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.

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Concurrent Oxygenation–Nitration of Aromatics with Peroxides–Nitric Acid[1]

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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; $k_{\text{toluene}}/k_{\text{benzene}}$ = 20–30). 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.

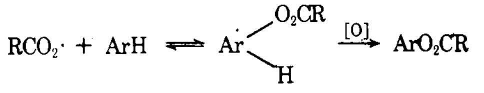
Previously it had been reported that significant amounts of aryl esters could be produced when peroxydicarbonates and aroyl peroxides were decomposed in toluene in the presence of a variety of promoters.[2] Among the effective promoting species were the metal salts $CuCl_2$,[3] ceric ammonium nitrate,[4] $FeCl_3$,[5] and others,[5,6] molecular oxidants O_2[7] and I_2,[8] and even radicals such as trityl.[9] In most of these cases an oxy radical was felt to be the substituting entity,

Table I
Product Analysis for Toluene–Dialkyl Peroxydicarbonate–Nitric Acid[a,b]

Products	System			
	HNO_3–SBP	HNO_3–IPP	IPP[c]	HNO_3[d]
$CH_3C_6H_4OCO_2R$	19	17	1	
o-:*m*-:*p*-	59:7:34	65:6:29		
$CH_3C_6H_4NO_2$	17	17		3
o-:*m*-:*p*-	20:76:4	18:77:5		60:5:35
$C_6H_5CH_2NO_2$	13	12[e]		0
$C_6H_5CH_2OCO_2R$	0	0	2	0
$C_6H_5CH_2OH$	6	8	Trace	0
C_6H_5CHO	15	18	2	3
C_6H_5COOH	<1	2[f]	<1	
$(C_6H_5CH_2\text{—})_2$	5	3[f]	36	0
CH_3COCH_3		50	58	
$CH_3CHOHCH_3$		105	130	
$CH_3C_6H_3(NO_2)_2$	<1	2[f]		<1

[a] Peroxide (5 mmol), nitric acid (10 mmol), and toluene (10 ml) in acetonitrile (50–75 ml), 60°, 24 hr. [b] Yields based on moles of peroxide limiting reagent; actual yield of nitration based on nitric acid is one-half the table value. [c] No nitric acid. [d] No peroxide, 72 hr. [e] The average of four widely varying runs. [f] Approximate yields.

and the oxidant served to rearomatize an initially formed cyclohexadienyl radical (eq 1).



$$RCO_2\cdot + ArH \rightleftharpoons \dot{A}r{<}^{O_2CR}_{H} \xrightarrow{[O]} ArO_2CR \qquad (1)$$

Nitrogen dioxide was also utilized to promote this type of reaction in a somewhat different manner characterized by a concomitant production of nitrated aromatics.[10] In connection with our studies on aromatic substitution by oxy species we have had occasion to study peroxide–aromatic combinations in the presence of nitric acid and have observed a similar oxygenation–nitration phenomenon. In light of the fact that peroxyacetyl nitrate (PAN), the best known member of the new class of PAN's produced in photochemical smog,[11] can be made from the reaction of nitric acid and peracetic acid,[12] we became particularly interested in determining the nature of the peroxide–nitric acid–aromatic reaction, and assessing whether or not PAN-type intermediates were involved. We wish to report our findings here.

The standard procedure involved combining peroxide, nitric acid, and toluene in a 1:2:20 molar ratio in excess acetonitrile at 60° for 12–24 hr. The products of the reaction with both diisopropyl peroxydicarbonate (IPP) and di-*sec*-butyl peroxydicarbonate (SBP) are listed in Table I. Control runs containing toluene with IPP alone or with nitric acid alone are also included for comparison.

The formation of significant amounts (17–19%) of tolyl alkyl carbonates shows that the nitric acid apparently can serve as an oxidant in promoting aromatic substitution, especially when compared to the peroxide control. Even more interesting was the fact that a similar amount of nitrotoluenes, comprised predominantly of the meta isomer, was formed in each case, in addition to small amounts of dinitrotoluenes. In contrast, the nitric acid control gave only a small amount of nitrotoluenes with an isomeric pattern which was in agreement with the literature reported values for electrophilic nitration involving nitronium ion.[13,14] Among other major products from IPP–HNO_3–toluene were acetone and 2-propanol, formed by degradation of the peroxide, as described elsewhere.[3] Most of the minor products were produced from side-chain reactions of toluene (*i.e.*, benzaldehyde, benzyl alcohol, α-nitrotoluene, benzoic acid, and bibenzyl). Many of the benzyl radicals were diverted from the dimerization path characteristic of the control run, into side-chain oxidation products typical of toluene nitrations with radicals present.[15]

With IPP a reaction series of different nitric acid to peroxide ratios over the range 0.5–5.0 was run. Both ring oxygenation and nitration increased from 6 to 20%, but the isomeric composition in each case remained essentially the same as in Table I. Side-chain oxidation and nitration also increased somewhat when greater amounts of nitric acid were used.

Other peroxides were decomposed in the presence of nitric acid–toluene to see how general this concurrent production of aryl esters and nitroaromatics was (Table II). The only peroxide other than the peroxydicarbonates which gave significant amounts of both types of aromatic substitution was benzoyl peroxide. In this case tolyl benzoates were produced with an isomer distribution and yield very similar to those of the tolyl carbonate esters while the nitrotoluenes showed a much higher ratio of meta isomer than usual,[14,15] but not as high as with the peroxydicarbonates. This is most likely due to some direct nitration of toluene by nitric acid at this greater reaction temperature and time.

In light of earlier reports[11] potential involvement of PAN's seemed most probable from systems involving peracids (eq 2), and two such candidates (perbenzoic and *m*-chloroperbenzoic acid) were treated with nitric acid and

$$CH_3CO_3H + HNO_3 \longrightarrow CH_3CO_3NO_2 + H_2O \qquad (2)$$

toluene. One can visualize a process analogous to eq 2 leading to peroxybenzoyl nitrate (PBN) from perbenzoic acid. However, under the conditions studied (80° in acetonitrile) little indication of PBN involvement was noted as most of the peracid decomposed to benzoic acid.[16] Small amounts (~1%) of two oxygenation products (cresols and tolyl benzoates) were obtained, suggesting the intermediacy of both the hydroxyl and benzoyloxy radical, respectively (eq 3).

$$C_6H_5CO_3H \longrightarrow C_6H_5CO_2\cdot + HO\cdot \qquad (3)$$

The former was rapidly nitrated, showing up in the final product mixture as nitrocresols and dinitrocresols (in 1% and trace quantities, respectively). Less than 1% of nitrotoluenes (ortho:meta:para = 47:24:29) were formed in this reaction as well as small amounts of methyl biphenyls, benzyl nitrate, and α-nitrotoluene, further substantiating the presence of some radicals (eq 3).

The reaction of *m*-chloroperbenzoic acid–HNO_3–toluene led to small amounts of the same or analogous products except that the nitrotoluene isomers (ortho:meta:para = 58:8:34) more nearly resembled those expected from nitric acid alone.[14]

Two peresters (*tert*-butyl perbenzoate and *tert*-butylperoxy isopropyl carbonate) were studied in like fashion. No oxygenation products were formed with either perester, although nitration did occur. The yields and isomer distribution for all the peroxides studied with nitric acid–toluene are summarized in Table II. Also listed are the relative rates of nitration in each case as obtained by performing toluene–benzene competitions. These intramolecular and intermolecular selectivities are compared to those obtained from nitric acid without any peroxide and to previous literature values for nitrations. For peroxides such as the peroxydicarbonates that decompose quite rapidly at 60° (see the literature values for the peroxide half-lives, Table II) the same high proportion of meta isomer (76–80%) was obtained whereas those peroxides which were reasonably sta-

Table II
Nitration of Toluene with Nitric Acid in the Presence of Peroxides[a]

				Ring nitrotoluenes					Temp for 10 hr
Registry no.	Peroxide	Temp, °C	Aryl esters, %[b]	%yield[b]	*o*-	*m*-	*p*-	k_{tol}/k_{ben} [c]	$t_{1/2}$ [d]
105-94-6	$(i\text{-PrOCO}_2)_2$	60	17	17	18	77	5	2.66	34
		80		*e*	17	78	5	3.04	
19910-65-7	$(sec\text{-BuOCO}_2)_2$	60	19	17	20	76	4	*e*	36
		50		*e*	17	80	3	2.33	
94-36-0	$(C_6H_5CO_2)_2$	60	9[f]	10	33	54	13	2.07	72
		80	12[g]	*e*	38	47	15	*e*	
93-59-4	$C_6H_5CO_3H$	60	1[h]	1	47	24	29	*e*	76[i]
937-14-4	$m\text{-ClC}_6H_4CO_3H$	80	1[j]	*e*	58	8	34	*e*	
2372-21-6	$t\text{-BuOOCO}_2\text{Pr-}i$	80	0	3	57	7	36	14.1	97
614-45-9	$t\text{-BuOOCOC}_6H_5$	80	0	14	57	6	37	22.4	105
78-67-1	AIBN[l]	80		5	61	5	34	20.5	
	None	60		3	60	5	35	33.7	
		80		14	60	5	35	29.7	
		30–60[k]			57–61	3–5	37–40	21–27	

[a] Peroxide (5 mmol), HNO_3 (10 mmol), and toluene (10 ml) in acetonitrile (50–75 ml). [b] Based on peroxide limiting reagent; actual yield of nitration based on nitric acid is one-half the table value. [c] Aromatic mixture of benzene (10 ml) and toluene (10 ml) used; value corrected to a 1:1 molar ratio of the two. [d] See ref 17. [e] Not determined. [f] Ortho:meta:para = 73:5:22; methyl biphenyls (3%) also formed. [g] Ortho:meta:para = 69:7:24; methyl biphenyls (25%) also formed. [h] Includes nitrocresols and tolyl benzoates. [i] Approximated from data in ref 16 and 18. [j] Nitrocresols. [k] See ref 13 and 14. [l] Azobisisobutyronitrile.

Table III
Product Analyses for Peroxide–Toluene–Nitrogen Oxides System[a]

	Nitrotoluenes				RCO_2Ar			
System	Yield	*o*-	*m*-	*p*-	Yield[b]	*o*-	*m*-	*p*-
HNO_3–IPP	17	18	77	5	17	64	5	31
HNO_3	3	60	5	35				
N_2O_4–IPP	18	21	66	13	21	62	10	28
N_2O_4	12	67	5	28				
N_2O_5–IPP[c]	20	33	55	12	48	55	15	30
N_2O_5[c]	19	62	4	34				
HNO_3–$(C_6H_5CO_2)_2$[d]	8	38	47	15	12	72	4	24
N_2O_4–$(C_6H_5CO_2)_2$[d]	33	57	13	30	16	69	9	22
N_2O_4–$(C_6H_5CO_2)_2$[d,e]	5	13	85	2	14	50	16	34

[a] Peroxide (5 mmol), nitrogen oxide (10 mmol), and toluene (100 mmol) in CH_3CN (50 ml) at 60°; see Experimental Section. [b] Based on moles of peroxide limiting reagent; actual yield based on nitric acid is one-half the yield reported. [c] Reference 15. [d] 80°. [e] From ref 10; NO_2:peroxide = 0.53; benzene also present as part of a competition run.

ble at 60° or even 80° gave isomeric compositions much more compatible with the usual nitronium ion intermediates.[14] Benzoyl peroxide, which was somewhat intermediate in stability of the peroxides studied, gave almost 50% of the meta isomer. Azobisisobutyronitrile, a nonperoxidic radical-producing agent having a similar half-life to that of benzoyl peroxide, failed to appreciably alter the usual pattern of nitric acid–toluene reaction.

The peroxide, IPP, was singled out for further mechanistic studies. Kinetic analyses were performed on the nitric acid promoted IPP decomposition at 60° utilizing both nmr and iodometric techniques. The rates obtained by both methods, 6.09 and 6.53×10^{-3} min^{-1}, respectively, were in excellent agreement and indicated roughly a twofold rate hindrance in comparison to that (13.6×10^{-3} min^{-1}) for the peroxide decomposition in the absence of nitric acid. The rate of by-product formation (acetone and 2-propanol) was also able to be followed by nmr, and coincided well with that of the peroxide decomposition. Nmr had previously been used to detect PAN formation from peracetic acid through the observance of a new methyl group signal.[19] In our case no sign of any species other than those due to the decomposing peroxide and forming 2-propanol and acetone were spotted by nmr. Attempts to detect an intermediate by uv spectroscopy were also futile. CIDNP effects were not observed while the peroxide–nitric acid decomposition was repeatedly monitored by nmr, even though such effects have been noted for a variety of peroxide systems.[20]

Other nitrogen oxides were studied with both IPP and benzoyl peroxide to see if they could function effectively to promote concurrent nitration and oxygenation of toluene (Table III). N_2O_4 and N_2O_5 served well as oxygenation promoters, as aryl esters were obtained in as good or better yields as in the HNO_3–peroxide reaction. Nitration also occurred in good yield and the preponderance of meta isomer was again evident in the peroxydicarbonate cases. However, with benzoyl peroxide a much greater amount of nitrotoluenes of lower meta content was produced, indicating that direct nitration of toluene with NO_2 was probably competing strongly. In the previous work,[10] where a deficiency of NO_2 relative to peroxide was used, the unusual nitrotoluene composition clearly showed up.

Nitration with N_2O_4 and N_2O_5 alone also led to nitrotoluenes in 18–20% yields, but with isomer values which were in excellent agreement with the literature values[13,14] for nitrations involving nitronium ions.

The similarity in reaction characteristics of the peroxide with the various nitrogen oxides suggests that a common species, most likely nitrogen dioxide, is involved in each case.

To determine the extent of free-radical involvement in both the nitration and oxygenation processes, a stable free radical, galvinoxyl,[21] was employed as a radical trapping agent in the IPP–HNO_3–toluene system (Table IV). As more scavenger was added the nitration could be diminished and wiped out, but the oxygenation persisted. It should be pointed out that even when a 1:1 ratio of galvinoxyl to peroxide was utilized, only enough scavenger was available to trap half of the potential oxy radicals; hence oxygenation could still occur. Indeed, when galvinoxyl was

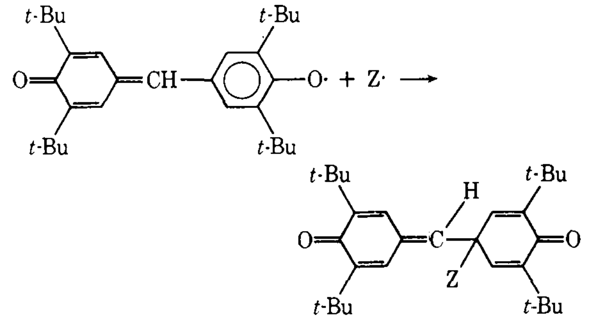
Table IV
Oxygenation-Nitration in the Presence of Galvinoxyl[a]

	$CH_3C_6H_4NO_2$		$CH_3C_6H_4OCO_2Pr\text{-}i$	
System	Yield	*o*:*m*:*p*	Yield	*o*:*m*:*p*
HNO_3-IPP (2:1)	17	18:77:5	17	64:5:31
HNO_3-IPP-galvinoxyl (2:1:0.3)	8[b]	20:77:5	13	60:11:29
HNO_3-IPP-galvinoxyl (2:1:1)	1		12	51:13:36
IPP-galvinoxyl (1:1)[c]			15	56:15:29

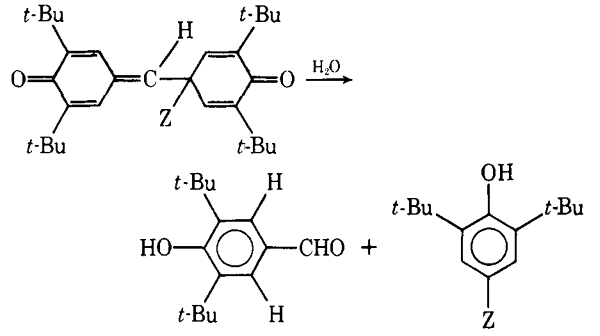
[a] Peroxide:HNO_3:toluene = 1:2:20 in excess CH_3CN at 60°; see Experimental Section. [b] Single run only. [c] No nitric acid.

used with the peroxide alone, tolyl esters with an isomer distribution typical of carbonate radical oxygenation[3,24] resulted, which suggests the involvement of galvinoxyl itself as an oxygenation promoter.

Product analyses carried out on the toluene-IPP-HNO_3 reaction with galvinoxyl were quite revealing. Large amounts of 2,6-di-*tert*-butyl-4 nitrophenol and 2,6-dinitrohydroquinone, formed from breakdown of the scavenged products of galvinoxyl with nitrogen dioxide and the isopropyl carbonate radical, respectively (eq 4 and 5), provide good evidence for the involvement of both radicals in the reaction. Furthermore, all of the galvinoxyl is apparently consumed, as evidenced by the disappearance of a product felt to be due to galvinoxyl breakdown on the chromatograph (see paragraph at end of paper regarding supplementary material).


(4)

Z = NO_2, *i*-$PrOCO_2$, H


(5)

IPP-Nitric Acid-Other Aromatics. The study of the peroxydicarbonate-nitric acid system was extended to other aromatics. In all cases aryl ester formation was accompanied by nitration products (Table V). The nitration pattern observed with the halobenzenes was found to be predominantly meta, in contrast to the usual ortho/para nitration with NO_2^+ (Table V), just as it was with toluene. Relative rate values closer to unity than is typical of nitrations involving NO_2^+ were also obtained for chlorobenzene and fluorobenzene as well as for toluene. Although anisole underwent both substitution reactions the nitration pattern was more typical of straightforward electrophilic nitration,[22] a process which likely competed strongly with this more reactive aromatic under the reaction conditions.

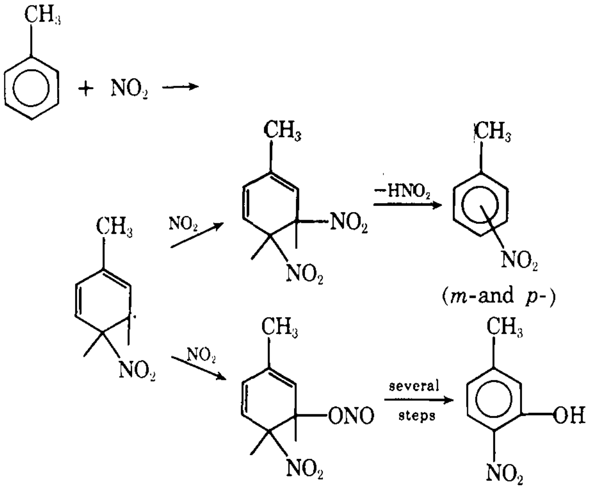
The isomer distributions and relative rates for the oxygenation products differed from those values noted earlier for the isopropyl carbonate radical,[3] except in the case of anisole. (See paragraph at end of paper regarding supplementary material.)

Discussion

Nitric acid effectively promotes aromatic oxygenation with certain peroxides, and in the process nitrates aromatics in an unusual manner. Although a number of mechanistic pathways can be considered for the two aromatic substitutions, most can be discounted.

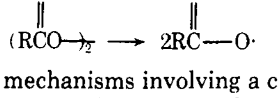
For example, independent electrophilic substitutions with nitronium ion can be ruled out on the basis of the much different nitration pattern, while the presence of cationic oxygen such as noted previously with peroxydicarbonate- $AlCl_3$[27] seems unlikely, as nitric acid retards peroxide decomposition rather than promoting heterolysis.

Independent radical substitution processes also do not adequately explain the results. Titov[28] has discussed radical nitrations involving substitution by NO_2 and subsequent trapping of the cyclohexadienyl radical as in eq 6 and 7.[29] However, it is unlikely that such a scheme pertains in our case, since we found no evidence for nitrocresols (eq 7) except in the peracid cases and there is no consistent rationale to account for the large preponderance of the meta-nitrated aromatic.



(6)
(7)

Oxy radical attack followed by subsequent oxidation to the aromatic (eq 1) is not a fully satisfactory mechanism for the oxygenation process either, since one would have anticipated obtaining the same pattern of substitution as noted for $CuCl_2$-,[3] I_2-,[8] and O_2[7]-promoted oxygenations. A complexed oxy radical (eq 8) is a possibility as the oxygenating species and would account for the greater selectivity observed.[5]



$$(\overset{\overset{\text{O}---\text{H}^+}{\|}}{\text{RC}}\text{O}\rightarrow)_2 \longrightarrow 2\overset{\overset{\text{O}---\text{H}^+}{\|}}{\text{RC}}\text{—O}\cdot \qquad (8)$$

A number of mechanisms involving a common nitrating-oxygenating species can be envisioned.

For example, peroxyacyl nitrates (eq 9) or acyl nitrates (eq 10) could be formed under the reaction conditions but

$$(RCO_2\rightarrow)_2 + HNO_3 \longrightarrow RCO_3NO_2 + RCO_2H \qquad (9)$$

$$C_6H_5CO_2\cdot + NO_2 \longrightarrow C_6H_5CO_2NO_2 \qquad (10)$$

being unstable could conceivably break down in such a manner as to nitrate and oxygenate toluene in the process. There is no prior literature analogy for this type of behav-

Table V

Nitration and Oxygenation of Aromatics with Nitric Acid–Diisopropyl Peroxydicarbonate

Aromatic	System	$ArNO_2$			$ArOCO_2Pr$-		
		Yield[a]	o-:m-:p-	$k_{ArH}/k_{C_6H_6}$	Yield[a]	o-:m-:p-	$k_{ArH}/k_{C_6H_6}$
$C_6H_5CH_3$	HNO_3–IPP[b]	17	18:77:5	2.66	17	64:5:31	12.4
	HNO_3[c]	3	60:5:35	33.7			
	$CuCl_2$–IPP[d]				85	57:15:28	3.77
C_6H_5Cl	HNO_3–IPP[b]	17	10:87:3	0.65	5	64:tr:36	0.85
	HNO_3–H_2SO_4[e]		31:tr:69				
	$CuCl_2$–IPP[f]				29	54:13:33	0.46
C_6H_5F	HNO_3–IPP[b]	16	28:58:16	0.32	7	41:36:23	0.65
	HNO_3–H_2SO_4[e]		20:0:80[g]				
	$CuCl_2$–IPP[f]				30	33:22:45	0.31
$C_6H_5OCH_3$	HNO_3–IPP[b]	31	39:0:61	57.4	16	59:tr:41	19.1
	HNO_3–H_2SO_4[h]		31:2:67				
	$CuCl_2$–IPP[d]				98	63:1:36	24.9

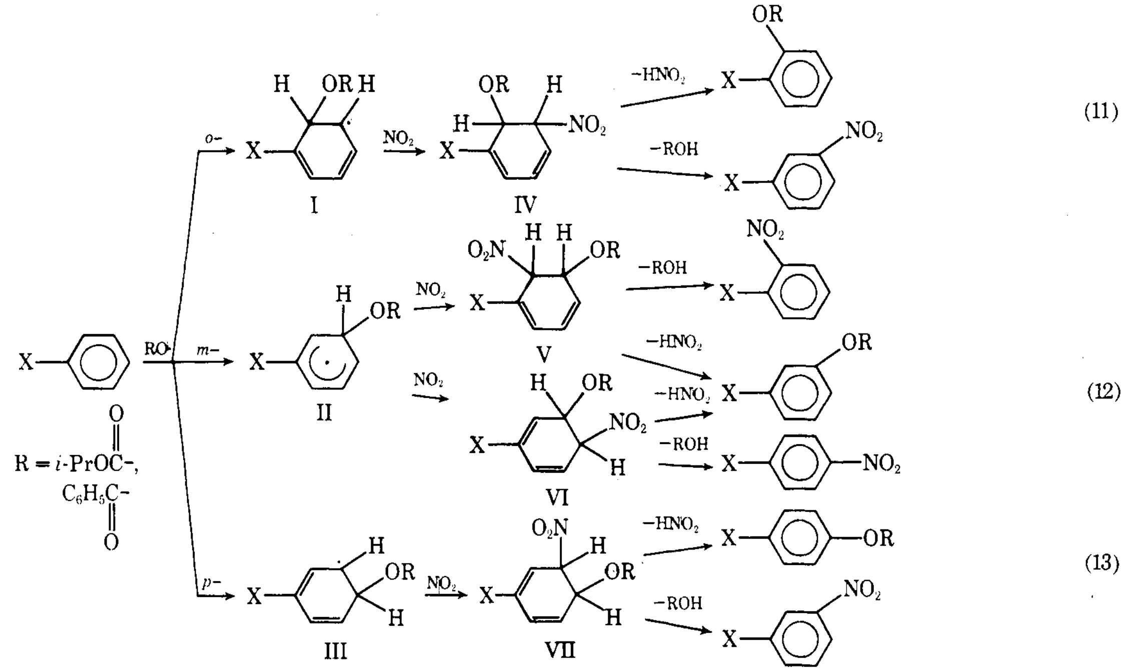
[a] Yield based on mol of products/mol of peroxide. [b] Peroxide (5 mmol), HNO_3 (10 mmol), and aromatic (10 ml) in acetonitrile (50 ml), 60°, 24 hr. [c] Acetonitrile solvent; for other values see ref 14 and 23. [d] See ref 24. [e] HNO_3 (0.05 mol), H_2SO_4 (0.05 mol), and aromatic (20 ml), 60°, 24 hr. [f] See ref 25. [g] Lit. value[26] 12:0:88. [h] See ref 22.

ior for peroxyacyl nitrates, but such a species might be expected to exhibit both peroxide and nitrate reactivity. Previously Fischer and coworkers[30] had demonstrated that protonated acetyl nitrate from acetic anhydride–nitric acid is the common intermediate responsible for both nitrating and acetoxylating aromatics such as toluene and *o*-xylene. Similar studies[15] of benzoyl nitrate interaction with toluene in the presence of acids did produce some tolyl benzoates, but gave the usual (ortho:meta:para = 60:5:35) nitrotoluene product pattern. However, we obtained no evidence for either type of intermediate, and neither species could suitably explain the predominance of *m*-nitrotoluenes in our system.

The mechanism which appears to be consistent with our experimental observations is analogous to that reported for benzoyl peroxide with nitrogen dioxide[10] and is shown in Scheme I, eq 11–13. It involves the usual reversible attack by the acyloxy radical (or possibly an acid-complexed acyloxy radical) onto the aromatic, giving the three possible cyclohexadienyl radical intermediates (I–III). These in turn are trapped efficiently by small amounts of nitrogen dioxide to produce various dihydroaromatics (IV–VII), which under the reaction conditions tend to rapidly rearomatize losing either nitrous acid or an alkyl hydrogen carbonate (alcohol + carbon dioxide). With toluene at least, the dihydroaromatic tended to partition itself to the aryl ester and nitrotoluene in roughly equal proportions. With the halobenzene, the corresponding intermediates (IV–VII) preferentially formed nitrohalobenzenes (eq 11–13, Table V). Since the oxy radical attacks toluene and the halobenzenes predominantly at ortho and para positions,[3,25] nitroaromatics formed in this manner would be predominantly the meta isomers (eq 11, 13). Only anisole of the aromatics failed to give meta nitration. Perhaps the greater reactivity

Scheme I

Concurrent Oxygenation–Nitration



of anisole toward nitric acid[14] caused the usual electrophilic nitration to occur in that case.

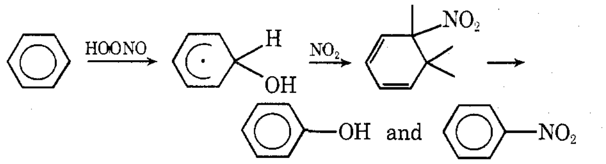
The scheme presented also accounts qualitatively for the unusual "apparent" relative reactivities of toluene and benzene toward both nitration and oxygenation. Since both types of substitution products resulted from initial attack by the oxy radicals onto the aromatic, one can calculate a composite partial rate factor for this process by taking into account the proposed scheme (Scheme I), the apparent partial rate factors for nitration and oxygenation and the molar yields of oxygenation relative to nitration (Table V). Plotting the resulting composite partial rate factors (describing initial oxy radical attack) *vs* the appropriate σ^+ values gave a surprisingly fair correlation with a slope of -1.87 (ρ value) and an average deviation of ±0.05 (see paragraph at end of paper regarding supplementary material).[31] This value compares quite closely to that obtained (-2.1) by doing a least-squares plot for the same points from isopropyl carbonate radical,[25] providing further evidence for this concurrent nitration–oxygenation scheme.

The fact that N_2O_4 and N_2O_5 also serve efficiently to promote oxygenation is consistent with the mechanism proposed, since both are reasonable sources of nitrogen dioxide.[32] The similarity of these systems to that with nitric acid seems to indicate that NO_2 is the species responsible in nitric acid for promoting aromatic substitution.

The results of the galvinoxyl trapping experiments are also in line with the proposed scheme. Galvinoxyl is known as an efficient scavenger of both carbon and oxygen free radicals, particularly the shorter lived ones such as *tert*-butoxy radical.[21] Despite the fact that potential carbonate radicals exceeded the amount of galvinoxyl used (Table IV), galvinoxyl reacted in ways other than just trapping the longer lived carbonate radicals in this system. It scavenged nitrogen dioxide, present in relatively small amounts in the peroxide–HNO_3 media to wipe out the nitroaromatic production (Table IV) and account for the 2,6-di-*tert*-butyl-4-nitrophenol found. Galvinoxyl also reacted with cyclohexadienyl radicals formed from oxy radical attack on the aromatic to promote aromatic oxygenation by either hydrogen atom abstraction[33] or electron transfer.[34] The small amount of 2,6-di-*tert*-butylphenol (eq 4 and 5) is consistent with hydrogen atom abstraction by galvinoxyl.

The reason for the rate-retarding effect of nitric acid on the peroxydicarbonate is uncertain. It could indicate acid complexing of the peroxide, since the breakdown of complexed peroxides is known to be slowed down.[5,6] A complexed radical formed therefrom could also account for the more selective nature of the oxygenation and essentially the same scheme (Scheme I) for nitration–oxygenation would hold.

There is prior analogy for the mechanism proposed which amounts to a radical addition-elimination mechanism. The reaction of pernitrous acid with aromatics giving nitration and hydroxylation in very low yields was felt to involve hydroxyl radical attack followed by nitrogen dioxide trapping (eq 14).[29,35]



(14)

Analogous addition–elimination mechanisms have been proposed for electrophilic aromatic substitutions, including aminations with trichloroamine–aluminum chloride,[36] concurrent nitration–acetoxylation by protonated acetyl nitrate,[30] and others.[37]

Experimental Section[38]

Reagent-grade solvents and chemicals were used directly, including deuterioacetonitrile (Merck Sharp and Dohme, 99%), which was checked for purity by nmr. The commercial peroxides,[39] checked out to be greater than 95% pure except for 85% *m*-chloroperoxybenzoic acid, were used without purification except for benzoyl peroxide, which was recrystallized from methanol–hexane. Peroxybenzoic acid was synthesized from benzoyl peroxide and hydrogen peroxide by a literature method;[40] the peracid was extracted into toluene, and the toluene stock solution was titrated and used directly in the appropriate reactions.

Tolyl alkyl carbonate authentics (not commercially available) were synthesized from the appropriate phenols and alkyl chloroformates as previously described.[4]

Nitrocresol product mixtures for comparative purposes were made by treating *o*- and *p*-cresol, respectively, with HNO_3 in acetonitrile at 60°. In the former case two major nitration products were found by gc–mass spectrum (*m/e* 153, base peak) and were assumed to be 4-nitro-2-methylphenol and 6-nitro-2-methylphenol. With *p*-cresol just one major nitration product (*m/e* 153), presumably 2-nitro-4-methylphenol, was produced.

Reactions of Aromatics with Nitric Acid–Peroxide. General Procedure. The peroxide (5 mmol) in the appropriate aromatic (10 ml) was mixed with acetonitrile (50 ml) containing the appropriate amount of nitric acid in a lightly stoppered flask, and immersed quickly in a constant-temperature bath for a 24-hr period or longer. At the end of this time, qualitative and quantitative product analysis was carried out on the reaction mixtures. For the competition studies, a mixture of benzene and the appropriate aromatic, both present in at least an 18-fold molar excess, was used with the peroxide and nitric acid. The aromatic:benzene product ratios (both nitration and oxygenation) corrected to equimolar reactant concentrations were used directly as a measure of the relative rates.

Other reactions were carried out with modifications of the general procedure. In the galvinoxyl run additional toluene was required to solubilize the radical trapping agent. Reactions with NO_2 were carried out in special reaction flask containing peroxide–toluene and solvent which was evacuated at liquid nitrogen temperatures. N_2O_4 was weighed out in a separate gas density bulb and then distilled into the reaction vessel. After the appropriate quantity of NO_2 was added, the vessel was sealed, placed in a constant-temperature bath for 24–48 hr at 60°, and then analyzed.

In all cases reactions were carried out in duplicate (unless otherwise indicated) and the yields reported are the average of two or more runs in close agreement.

Kinetic Studies. A. By Iodometry. A method described elsewhere[4] was used. In the runs containing nitric acid, the end point became harder to detect as the decomposition approached midway, owing to the continued development of colored nitrotoluenes. In these cases, titration was carried out to the color of blanks containing the calculated amount of nitrotoluenes.

B. By Nmr. Prior to carrying out a kinetic study by nmr (Perkin-Elmer Hitachi Model R-20), we demonstrated that the signals from the expected products and starting peroxide did not interfere with each other. A control run with HNO_3 in CD_3CN indicated that the nitrile underwent proton exchange but did not interfere with the signals to be followed.

The kinetic run itself was performed on the reaction of diisopropyl peroxydicarbonate with HNO_3 in the absence of aromatic in deuterated acetonitrile. One milliliter of a peroxide solution in CD_3CN (4.5 *M*) was mixed with HNO_3 in an nmr tube to give a peroxide:HNO_3 molar ratio of 1:2. The tube was set into the nmr probe which was thermostatted at a constant temperature of 60 ± 0.5°. The intensities of the following major signals were monitored: isopropyl group doublet from the reactant peroxide (δ 1.28), isopropyl group doublet from 2-propanol (product) (δ 1.04), and methyl group singlet from acetone (product). The changes in integration heights of the signals were followed *vs.* time to obtain changes in concentration of both reactant and products. To take care of any possible error due to instrumental instability, the field homogeneity was checked throughout the experiment. The study was repeated with *p*-dichlorobenzene added as an inert material to the reaction mixture for use as an internal intensity standard. The intensities of the signals could then be adjusted when any fluctuation of the *p*-dichlorobenzene marker occurred. Little correction had to be made and reasonable agreement was noted for the data from the two runs.

Nitration of Halobenzenes. HNO_3 (3.2 ml, 0.05 mol) and

H_2SO_4 (2.65 ml, 0.05 mol) were mixed, cooled, and added to the halobenzenes (fluoro- and chlorobenzene). The mixtures were vigorously shaken at intervals over a 24-hr period at 60°. The products (two) from fluorobenzene was collected by preparatory gc (column A) and analyzed by ir and mass spectrum. The smaller product, ortho, gave an out-of-plane C–H bending signal at 755 cm^{-1}, while the larger para product had the corresponding signal at 840 cm^{-1}. Both had a mass spectrum with *m/e* 141 (molecular ion) and 95 (base peak). The nitrochlorobenzene products were compared to authentics and also analyzed by mass spectrum (*m/e* 157).

Analytical Procedures. A. Product Identification. The product mixture from the reaction of 50 mmol of diisopropyl peroxydicarbonate and 100 mmol of nitric acid with toluene in acetonitrile was concentrated on a rotary evaporator, and the concentrate was separated into a number of components by preparative gc (Varian Model 90-P, thermal conductivity detector, column A, 6 ft × 0.25 in. 3% SE-30 on Chromosorb W). The major product gave an ir consistent with *m*-nitrotoluene contaminated with a small amount of ortho and para isomers. The second largest product was shown by ir to be *o*-tolyl isopropyl carbonate. From other analogous reaction mixtures gc-mass spectral analysis was performed using a Finnegan Model 3000 G.C. peak identifier with a quadrupole mass filter. Mass spectra at 70 eV of the reaction products eluted from three different columns (B, 6 ft × 0.125 in. stainless steel, 3% OV-1 on Chromosorb W: C, 10 ft × 0.125 in. copper, 10% OV-225 on Chromosorb W, AW-DMCS; D, 10 ft × 0.125 in. copper, 20% SE-30 on Chromosorb W, AW-DMCS) indicated the presence of benzaldehyde (*m/e* 106), benzyl alcohol (*m/e* 108), benzoic acid (*m/e* 122), nitrotoluenes (*m/e* 137), tolyl isopropyl carbonates (*m/e* 194, fragments at *m/e* 135, 108, and 43), bibenzyl (*m/e* 182), and traces of dinitrotoluenes (*m/e* 182). Other minor high boilers were detected, but were not identified. Column D programmed at 160–240° was utilized in like manner to separate and identify the nitroanisoles (*m/e* 153) and anisyl isopropyl carbonates from anisole, chloronitrobenzenes (*m/e* 157) and chlorophenyl isopropyl carbonates from chlorobenzene, and fluorophenyl isopropyl carbonates (*m/e* 198) and fluoronitrobenzene (*m/e* 141) from fluorobenzene.

Column D was used with the gc-mass spectrum to identify the benzoyl peroxide reaction products, benzoic acid (*m/e* 122), nitrotoluenes (*m/e* 137), methyl biphenyls (*m/e* 168), phenyl benzoate (*m/e* 198), and tolyl benzoates (*m/e* 212), while both columns C and D were used to identify benzyl nitrate (*m/e* 153), nitrotoluenes (*m/e* 137), benzoic acid (*m/e* 122), nitrocresols (*m/e* 153), methyl biphenyls (*m/e* 168), and tolyl benzoates (*m/e* 212) from the perbenzoic acid runs. Column B was used to pin down the galvinoxyl reaction products. In addition all nitration and oxygenation products were matched with authentic materials by gc retention times on at least two different columns (C and D). Nitrocresol and nitrofluorobenzene isomers were identified by comparison to the product mixtures from the nitrations of *o*- and *p*-cresol and fluorobenzene.

B. Quantitative Analysis. Reaction product yields were determined by adding a known quantity of a marker (usually phenyl isopropyl carbonate) to a one-tenth portion of the reaction mixture and analyzing by gc (Varian Models 1400 and 600D with flame ionization detectors; columns B and C). The appropriate correction factors for detector response were determined from standard mixtures and applied to convert product to marker area ratios to mole ratios.

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Registry No.—Toluene, 108-88-3; nitric acid, 7697-37-2.

Supplementary Material Available. Qualitative and quantitative galvinoxyl product analyses (by gc–mass spectrum), partial rate factors for nitration and oxygenation, and a Hammett $\rho\sigma$ treatment for concurrent nitration–oxygenation will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D.C. 20036. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche, referring to code number JOC-74-3336.

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