meta isomer. Extrapolation of each isomer back to zero CAN content leads to an all-around isomer composition of ortho:meta:para = 58:6:36, which is very similar to that found using just nitric acid as the promoter.<sup>14</sup> This value is quite different from that obtained (ortho:meta:para = 57:15:28) with CuCl<sub>2</sub> as a catalyst where free oxy radicals are believed to be the substituting entity.<sup>2</sup>

Little effect of temperature on the CAN-promoted oxygenation was noted in the range of 50–70°. Slightly more tolyl isopropyl carbonates with a more selective isomer distribution (ortho:meta:para = 59:10:31) were obtained at 50° but the reaction required more time (48 hr).

**Table III**  
**Products as a Function of Ceric Ammonium Nitrate: Peroxide Ratio<sup>a</sup>**

CAN:peroxide molar ratio	Products, % <sup>b</sup>												
	Tolyl isopropyl carbonates				Carbon dioxide	Isopropyl alcohol	Acetone	Benzaldehyde	Benzyl alcohol	Nitrotoluenes	Bibenzyl	Σ( <i>t</i> -Pr) <sup>c</sup>	Σ(CO <sub>2</sub> ) <sup>d</sup>
Yield	Ortho	Meta	Para										
0	1				212	119	55	0	0	0	18	87	106
0.5	38	58.5	7.1	34.4	174	101	44	3	13	3.6 <sup>e</sup>	0.05	91	106
1.0	84	58.0	8.3	33.7	116	84	32	1	6	2.5 <sup>f</sup>	0 <sup>g</sup>	100	100
1.5	121	58.3	9.4	32.3	104	39	17	1	3	1.5	0 <sup>g</sup>	90	112
2.0	143	59.1	10.4	30.5	80	28	13	1	1	0.5	0	99	112
2.5	152	58.6	12.3	29.1	66	28	14	2	0.5	0.5	0	97	109

<sup>a</sup> Toluene:diisopropyl peroxydicarbonate = 50:1, 24 hr, 60°, acetonitrile solvent (see general procedure). <sup>b</sup> Yields based on mol product/mol peroxide. <sup>c</sup> Material balance based on two isopropyl groups/mol peroxide. <sup>d</sup> Material balance based on two CO<sub>2</sub> groups/mol peroxide. <sup>e</sup> Ortho:meta:para = 13:78:9. <sup>f</sup> Predominantly meta; not quantitatively determined. <sup>g</sup> Trace of bibenzyl present.

**Table IV**  
Decomposition Rates for Diisopropyl Peroxydicarbonate in Acetonitrile as a Function of Metal Salt<sup>a</sup>

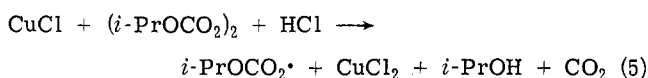
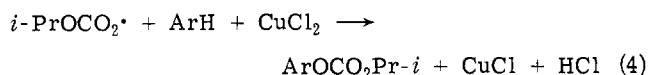
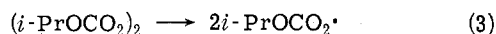
Salt	Temp, °C	$k \times 10^3, \text{ min}^{-1}$	$t_{1/2}, \text{ min}$
None <sup>c</sup>	50	6.45	108
CuCl <sub>2</sub> <sup>c</sup>	50	66	10.4
None	60	13.6	48
CAN <sup>d</sup>	60	4.9	140
CKN <sup>e</sup>	60	5.6	127

<sup>a</sup> Average of duplicates in good agreement. <sup>b</sup>  $\pm 10\%$ . <sup>c</sup> Reference 2 (toluene:peroxide:catalyst = 17.3:1:0.3). <sup>d</sup> Toluene:peroxide:CAN = 25:1:2. <sup>e</sup> Toluene:peroxide:CKN = 25:1:2, single determination.

**Peroxide Decomposition Rates.** The rates of peroxide decomposition in the presence of a number of cerium salts were followed iodometrically. The rate curves plotted nicely as first-order reactions in peroxide with the exception of cerous nitrate (*vide infra*). Previously, first-order kinetics for the thermolysis of diisopropyl peroxydicarbonate in acetonitrile<sup>2</sup> and other solvents<sup>15</sup> had been reported. The rate of formation of aryl carbonate esters was also followed at 50° by glpc, and agreed well with the rate of peroxide decomposition.

Inspection of Table IV shows that the rates of peroxide breakdown at 60° with the ceric salts were slowed in comparison to the rate in the absence of these promoters. The similarity of rates in the presence of ceric ammonium nitrate and ceric potassium nitrate (CKN) indicates both the apparent importance of the hexanitratocerate ion and unimportance of the cationic species in the rate-retarding effect of the ceric salts. This rate-slowing effect stands in marked contrast to the accelerating effect of cupric chloride on the decomposition (50°) of the same peroxide (Table IV). Whereas cupric chloride accelerates the rate of peroxide decomposition by a factor of 10 in relation to the thermolysis rate, CAN and CKN retard the decomposition by a factor of about 3.

With cupric chloride, rate acceleration is attributed to the ability of cuprous ion formed in the radical oxidation step (eq 4) to induce peroxide decomposition (eq 5), lead-



ing to a redox chain mechanism. Unlike cuprous ion, cerous ion is oxidized only with very strong oxidizing agents,<sup>16</sup> and is not effective in breaking down the peroxide, explaining the lack of rate enhancement shown by the cerium salts.

To determine if the rate-retarding effect depends on the relative CAN concentration, additional kinetic studies of peroxide decomposition were made on systems containing CAN:peroxide ratios of 0.5, 1.0, 1.5, and 2.5. The rates in all cases were identical within experimental error, indicating perhaps a medium effect rather than a stoichiometric peroxide-CAN complex.

The actual decrease in the peroxide breakdown rate is not understood at this point, but has been noticed in other peroxide decompositions using metal salts of strong acids.<sup>6</sup>

**Other Cerium Salts.** Several additional cerium salts were tested for their effectiveness as oxygenation promoters. Table V summarizes the results. Ceric potassium ni-

**Table V**  
Reaction of Toluene and Diisopropyl Peroxydicarbonate with Other Cerium Promoters<sup>a</sup>

Promoting salt	Tolyl isopropyl carbonates, % <sup>b</sup>				Rate <sup>c</sup> $\times 10^3, \text{ min}^{-1}$
	Yield	Ortho	Meta	Para	
K <sub>2</sub> Ce(NO <sub>3</sub> ) <sub>6</sub>	130	60	10	30	5.6
Ce(NO <sub>3</sub> ) <sub>3</sub> ·6H <sub>2</sub> O <sup>d, e</sup>	33	59	7	34	7.5 <sup>f</sup>
Ce(NO <sub>3</sub> ) <sub>3</sub> ·2H <sub>2</sub> O <sup>e</sup>	44	60	6	34	
Ce(NO <sub>3</sub> ) <sub>4</sub> <sup>e, g</sup>	14	61	6	33	12.0
HNO <sub>3</sub> <sup>h</sup>	11	58	6	36	6.4
Ce(OH) <sub>4</sub> <sup>i</sup>	1				31.0
Ce(ClO <sub>4</sub> ) <sub>3</sub>	1				11.0
CeCl <sub>3</sub> , Ce(NH <sub>4</sub> ) <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> , Ce(acac) <sub>3</sub> , H <sub>2</sub> Ce(SO <sub>4</sub> ) <sub>2</sub> } <sup>i</sup>	1				

<sup>a</sup> Toluene:peroxide:promoter = 25:1:2, unless otherwise stated; acetonitrile solvent, 60°, 24 hr. <sup>b</sup> Yields based on mol product/mol peroxide. <sup>c</sup>  $\pm 10\%$ . <sup>d</sup> Other products included acetone (26%), isopropyl alcohol (120%), CO<sub>2</sub> (97%), bibenzyl (2.1%), and small quantities of benzyl alcohol, benzaldehyde, and two unidentified compounds. <sup>e</sup> Initially homogeneous; gradually became heterogeneous. <sup>f</sup> Nonlinear curve, approximate value  $\pm 15\%$ . <sup>g</sup> Toluene:peroxide:ceric nitrate = 25:1:0.38. Nitrotoluenes (about 10%, mainly meta) were present. <sup>h</sup> HNO<sub>3</sub>:peroxide = 6:1. Other products: acetone (28%), isopropyl alcohol (97%), CO<sub>2</sub> (103%), nitrotoluenes (10%, ortho:meta:para = 17:78:5), bibenzyl (2%), benzyl alcohol, benzaldehyde, and an unidentified component; see ref 14. <sup>i</sup> Heterogeneous throughout.

trate proved to be nearly as effective as CAN. Of the other salts tested only cerous nitrate and ceric nitrate showed any indication of promoting oxygenation.

In view of the sluggishness of cerous toward oxidation one might predict that cerous nitrate would not affect the decomposition of the peroxide or promote the oxygenation of aromatics. Experimental results fail to support either prediction. As shown in Table V, cerous nitrate causes a rate-inhibiting effect intermediate between the uncatalyzed and the CAN-promoted reactions, although the curve is more eccentric. This behavior is attributable to precipitation of a ceric oxide hydrate formed as the cerous nitrate hydrolyzed during the reaction. During the stages of ceric oxide precipitation, the rate actually increased owing to Ce(OH)<sub>4</sub>'s ability to accelerate peroxide decomposition (Table V).

The formation of an appreciable amount of tolyl isopropyl carbonates with Ce(NO<sub>3</sub>)<sub>3</sub> remains a puzzle. Cerous ion itself is not expected to be a good oxidant, and other potential promoters formed during the reaction can be ruled out, *i.e.*, Ce(OH)<sub>4</sub> and nitric acid. The former does not appear to be capable of promoting oxygenation (Table V). Although nitric acid is known to promote oxygenation<sup>14</sup> and does form in appreciable amounts from cerous nitrate during the reaction, the conspicuous absence of nitrotoluenes among the reaction products suggest that it is not involved in promoting aromatic substitution by an oxy species.<sup>14</sup>

The involvement of nitric acid as a promoter seems more plausible (Table V) for the ceric nitrate reactions, since both tolyl ester and nitrotoluene yields and isomer distributions resemble each other. Considering the experimental details, this conclusion can be easily rationalized. Because of unavoidable hydrolysis ceric nitrate does not exist in solid form;<sup>17</sup> rather, it was used as supplied commercially (0.95 M) in nitric acid. Very early in the reaction the deep red color of the ceric solution turned yellow and significant amounts of hydrated ceric oxide precipitated. Significant amounts of nitric acid remained in solution to promote oxygenation.<sup>14</sup>

Ceric hydroxide, even though only partially soluble in ac-

**Table VI**  
Toluene Reaction with Peroxide-Ceric  
Ammonium Nitrate

Peroxide <sup>a</sup>	Temp, °C time, hr	Aromatic substitution product	Yield, % <sup>b</sup>	<i>k<sub>t</sub>/k<sub>p</sub></i>
( <i>i</i> -PrOCO <sub>2</sub> ) <sub>2</sub>	60 (24)	<i>i</i> -PrOCO <sub>2</sub> C <sub>6</sub> H <sub>4</sub> CH <sub>3</sub> (58:11:31) <sup>d</sup>	161	6.35
( <i>sec</i> -BuOCO <sub>2</sub> ) <sub>2</sub>	50 (24)	<i>sec</i> -BuOCO <sub>2</sub> C <sub>6</sub> H <sub>4</sub> CH <sub>3</sub> (59:12:29) <sup>d</sup>	181	7.1
(C <sub>6</sub> H <sub>5</sub> CO <sub>2</sub> ) <sub>2</sub>	80 (96)	C <sub>6</sub> H <sub>5</sub> CO <sub>2</sub> C <sub>6</sub> H <sub>4</sub> CH <sub>3</sub> <sup>c</sup> (56:14:30) <sup>d</sup>	53	

<sup>a</sup> Toluene:CAN:peroxide = 19-25:2:1, acetonitrile solvent.  
<sup>b</sup> Based on 1 mol of product/mol of peroxide. <sup>c</sup> Other aromatic substitution products were methylbiphenyls (ortho:meta:para = 68:23:9), 38%, and nitrotoluenes (ortho:meta:para = 60:5:35), 59%. <sup>d</sup> Ortho:meta:para ratio.

etonitrile, caused the greatest acceleration of peroxide decomposition of the cerium salts tested (Table V), even though it did not promote oxygenation.

Of the other cerium salts studied only minor modifying effects on peroxide decomposition were noted, and no candidate was significantly efficient in promoting oxygenation. With cerous chloride, ceric sulfate, and ceric ammonium sulfate very little of the salt appeared to dissolve in acetonitrile, while cerous acetylacetone was about half in solution. Only with cerous perchlorate was the desired amount of salt able to be utilized.

This work points up the apparent importance of the intact hexanitrate cerium(IV) complex for the efficient promotion of this oxygenation reaction. This complex possesses considerable solvolytic stability,<sup>18</sup> and yet is a vigorous oxidizing agent as expected for a tetravalent metal.<sup>19</sup> Previously oxygenation had been promoted by another anionic complex, the hexachloroiridate ion (IrCl<sub>6</sub><sup>2-</sup>).<sup>3</sup>

**Nature of the Substituting Species.** To learn more about the nature of the substituting entity subsequently involved in aromatic substitution, relative rate reactions were carried out. Equimolar quantities of toluene and benzene at a tenfold and again at a 20-fold molar excess relative to peroxide were subjected to the peroxide-CAN mixture, yielding a relative rate value,  $k_{C_6H_5CH_3}/k_{C_6H_6} = 6.35$ . This value is about twice that attributed to a free isopropoxycarboxy radical ( $k_t/k_p = 3.77$ ),<sup>20</sup> which itself is somewhat electrophilic. The increased selectivity observed in this system is not understood, but may be due to a medium effect or to nitric acid intervention. Other metal salts containing nitrate ligands have given quite similar isomer distributions and relative rates.<sup>6</sup>

**Other Peroxides.** CAN-promoted reactions of toluene with di-*sec*-butyl peroxydicarbonate and benzoyl peroxide were also looked at. The results are summarized in Table VI along with the diisopropyl peroxydicarbonate reaction. The di-*sec*-butyl peroxydicarbonate reaction gave an even better yield of aryl ester with an isomer distribution and relative rate very much like that from IPP. The aromatic substitution became less effective with benzoyl peroxide, owing largely to the wasting of CAN in nitrating toluene, which occurred at the higher temperature required (80°) for the benzoyl peroxide to undergo thermolysis (Table VI).

**Radical Trapping Studies.** Radical trapping experiments were performed with acrylamide and acrylonitrile<sup>21,22</sup> in an effort to determine the extent of involvement of free oxy radicals (Table VII). In a control system containing toluene, acrylonitrile, and peroxydicarbonate, considerable polyacrylonitrile precipitated from the reaction mixture. In a further control, CAN in the absence of perox-

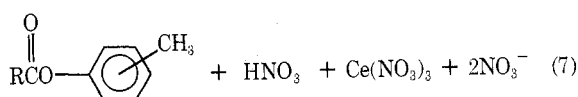
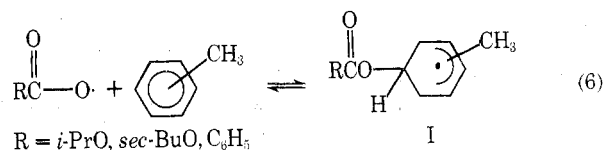
**Table VII**  
Radical Trapping Studies<sup>a</sup>

Catalyst	Molar ratio <sup>b</sup>	Trapping agent	Molar ratio <sup>b</sup>	CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> OCO <sub>2</sub> Pr- <i>t</i> yield <sup>b</sup>
None <sup>c</sup>		None		1 <sup>d</sup>
None		CH <sub>2</sub> =CHCN	9	1 <sup>e</sup>
CAN	2.25	None		149
CAN	2.25	CH <sub>2</sub> =CHCN	15	127 <sup>f</sup>
CAN	2.25	CH <sub>2</sub> =CHCONH <sub>2</sub> <sup>g</sup>	15	132
CuCl <sub>2</sub> <sup>c</sup>	0.3	None		85
CuCl <sub>2</sub>	0.3	CH <sub>2</sub> =CHCN	9	83 <sup>f</sup>

<sup>a</sup> Toluene:peroxide = 20:1, acetonitrile solvent, 60°. <sup>b</sup> Based on mol/mol of peroxide. <sup>c</sup> From ref 2. <sup>d</sup> Bibenzyl, 38%, was the major aromatic product. <sup>e</sup> Solution became heterogeneous as polyacrylonitrile (identified by ir) precipitated; only 1% bibenzyl was formed. <sup>f</sup> No polymer precipitate formed although the solution did darken. <sup>g</sup> Heterogeneous; no polymer precipitate formed, and solution ended up light yellow as was usual for CAN oxygenations.

ide was found to be ineffective as an initiator for polyacrylonitrile formation. When the CAN-promoted oxygenation of toluene was performed with a 15-fold molar excess of acrylonitrile or acrylamide no insoluble polymer was formed nor was the alkyl tolyl carbonate yield lowered appreciably (Table VII). These results suggest either the absence of or a very low concentration of free oxy radicals in the CAN-promoted oxygenation. However, a similar lack of polymerization was noted when the cupric chloride catalyzed oxygenation was subjected to acrylonitrile trapping (Table VII). It appears that in both the CAN and CuCl<sub>2</sub>-peroxide reactions that oxy radicals are rapidly scavenged by toluene and oxidized to aryl esters, thus keeping the free oxy radical concentration too low to promote polymerization.

**Mechanism.** Based on the experimental results the following mechanism (eq 6) is proposed for the tolyl ester formation following an initial homolytic breakdown of the peroxide (eq 3).



A fast reversible attack on the aromatic by oxy radical or a complexed oxy radical (eq 6) is followed by oxidation of the cyclohexadienyl radical intermediate by Ce<sup>IV</sup>. The greater selectivity of the attacking entity compared to the free oxy radical<sup>2,20</sup> as indicated by the relative rate and isomer distribution patterns is not understood, but may be due to the increased polarity of the solvent system (nitric acid formation, eq 2),<sup>6</sup> or to complexing of the oxy radical by the cerium species. Alternatively the strong ceric oxidant may be capable of effecting an electron transfer from the oxy radical itself to produce an oxy cation which can then attack the ring. Although such electron transfers are well known for alkyl radicals with ferric,<sup>23</sup> cupric,<sup>24</sup> and ceric<sup>25</sup> ions, the analogous process with oxy radicals is unprecedented and would be expected to be energetically unfavorable.<sup>26</sup> An analogous situation (complexed oxy radical or oxy cation) was considered for the ferric chloride promoted oxygenation of toluene with diisopropyl peroxydicarbonate.<sup>3</sup>

The oxidation step (eq 7) involves  $\text{Ce}^{\text{IV}}$  in a less familiar role of radical oxidant rather than in its well-known function as oxidant of various organic compounds (e.g., alcohols<sup>21,27</sup> and arenes<sup>28</sup>).

### Experimental Section

Reagent grade chemicals and metal salts were used directly. The peroxydicarbonates<sup>29</sup> were found to possess >85% theoretical oxygen by iodometry,<sup>30</sup> and were used directly except in those cases involving the study of isopropyl alcohol and acetone yields. Here the peroxide in toluene was thoroughly irrigated with ice water, dried over sodium sulfate, and analyzed iodometrically before usage.

**Aryl Alkyl Carbonate Syntheses.** Carbonate esters were synthesized using a modification of a literature procedure.<sup>31</sup> Chloroform rather than ethyl ether was used as the solvent for the pyridine-promoted condensation to avoid precipitating the pyridine hydrochloride by-product. The tolyl isopropyl carbonates were shown to be >99.5% pure by gc after work-up and their ir spectra were identical with reference spectra.<sup>32</sup>

Phenyl and the isomeric tolyl *sec*-butyl carbonates were prepared from *sec*-butyl chloroformate (synthesized by a literature method<sup>30</sup>) and phenol or the appropriate cresols in the same manner, and were shown to be greater than 99% pure by gc after work-up and distillation. All gave similar characteristic ir signals at 1750 ( $\text{C}=\text{O}$ ) and 1270–1260 and 1230–1210  $\text{cm}^{-1}$  ( $\text{C}-\text{O}$ ), and the tolyl *sec*-butyl carbonates had nearly identical nmr spectra: 0.95 (3 H, t), 1.25 (3 H, d), 1.50 (2 H, quintet), 2.2 (3 H, s), 4.6 (1 H, sextet), and 6.95 ppm (4 H, broad singlet).

**General Procedure for Aromatic Oxygenation.** Reactions for the system toluene-peroxide-CAN (25–50:1:2.25) were carried out as follows. CAN (0.0094 mol) was transferred with 80 ml of acetonitrile and 16 ml of toluene to a three-neck flask (250 ml) equipped with stirrer, condenser, and gas-inlet fitting. The assembled flask was immersed in a 60° constant-temperature oil bath, the salt was allowed to dissolve as the mixture was stirred, and the system was allowed to equilibrate for 5 min while being flushed with nitrogen (about 75 ml/min). After the system had been thoroughly purged, a gas train consisting of a Drierite trap leading into an Ascarite trap was attached to the top of the condenser. By momentarily removing the gas-inlet fitting, a toluene solution (4.00 ml) of diisopropyl peroxydicarbonate (1.04 M) was quickly pipetted into the stirred flask, and a nitrogen sweep of 10 ml/min was then established using a soap-bubble flow meter temporarily attached to the outlet end of the Ascarite trap. After 24 hr, the flask assembly was removed from the bath and allowed to cool to ambient, and the solution was carefully decanted into a volumetric flask (100 ml). The 3–4 g of salted-out cerous nitrate which remained was rinsed with sufficient 1-ml portions of acetonitrile to bring the volume to the mark.

Separate aliquots were then taken and analyzed directly by gc for product yield and light boilers. In some cases an aliquot was worked up to remove salts and the organic phase was titrated iodometrically to verify the absence of residual peroxide. In still other cases the tolyl isopropyl products were isolated by a procedure given elsewhere,<sup>32</sup> and qualitatively identified by infrared analysis.<sup>32</sup> Although most reactions were stirred and slowly purged with nitrogen, no decrease in product yield was noted when these steps were omitted, but the side-product ratios appeared to be altered somewhat.

Radical trapping studies were made using the general procedure and adding a 9–15 molar excess (to peroxide) of freshly distilled acrylonitrile or solid acrylamide to the system. All reacted solutions were visually examined for insoluble polymer, and after diluting to 100 ml with acetonitrile the solutions were analyzed by gc for aryl esters and by-products.

A slight alteration of the general procedure was employed for relative rate studies. The appropriate amounts of toluene and benzene (10–20 molar excess) were stirred in the assembled flask with the CAN-acetonitrile. A solution of peroxide in acetonitrile was then added, and the reaction was carried out as usual.

The oxygenation reaction was tried in a few other solvents (ethanol, 4-methyl-2-pentanone, and acetone) with discouraging results attributed to the oxidation of these by CAN.<sup>19</sup> Some 3–4% oxygenation was found in ethanol as the solvent, only a trace with acetone, and none with 4-methyl-2-pentanone.

Product yields are the average of duplicate experiments in good agreement, and these yields are based on a stoichiometry of 1 mol

of aryl ester products/mol of peroxide. This permits a direct comparison to those from diisopropyl peroxydicarbonate-cupric chloride.<sup>2</sup> Aryl ester and side-product yields were determined by gc.

**Identification of Organic Products.** Comparisons between the retention times for product components and authentic materials on two or more dissimilar gc columns and noting peak enhancements upon adding authentic compounds to reaction product mixtures comprised the basic approach for product identification. In this way benzaldehyde, benzyl alcohol, isomeric tolyl isopropyl carbonates, tolyl *sec*-butyl carbonates, tolyl benzoates, methyl biphenyls, and nitrobenzenes and bibenzyl were identified (gc columns 1 and 3). Using a similar approach, light-boiling products (acetone and isopropyl alcohol) were characterized (gc column 2).

**Identification of Inorganic Products.** The inorganic components were extracted from the reaction mixture with water as follows. The solution and precipitate were transferred with acetonitrile and water rinses to a separatory funnel (500 ml) containing toluene (25 ml). This solution was extracted with water (200 ml, 2 × 100 ml, 50 ml), and the combined aqueous phase was then washed once with toluene (10 ml) and made up to 500 ml. The combined toluene phase was diluted to 50 ml and saved for gc analysis. Using suitable aliquots from the aqueous extract (usually 50 ml), appropriate analytical tests were carried out to characterize the various inorganic components. Nitric acid was determined potentiometrically with standard alkali (0.100 N NaOH) by titrating duplicate 50-ml aliquots of the aqueous extract. The end points were estimated graphically from the titration curves.

Nonvolatile nitrate was determined spectrophotometrically by modifying a literature procedure.<sup>9</sup> From the 500-ml aqueous extract a 2-ml aliquot was transferred to a 50-ml beaker, and the contents were evaporated to dryness on the steam table. To the dried residue was added 1.0 ml of the phenoldisulfonic acid reagent, and after the salt was dissolved by gentle heating and stirring, the mixture was diluted to 250 ml with water and the absorption of this solution was measured at 407 nm in a 1-cm cell. The nitrate content of this solution was determined by reference to a similarly prepared nitrate calibration curve (0, 0.5, 1.0, and 1.5  $\mu\text{g N/ml}$ ).

The nitric acid nitrate and the nonvolatile nitrate were added to obtain the total nitrate in the inorganic reaction products.

Ammonium ion was determined on the vacuum-dried salt (2 hr, 80°) from a 50-ml aliquot of the aqueous extract by dissolving the salt in 0.5 M NaOH, distilling the liberated ammonia into standard sulfuric acid (0.050 N), and back titrating with standard base.

Cerium was determined on a 5-ml aliquot of the aqueous extract by measuring its ultraviolet absorption peak at 253.6 nm in 1 N sulfuric acid following a procedure given in the literature.<sup>8</sup>

**Carbon Dioxide Analysis.** This analysis was made by flushing the reaction gasses through preweighed Ascarite traps and noting the weight gain.<sup>2</sup> Because of the long reaction times (usually 24 hr) the nitrogen flow had to be restricted to 10–15 ml/min and the condenser temperature maintained below 5° to obtain satisfactory results. The material balance calculations for carbon dioxide yields by this method were 100–112%.

**Kinetic Studies.** All studies were made at 60° on solutions prepared, sometimes with modifications, as described in the general procedure. In studying the effects of various promoters on the peroxide decomposition rate, an initial toluene/peroxide ratio of 25 was provided in all cases. Aliquots (10 ml) were withdrawn by pipet at predetermined intervals and quickly delivered into separatory funnels (125 ml) containing ice-cold 1.0 N sulfuric acid (50 ml). Chilled toluene (10 ml) was added; the solution was gently mixed for 30 sec. After the phases were allowed to separate for 1 min, the aqueous lower phase was discarded and toluene layer was then washed with 10% sodium carbonate (25 ml, 2 × 15 ml) and water (2 × 15 ml). The toluene layer was then delivered with acetone rinses into a titrating flask containing potassium iodide (about 3 g) in acetone (50 ml), and titrated with standard 0.1 N sodium thiosulfate. In some cases 5-ml aliquots were withdrawn, in which case 0.05 N sodium thiosulfate titrant was used. Reactions without any interfering metal salts were also worked up in this manner before iodometry.

**Gas Chromatography Procedures.** Gc analyses were made on the following instruments: Hewlett-Packard Models 700 and 5750 B and Varian Models 1400 and 600 D, all equipped with flame ionization detectors and the following columns (all 0.125 in. o.d. stainless steel): column 1, 15 ft 10% Bentone 34-diisodecyl phthalate (50:50) on Diatoport S; column 2, 8 ft 20% Carbowax 400 on Chromosorb W; column 3, 10 ft 20% SE-30 on Chromosorb W; column 4, 12 ft 10% OV-225 on Chromosorb W; column 5, 6 ft Poropak Q.

Product yields for the diisopropyl peroxydicarbonate runs were

determined from duplicate analyses on columns 1 and 3 at 160° after adding an external standard, phenyl isopropyl carbonate, to a reaction aliquot. Isomer distributions were also studied on column 4 in addition to columns 1 and 3. Relative rates were analyzed on column 1 directly using a predetermined response factor. Light-boiling materials (acetone, isopropyl alcohol) were determined on columns 2 and 5 using methyl ethyl ketone in acetonitrile as an external standard.

Products from both benzoyl peroxide and di-*sec*-butyl peroxydicarbonate systems were determined on column 3 using phenyl benzoate and phenyl isopropyl carbonate, respectively, as external standards.

In all cases appropriate detector response factors were determined for the products relative to the marker by running a series of standards.

**Acknowledgment.** We thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this work.

**Registry No.**—Diisopropyl peroxydicarbonate, 105-64-6; toluene, 108-88-3; ceric ammonium nitrate, 16777-21-3;  $K_2Ce(NO_3)_6$ , 17126-44-2.

### References and Notes

- Presented at the 28th Annual Southwest Regional Meeting of the American Chemical Society, Baton Rouge, La., Dec 1972. A preliminary account of this work has appeared: M. E. Kurz, E. M. Steele, and R. L. Vecchio, *J. Chem. Soc., Chem. Commun.*, 109 (1973); taken in part from the M.S. Thesis of E.M.S., Illinois State University, 1972.
- M. E. Kurz and P. Kovacic, *J. Amer. Chem. Soc.*, **89**, 4960 (1967).
- M. E. Kurz and P. Kovacic, *J. Org. Chem.*, **33**, 268 (1968).
- P. Kovacic, C. G. Reid, and M. J. Brittain, *J. Org. Chem.*, **35**, 2152 (1970).
- T. Nakota, K. Tokumaru, and O. Simamura, *Bull. Chem. Soc. Jap.*, **43**, 3590 (1970).
- M. E. Kurz and S. S. Schultz, unpublished work.
- W. C. Pierce, E. L. Haenisch, and D. T. Sawyer, "Quantitative Analysis," Wiley, New York, N. Y., 1958, Chapter 8.
- H. L. Greenhaus, A. M. Feibush, and L. Gordon, *Anal. Chem.*, **29**, 1931 (1957).
- "Official Methods of Analysis of the AOAC," 10th ed, 1965, Section 31.005, p 522.
- "The Merck Index," 8th ed, P. G. Stecher, Ed., Merck & Co., Rahway, N. Y., 1968, p 224.
- W. S. Trahanovsky and J. Cramer, *J. Org. Chem.*, **36**, 1890 (1971).
- H. C. McBay and O. Tucker, *J. Org. Chem.*, **19**, 869 (1954); L. M. Terman, *Russ. Chem. Rev.*, **34**, 185 (1965).
- G. A. Olah and S. J. Kuhn, "Friedel-Crafts and Related Reactions," Vol. III, G. A. Olah, Ed., Wiley, New York, N. Y., 1964, p 1453; J. G. Hoggett, R. B. Moodie, J. R. Penton, and K. Schofield, "Nitration and Aromatic Reactivity," Cambridge University Press, New York, N. Y., 1971.
- M. E. Kurz, R. Fozdar, and S. S. Schultz, *J. Org. Chem.*, **39**, 3336 (1974).
- S. G. Cohen and D. B. Sparrow, *J. Amer. Chem. Soc.*, **72**, 611 (1950).
- F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry," Interscience, New York, N. Y., 1962, Chapter 31.
- F. Ephraim, "Inorganic Chemistry," Chemical Publishing Co., New York, N. Y., 1954, Chapter 15.
- G. F. Smith, V. R. Sullivan, and G. Frank, *Ind. Eng. Chem., Anal. Ed.*, **8**, 449 (1936).
- W. H. Richardson, "Oxidation in Organic Chemistry," K. B. Wiberg, Ed., Academic Press, New York, N. Y., 1965, Chapter IV, Part A; G. F. Smith, "Cerate Oxidimetry," G. Frederick Smith Chemical Co., Columbus, Ohio, 1942.
- M. E. Kurz, P. Kovacic, A. K. Bose, and I. Kugajevsky, *J. Amer. Chem. Soc.*, **90**, 1818 (1968).
- P. M. Nave and W. S. Trahanovsky, *J. Amer. Chem. Soc.*, **90**, 4755 (1968); **93**, 4536 (1971).
- G. Mino, S. Karzerman, and E. Rasmussen, *J. Amer. Chem. Soc.*, **90**, 4755 (1968).
- O. Bamford, A. Jenkins, and R. Johnston, *Proc. Roy. Soc., Ser. A*, **239**, 214 (1957).
- J. K. Kochi in "Free Radicals," Vol. I, J. K. Kochi, Ed., Wiley, New York, N. Y., 1973, Chapter 11.
- W. S. Trahanovsky and M. D. Robbins, *J. Amer. Chem. Soc.*, **93**, 5256 (1971).
- H. E. DeLaMare, J. K. Kochi, and F. F. Rust, *J. Amer. Chem. Soc.*, **85**, 1437 (1963).
- W. S. Trahanovsky and L. B. Young, *J. Chem. Soc.*, 5777 (1965); W. S. Trahanovsky, L. B. Young, and G. L. Brown, *J. Org. Chem.*, **32**, 3865 (1967); W. S. Trahanovsky and J. Cramer, *ibid.*, **36**, 1890 (1971).
- W. S. Trahanovsky and L. B. Young, *J. Org. Chem.*, **31**, 2033 (1966); W. S. Trahanovsky, M. D. Robbins, and D. Smick, *J. Amer. Chem. Soc.*, **93**, 2086 (1971).
- We are grateful to the Pittsburg Plate Glass Co., Barberton, Ohio, and the B. F. Goodrich Co., Henry, Ill., for generous samples of these peroxides.
- F. Strain, W. E. Bissinger, W. R. Dial, H. Rudolf, B. J. DeWitt, H. C. Stevens, and J. H. Langston, *J. Amer. Chem. Soc.*, **72**, 1254 (1950).
- D. S. Tarbell and E. J. Longosz, *J. Org. Chem.*, **24**, 774 (1959).
- M. E. Kurz, Ph.D. Dissertation, Case Institute of Technology, 1967.

## Concurrent Oxygenation-Nitration of Aromatics with Peroxides-Nitric Acid<sup>1</sup>

Michael E. Kurz,\* Rabindra L. Fozdar, and Stephen S. Schultz

Department of Chemistry, Illinois State University, Normal, Illinois 61761

Received February 26, 1974

Treatment of toluene with peroxydicarbonates or benzoyl peroxide in the presence of nitric acid led to the concurrent production of aryl esters and nitrotoluenes in 10–20% yields. More selectivity was noted in the aryl ester product formation than was previously reported for the free carbonate radical from diisopropyl peroxydicarbonate. Most striking, though, was the nitrotoluene isomer distribution (ortho:meta:para = 18:77:5) and relative rate (2.66), which contrasted markedly with that for the nitronium ion (ortho:meta:para = 60:5:35;  $k_{\text{toluene}}/k_{\text{benzene}} = 20\text{--}30$ ). Other aromatics (*e.g.*, chloro- and fluorobenzene) behaved similarly with nitric acid-peroxydicarbonates. Analogous reactions of toluene-nitric acid with a variety of other peroxides indicated that only those capable of forming oxy radicals at a reasonable rate gave rise to the unusual nitration pattern. Nitric acid was shown to inhibit the peroxydicarbonate decomposition rate by a factor of 2.  $N_2O_4$  and  $N_2O_5$  functioned effectively in promoting this concurrent nitration-oxygenation when used instead of nitric acid, indicating the importance of nitrogen dioxide in the reaction scheme. Reactions run with the stable free radical, galvinoxyl, as a trapping agent eliminated the nitration, further implicating nitrogen dioxide as the nitrating species. No evidence for the intermediacy of peroxyacyl nitrates or acyl nitrates was obtained even from peracids treated with various nitrating agents. A mechanism is proposed which involves attack by oxy radicals (or complexed oxy radical) onto the aromatic to form a cyclohexadienyl radical which is trapped by nitrogen dioxide. Under the reaction conditions the resulting dihydroaromatic can either lose  $HNO_2$  to form an aryl ester, or lose  $RCO_2H$  to form a nitro aromatic. The result of a  $\rho\sigma$  plot using composite partial rate factors tends to support the mechanism proposed.

Previously it had been reported that significant amounts of aryl esters could be produced when peroxydicarbonates and aryl peroxides were decomposed in toluene in the presence of a variety of promoters.<sup>2</sup> Among the effective

promoting species were the metal salts  $CuCl_2$ ,<sup>3</sup> ceric ammonium nitrate,<sup>4</sup>  $FeCl_3$ ,<sup>5</sup> and others,<sup>5,6</sup> molecular oxidants  $O_2$ <sup>7</sup> and  $I_2$ ,<sup>8</sup> and even radicals such as trityl.<sup>9</sup> In most of these cases an oxy radical was felt to be the substituting entity,