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Nitration by Aroyl Nitrates

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Aroyl nitrates, prepared from the corresponding aroyl chloride and silver nitrate, were allowed to react with toluene in acetonitrile solvent. Nitrotoluenes were produced, the isomeric pattern of which varied depending on the conditions. At lower temperatures (25–60°), or with acid promoters, benzoyl nitrate underwent ionic decomposition, probably by way of dinitrogen pentoxide. The invariability in the resulting nitrotoluene distribution using a variety of para-substituted benzoyl nitrates and benzoyl nitrate with a number of acid catalysts and the similarity of this orientation to literature values indicates that the nitronium ion is the electrophile responsible for the aromatic substitution process. At higher temperatures (80°) or in the presence of added peroxides, radical products became more evident from the benzoyl nitrate–aromatic reaction. With *o*-xylene, small yields of 4-benzoyloxy-*o*-xylene were obtained implicating direct reaction between *o*-xylene and the aroyl nitrate. Spectral analyses on benzoyl nitrate solutions were performed. The mechanism of these reactions is discussed.

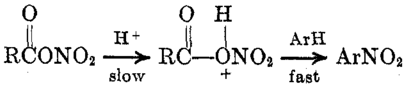
Despite the rather common use of benzoyl and acetyl nitrate (*i.e.*, nitric acid–acetic anhydride mixtures) as aromatic nitrating agents, mechanistic studies have led to conflicting reports concerning the mechanism of these reactions. A number of equilibria (eq 1 and 2) have been demonstrated[2–4] for these reagents in

$$2RCONO_3 \rightleftharpoons (RCO)_2O + N_2O_5 \quad (1)$$

$$N_2O_5 \rightleftharpoons NO_2^+ + NO_3^- \quad (2)$$

solution and evidence has been obtained for the formation of N_2O_5[5,6] from the nitrate under certain conditions. The acyl nitrate itself, N_2O_5, and NO_2^+ have each been suggested as the reagent responsible for the nitrating action of acyl nitrates.[2,3,7,8]

Most of the more recent investigations have utilized the acetic anhydride–nitric acid combination as a source of acetyl nitrate leading in many cases to the possibility of yet a fourth nitrating agent, protonated acetyl nitrate (eq 3). Not only has this species been proposed as the electrophile in nitrations,[9] but it has also been intimated as the substance responsible for the concomitant nitration and acetoxylation of *o*-xylene.[10] Recent MO calculations support this contention.[11,12]



$$R\overset{O}{\overset{\|}{C}}ONO_2 \xrightarrow[\text{slow}]{H^+} R\overset{O}{\overset{\|}{C}}-\underset{+}{\overset{H}{\overset{|}{O}}}NO_2 \xrightarrow[\text{fast}]{ArH} ArNO_2 \quad (3)$$

In addition to ionic decomposition, benzoyl nitrate has been shown to decompose thermally to radical intermediates.[13] Among the products found in the presence of aromatics were the corresponding nitrated compounds, but no isomer distributions were reported. It seems possible that radical nitration is occurring, the mechanism of which has been reviewed extensively by Titov.[14]

Since there is still uncertainty concerning the mechanism of acyl nitrate reactions, our purpose was to study them further in the hope of clarifying the manner in which they exert their nitrating action.

Results and Discussion

We decided to investigate reactions of benzoyl nitrate, since systematic structural changes could be conveniently accomplished with this reagent.

Stock solutions of benzoyl nitrate in acetonitrile were prepared by the method of Francis[15] (eq 4) and some re-

$$C_6H_5COCl + AgNO_3 \xrightarrow{CH_3CN} C_6H_5CONO_3 + AgCl\downarrow \quad (4)$$

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[1] Taken in part from the M.S. thesis of L. T. A. Yang, Illinois State University, Normal, Ill., 1972; presented at the Great Lakes Regional Meeting of the American Chemical Society, Houghton, Mich., June 23, 1972.

[2] V. Gold, E. D. Hughes, and C. K. Ingold, *J. Chem. Soc.*, 2467 (1950); G. A. Benford and C. K. Ingold, *ibid.*, 929 (1938); E. D. Hughes, C. K. Ingold, and R. I. Reed, *ibid.*, 2400 (1950).

[3] M. A. Paul, *J. Amer. Chem. Soc.*, **80**, 5329, 5332 (1958).

[4] R. Vandoni and R. Viola, *Mém. Serv. Chim., État. (Paris)*, **32**, 80 (1945).

[5] J. Chedin and S. Feneant, *C. R. Acad. Sci.*, **229**, 115 (1949).

[6] R. A. Marcus and J. M. Fresco, *J. Chem. Phys.*, **27**, 564 (1957).

[7] A. K. Sparks, *J. Org. Chem.*, **31**, 2299 (1966).

[8] R. O. C. Norman and G. K. Radda, *J. Chem. Soc.*, 3030 (1961); J. R. Knowles and R. O. C. Norman, *ibid.*, 3888 (1961).

[9] F. G. Bordwell and E. W. Garbisch, Jr., *J. Org. Chem.*, **27**, 2322 (1962).

[10] A. Fischer, A. J. Read, and J. Vaughan, *J. Chem. Soc.*, 3691 (1964); D. J. Blackstock, M. P. Hartshorn, A. J. Lewis, K. E. Richards, J. Vaughn, and G. J. Wright, *J. Chem. Soc. B*, 1212 (1971).

[11] N. Bodor and M. J. S. Dewar, *Tetrahedron*, **25**, 5777 (1969).

[12] P. Kriepler and S. E. Buttrill, Jr., *J. Amer. Chem. Soc.*, **92**, 1123 (1970).

[13] L. R. Barlow, *Tetrahedron*, **24**, 4913 (1968).

[14] A. I. Titov, *Tetrahedron*, **19**, 577 (1963).

[15] F. E. Francis, *J. Chem. Soc.*, **89**, 1 (1906).

actions were performed utilizing these solutions. This method proved unsatisfactory for substituted benzoyl nitrates owing to their ready hydrolysis and decomposition upon aging.

To circumvent this problem, many of the reactions of aroyl nitrates were performed *in situ* from silver nitrate and aroyl chloride under the reaction conditions desired. Acetonitrile was selected as solvent. This method provided for the preparation and immediate reaction of benzoyl nitrates, ensuring a known concentration of the nitrate ester. Quantitative determinations of the original benzoyl nitrate concentration were performed by the gravimetric analysis of the silver chloride precipitate at the end of each reaction.

Several preliminary studies of the reaction of benzoyl nitrate, prepared *in situ*, with toluene gave as products nitrotoluenes, benzaldehyde, and benzoic acid. Since the yield and isomer pattern of the nitrotoluenes was somewhat erratic, a number of reaction variables were checked to determine the best standard conditions. In Table I is shown the effect of carrying out the reaction at different temperatures.

TABLE I

TEMPERATURE EFFECT ON THE REACTION OF TOLUENE WITH BENZOYL NITRATE[a]

Temp, °C	Products					
	C_6H_5-CHO	C_6H_5-CH_2NO_2	Nitrotoluenes			
			% yield	*o*-	*m*-	*p*-
25[b]			51	62	4	34
35			50	62	4	34
50	1	2	44	58	6	36
60	3	1	41	57	5	38
80[c]	7[d]	3	13	54	13	33[e]

[a] Benzoyl nitrate, prepared *in situ*, was allowed to react at the appropriate temperature for 18–96 hr until all of the nitrate was consumed; see Experimental Section. [b] No difference in yields of isomers for reactions performed under oxygen or under nitrogen. [c] By blanketing the reacting mixture with nitrogen, yields of up to 25% (ortho:meta:para 59:8:33) could be accomplished. [d] Benzyl alcohol (3%) and nitrobenzene (2%) were also found. [e] The average of six runs with varying isomer composition (ortho, 49–58; meta, 8–24; para, 27–38).

A progressive decrease in yield with a slight increase in *m*-nitrotoluene distribution was noted as the reaction temperature was raised to 80°. The lower yields of nitration product were consistent with the observed increase in nitrogen dioxide fume evolution at the higher temperatures. These refluxing reactions were quite susceptible to the type of atmosphere under which they were run, with lower yields and a higher proportion of meta derivative formed when oxygen was present. On the other hand, benzoyl nitrate–toluene interaction at room temperature was little affected, regardless of whether it was run under nitrogen or oxygen. The effect of oxygen on this reaction at high temperatures suggests that radical intermediates might be involved, since free-radical reactions are often inhibited by oxygen.[16] At lower temperatures, seemingly ionic decomposition (not nearly so sensitive to air) was predominant.

As the amount of nitrotoluenes dropped off at higher temperatures, the by-products, benzaldehyde, benzyl alcohol, α-nitrotoluene, and nitrobenzene, began to appear. Their presence along with that of nitrogen dioxide would tend to further indicate the intervention of radical intermediates.

There are two potential sources of these by-products, both involving radicals: (a) the homolysis of benzoyl nitrate (eq 5) ultimately leading to nitrogen dioxide and

$$C_6H_5CONO_3 \longrightarrow C_6H_5CO_2\cdot + NO_2 \qquad (5)$$

phenyl radicals (eq 6), or (b) breakdown of dinitrogen

$$C_6H_5CO_2\cdot \longrightarrow C_6H_5\cdot + CO_2 \qquad (6)$$

pentoxide present in the system (eq 1) to dinitrogen tetroxide (eq 7)[17] which could occur by way of an

$$2N_2O_5 \rightleftharpoons 2N_2O_4 + O_2 \qquad (7)$$

initial homolysis (eq 8).

$$N_2O_5 \rightleftharpoons NO_2 + NO_3 \qquad (8)$$

The former pathway (eq 5 and 6) does not appear to be involved under these conditions, as no carbon dioxide was produced from a number of representative toluene–aroyl nitrate reactions at 60 and 80°. Also no phenylation products or other higher boilers were noted in any of these cases.

The possible involvement of dinitrogen pentoxide was scrutinized by performing a temperature study with toluene and the nitrogen oxide itself under analogous conditions (Table II). Nitration was achieved with this reagent and the same aromatic by-products were also formed. The nitrotoluene yields ranged near 20% in most cases and the isomer distributions stayed quite constant and similar to that attributed to the nitronium ion (*vide infra*).

Use of a mixture of dinitrogen pentoxide–benzoic anhydride or of dinitrogen tetroxide instead of the pure pentoxide led to similar results. Thus apparently either of these oxides of nitrogen could account for much of the nitration observed at the higher temperatures but cannot account totally for the room-temperature reactions of benzoyl nitrate with toluene.

Whatever the radicals first generated, side-chain abstraction from toluene would produce benzyl radicals capable of reacting with nitrogen dioxide to produce either α-nitrotoluene (eq 9) or benzyl nitrite (eq 10).

$$\mathrm{Rad}\cdot + C_6H_5CH_3 \longrightarrow C_6H_5CH_2\cdot \begin{array}{ll} \xrightarrow{\cdot NO_2} C_6H_5CH_2NO_2 & (9) \\ \xrightarrow{\cdot ONO} C_6H_5CH_2ONO & (10) \end{array}$$

This latter compound was not found, but could break down to form benzyloxy radicals (eq 11) and

$$C_6H_5CH_2ON{=}O \xrightarrow{-NO} C_6H_5CH_2O\cdot \qquad (11)$$

ultimately benzaldehyde and benzyl alcohol (eq 12).

$$2C_6H_5CH_2O\cdot \longrightarrow C_6H_5CHO + C_6H_5CH_2OH \qquad (12)$$

The isomer distribution of nitrotoluenes from the lower temperature studies in this research was quite similar to that noted for electrophilic aromatic nitration (*vide infra*). This suggests that at low temperature benzoyl nitrate undergoes ionic decomposition.

Thus the temperature study suggests that benzoyl nitrate or dinitrogen pentoxide derived thereof can undergo both an ionic and radical mode of decomposi-

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[16] J. March, "Advanced Organic Chemistry: Reactions, Mechanisms, and Structure," McGraw-Hill, New York, N. Y., 1968, p 522.

[17] A. R. Cooksey, K. J. Morgan, and D. P. Morrey, *Tetrahedron*, **26**, 5101 (1970).

TABLE II

TEMPERATURE EFFECT ON THE REACTION OF DINITROGEN PENTOXIDE WITH TOLUENE[a]

	Products						
				Nitrotoluenes			
Temp, °C	C_6H_5CHO	$C_6H_5CH_2OH$	$C_6H_5CH_2NO_2$	% yield	o-	m-	p-
25	<1	1	0	11	63	3	34
25[b]	1	2	0	20	64	3	33
50	13	7	0	19	68	4	28
60	3	1	1	19	62	4	34
60[c]	8	1	9	9	61	6	33
80	1	2	18	40	62	4	34

[a] Dinitrogen pentoxide was allowed to react at the appropriate temperature for 72–96 hr until all of the oxide was consumed (see Experimental Section). [b] N_2O_5 (0.0045 mol) + $(C_6H_5CO)_2O$ (0.005 mol). [c] Dinitrogen tetroxide was used instead of dinitrogen pentoxide.

TABLE III

REACTION OF BENZOYL NITRATE WITH TOLUENE AND DIISOPROPYL PEROXYDICARBONATE

		Products[a]					
		Nitrotoluenes					
Temp, °C	Peroxide/ $C_6H_5CONO_3$ molar ratio	% yield	o-	m-	p-	C_6H_5CHO[b]	Tolyl isopropyl carbonates
35	0	50	62	4	34	0	
35	0.5	37	58	9	33	6	3
35	1	43	53	15	32	4	6
35	2	26	56	18	26	14	8
50	0	44	58	6	36	1	
50	0.5	39	55	11	34	3	3
50	1	45	55	13	32	4	3
50	2	25	48	26	26	5	9
50	1[c]	15	43	30	27	36[d]	34[e]
60	0	41	57	5	38	3	
60	1	22	59	17	24	2	6
60	2	34	53	20	27	5	8
60	1[c]	20	33	55	12	27[f]	48[g]
80	1[h]	7	34	52	14	10	
80	0.5[i]	6	49	20	31	3	
80	0.5[j]	8	53	19	28	11	

[a] Benzoyl nitrate was prepared *in situ* with the peroxide and toluene in acetonitrile at the appropriate temperature; yields are based on moles of product per mole of nitrate; see Experimental Section. [b] Trace amounts of benzyl alcohol were also found in most cases. [c] Dinitrogen pentoxide was used in place of benzoyl nitrate. [d] Benzyl alcohol (16%) and α-nitrotoluene (9%) were also found. [e] Ortho:meta:para = 53:18:29. [f] Benzyl alcohol (19%) and α-nitrotoluene (16%) were also found. [g] Ortho:meta:para = 55:15:30. [h] Benzoyl peroxide was used instead of diisopropyl peroxydicarbonate. [i] Azobisisobutyronitrile used instead of the peroxydicarbonate. [j] *tert*-Butyl perbenzoate was used instead of the peroxydicarbonate.

tion. At higher temperatures the latter reaction predominates.

Confirmation of radical involvement in benzoyl nitrate decompositions was sought by examining the effect of radical initiators on the nitrating properties of benzoyl nitrate. Diisopropyl peroxidicarbonate was selected as the radical source owing to its ready formation of radicals even at lower temperatures.[18]

The addition of increasing proportions of radicals would be expected to favor the radical decomposition pathway. As can be seen from Table III, the proportion of *m*-nitrotoluene increased steadily with increasing peroxide concentrations at all the temperatures studied. The less selective pattern reflected in the nitrotoluene isomer distributions under these conditions indicates either the involvement of a homolytic aromatic substitution pathway which is generally characterized by more statistical, less selective isomeric compositions than ionic substitutions,[19] or the production of a different nitrating agent from the peroxide–nitrate interaction.[20]

The yield of nitrotoluenes produced with increased radical initiator concentrations in general was lower, and greater amounts of the side products, benzaldehyde and tolyl isopropyl carbonates, were found. Interestingly, no sign of α-nitrotoluene was found in these cases. Utilization of dinitrogen pentoxide in place of benzoyl nitrate led to some nitration with characteristically high proportions of meta, but also to much larger amounts of α-nitrotoluene, benzaldehyde, and benzyl alcohol. This difference in product amounts suggests that dinitrogen pentoxide itself cannot solely account for benzoyl nitrate reactions.

Having established that benzoyl nitrate can react with aromatics by both radical and ionic pathways, we sought to investigate more closely the nature of the substituting entity under ionic conditions.

A number of potential substituting moieties have been proposed for both benzoyl and acetyl nitrate systems: the nitronium ion, dinitrogen pentoxide, protonated acyl nitrate, or even the acyl nitrate itself.[11,21] Our approach to the problem was to nitrate toluene with a series of substituted benzoyl nitrates and study the electronic effects of substituents on the pattern of nitration. It was hoped that this would allow us to distinguish between nitration intermediates formed

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(18) W. A. Strong, *Ind. Eng. Chem.*, **12**, 33 (1964).

(19) G. H. Williams, "Homolytic Aromatic Substitution," Pergamon Press, New York, N. Y., 1960.

(20) Recently (M. E. Kurz, unpublished work) it has been shown that the decomposition of peroxydicarbonates with nitric acid in the presence of toluene leads to aryl esters and nitrotoluenes. The predominance of the meta isomer in the latter product suggests a nitrating agent other than the nitronium ion in this case.

(21) J. G. Hoggett, R. B. Moodie, J. R. Penton, and K. Schofield, "Nitration and Aromatic Reactivity," Cambridge University Press, London, 1971.

TABLE IV

REACTIONS OF PARA-SUBSTITUTED BENZOYL NITRATES WITH TOLUENE[a]

Registry no.	p-$XC_6H_4CONO_3$, X =	Nitrotoluenes % yield[b]	o-	m-	p-	$k_{toluene}/k_{benzene}$[c]
39835-16-0	NO_2	34	60.9	5.4	33.7	26.9
39835-17-1	Cl	31	61.4	5.3	33.3	22.3
	H	41	61.1	4.8	34.1	27.1
39835-18-2	OCH_3	40	60.7	5.3	34.0	25.9
39247-26-2	CH_3	30	60.9	5.3	33.8	26.4
	N_2O_5[d]	19	63	5	32[e]	21

[a] Acetonitrile solvent, 60°. [b] Benzaldehyde, 1–7%, and α-nitrotoluene, trace–2%, were also found as well as the appropriately substituted benzoic acid. [c] The average of competition experiments carried out at toluene to benzene ratios of 0.83 and 0.207. [d] N_2O_5 was used instead of $C_6H_5CONO_3$. [e] Duplicate values were in poorer agreement in this case; values are ±2%.

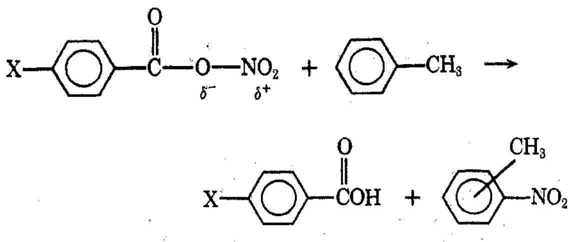
from the acyl nitrate and those actually involving the intact acyl nitrate structure.

A series of aroyl nitrates was prepared *in situ* from silver nitrate and substituted aroyl chloride in the presence of toluene at 60°. The results (Table IV) showed essentially constant nitrotoluene yields and isomer distributions (*i.e.*, ortho:meta:para = 61:5:34). Small amounts of α-nitrotoluene and benazldehyde also were produced. Reactions were also performed at 80° with lower but erratic yields found in all cases.

Subsequently, the competitive method of rate determinations was employed to determine the relative rate of benzene and toluene nitration, using substituted benzoyl nitrates. A large molar excess of both toluene and benzene in a variety of starting ratios was subjected to the nitrating agent. The results (Table IV) showed high substrate selectivity (*i.e.*, $k_{toluene}/k_{benzene}$ of 25 ± 3) accomplished with high positional selectivity (low meta isomer content).

In all of the cases investigated, *i.e.*, p-nitrobenzoyl, p-chlorobenzoyl, benzoyl, p-methoxybenzoyl, and p-methylbenzoyl nitrate, essentially the same nitration orientation was observed. Furthermore, the relative rate of nitration in each case was very similar.

If the aroyl nitrate itself is the nitrating agent under these conditions, one would expect the electronic influence of the substituents to affect the electrophilicity of the aroyl nitrate to different degrees and cause the ratio of isomeric nitrotoluenes to be different (eq 13). With electron-withdrawing groups substituted in the para position of benzoyl nitrate, the polarity of the O–N bond should be enhanced, resulting in a higher proportion of o- and p-nitrotoluenes. On the other hand, electron-donating groups should decrease the electrophilicity of the aroyl nitrate, as would be evidenced by higher meta nitration.



(13)

Since we found no change with the different agents, it appears that a common intermediate is involved in each case. It would seem, therefore, that the aroyl nitrate itself is not the actual nitrating species with toluene.

Nitration by dinitrogen pentoxide under similar conditions (Table IV) gave relative rate and isomer values reasonably similar to those from the aroyl nitrate reactions. Furthermore, these values compared closely to typical toluene nitration values in the literature ($k_{toluene}/k_{benzene}$ = 21–27, and ortho:meta:para = 57–61:3–5:37–40) for nitric acid,[22,23] mixed acid,[24] acetyl nitrate,[17,22] and benzoyl nitrate.[25] The similarity of our isomer distributions and relative rates with these literature values, which in some cases have been attributed to the nitronium ion,[22,23] suggests that this same species formed by way of dinitrogen pentoxide (eq 1 and 2) is the actual nitrating entity from benzoyl nitrates.

To determine whether protonated benzoyl nitrate can be involved in these reactions, nitrations were also carried out with acid catalysts (Table V).

TABLE V

ACID-PROMOTED REACTION OF BENZOYL NITRATE WITH TOLUENE[a]

Acid promoter	Nitrotoluenes % yield	o-	m-	p-	$k_{toluene}/k_{benzene}$[b]
None[c]	41	59.6	4.3	36.1	28.1
$HClO_4$	53	56.3	4.4	39.3	18.6
H_2SO_4	64	62.1	3.4	34.5	35.3
$AlCl_3$[d]	45[e]	60.6	3.2	36.2	32.3
BF_3[d,f]	55	66.4	2.7	30.9	58.0

[a] Catalyst: benzoyl nitrate molar ratio 2:1, acetonitrile (73%)–aromatic (27%) solvent, 25°. [b] The average of at least duplicate runs performed at toluene to benzene molar ratios of 0.83 and 0.207. [c] No difference in isomer distribution and relative rates for reactions carried out in predominantly acetonitrile or predominantly aromatic solvent. [d] Acetonitrile (33%)–aromatic (67%) solvent. [e] Chlorotoluenes produced in fair amounts. [f] Below 0°, BF_3 concentration unknown, but in excess of benzoyl nitrate.

Although the reaction rate was accelerated with all of the acid catalysts, rather minor differences in the nitration products resulted. The slight isomer distribution changes with boron trifluoride and aluminum chloride may in part be due to changes in the medium as well as to the lower reaction temperature in the latter case.

A number of benzoyl nitrate reactions with o-xylene both with and without added catalyst were studied to see if benzoyloxylation, analogous to the acetoxylation reported for acetyl nitrate,[10] could occur (Table VI). Even without catalysts, a small amount of benzoyl-

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[22] C. K. Ingold, A. Lapworth, E. Rothstein, and D. Ward, *J. Chem. Soc.*, 1959 (1931).

[23] H. Cohn, E. D. Hughes, M. H. Jones, and M. G. Peeling, *Nature (London)*, **169**, 291 (1952).

[24] P. H. Griffiths, W. A. Walkey, and H. B. Watson, *J. Chem. Soc.*, 631 (1934).

[25] W. W. Jones and M. Russell, *J. Chem. Soc.*, 921 (1947).

TABLE VI

REACTION OF BENZOYL NITRATE WITH *o*-XYLENE

Catalyst (ratio)	Temp, °C	Products[a]			
		Nitro-*o*-xylenes[b]	4-Benzoyloxy-*o*-xylene	*o*-Tolualdehyde	2-Methylbenzyl alcohol
None	0	17	3	1	1
None	25	22	7	5	4
None	50	22	4	4	1
BF_3[c]	25	38	14	3	0
$AlCl_3$ (2.0)	50	59	0	0[d]	0
$HClO_4$ (2.0)	50	53	0	10	10

[a] Benzoyl nitrate (0.00125 mol) was added to the solution of *o*-xylene and catalyst in acetonitrile at the appropriate temperature. [b] Isomeric mixture of varying composition containing predominantly 3- and 4-nitro-*o*-xylene contaminated with some α-nitro-*o*-xylene. [c] Exact amount not known; an excess of BF_3 was used. [d] 4-Chloro-*o*-xylene (135%) was also formed.

oxylation (3–7%) accompanied the expected nitration. This result would tend to indicate that the aroyl nitrate structure itself is interacting with the aromatic to some extent, as it is hard to visualize the ester product arising from dinitrogen pentoxide and benzoic anhydride.

Addition of boron trifluoride at 25° enhanced the aryl ester yield as well as that of the nitroxylenes. On the other hand, only nitroxylenes were produced with aluminum chloride and perchloric acid at 50°.

In this case, some sort of benzoyl nitrate–boron trifluoride complex analogous to that proposed with acetyl nitrate[11,12] might be involved in both the nitration and benzoyloxylation processes.

In an effort to learn more about the possible nitrating species available in these aroyl nitrate systems, nmr and uv spectra were observed for a variety of potential moieties in acetonitrile.

The aromatic region of the benzoyl nitrate nmr spectrum, when compared to that of benzoic anhydride and benzoic acid, indicated that these latter compounds are not present to a great extent in benzoyl nitrate solution. Addition of dinitrogen pentoxide alone or with a trace of benzoic acid to the benzoic anhydride did not substantially alter the anhydride's nmr spectrum. A more sensitive probe for the presence of benzoic acid (a by-product of benzoyl nitrate decomposition) was integration of the hydroxyl proton (11.3 ppm) *vs.* the total aromatic signal. Using this method, we found that, while fresh solutions of benzoyl nitrate contained just trace amounts of benzoic acid, its concentration steadily increased with solution aging.

The uv spectra of a variety of potential species in the benzoyl nitrate system are shown in Figure 1. A fresh solution of benzoyl nitrate in acetonitrile at room temperature showed two broad bands of equal intensity (ϵ ~500) at 272 and 279 nm. Benzoic acid gave absorption bands at 272 nm (ϵ ~910) and 279 (~690) also, but of considerably different intensity.[26] Aged solutions of benzoyl nitrate (*e.g.*, 2 weeks), still containing active nitrating power, gave spectra very much resembling that of benzoic acid.

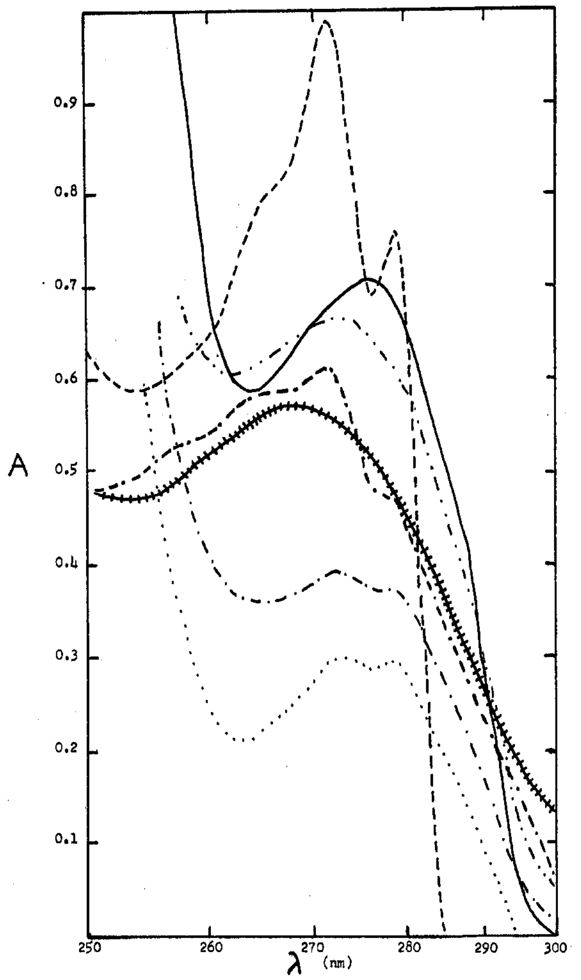
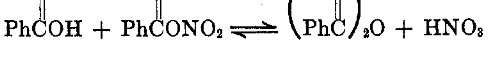


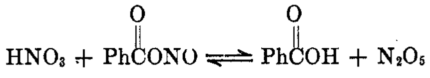
Figure 1.—Uv spectra in acetonitrile of ·······, benzoyl nitrate (0.0005 *M*), fresh; —·—·—, benzoyl nitrate (0.0005 *M*), aged; ——, benzoic anhydride (0.00025 *M*); ++++++++++, dinitrogen pentoxide (0.0012 *M*); ··—··—, benzoic anhydride:dinitrogen pentoxide (1:2); —·—·—, benzoic anhydride:dinitrogen pentoxide:benzoic acid (2:2:1); — — — —, benzoic acid (0.0009 *M*).

Pure dinitrogen pentoxide absorbed at 269 nm (ϵ ~475) while benzoic anhydride showed a broad absorption [λ_{max} 277 nm (ϵ ~2830)]. Synthetic mixtures of dinitrogen pentoxide–benzoic anhydride showed only a single absorption maxima which gradually shifted from 277 (pure anhydride) to 270 nm as higher dinitrogen pentoxide:anhydride ratios were utilized. However, when benzoic acid was added to this mixture, the resulting spectrum resembled that of benzoyl nitrate. Although the uv data is consistent with either benzoyl nitrate or anhydride as the main component in solution with benzoic acid as a contaminant, the combined uv–nmr studies would tend to favor the former case.

These findings are consistent with the previous work of Ingold and coworkers,[2] who showed that the equilibrium (eq 1) which is actually comprised of two steps (eq 14 and 15) is shifted to the left.



$$PhC(=O)OH + PhC(=O)ONO_2 \rightleftharpoons (PhC(=O))_2O + HNO_3 \qquad (14)$$



$$HNO_3 + PhC(=O)ONO \rightleftharpoons PhC(=O)OH + N_2O_5 \qquad (15)$$

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(26) D. Pasto and C. Johnson, "Organic Structure Determination," Prentice-Hall, Englewood Cliffs, N. J., 1969, p 101.

Discussion

Reactions involving aroyl nitrates are complicated by a series of possible equilibria (eq 1, 2, 13, 14) involving the nitrate itself and dinitrogen pentoxide–benzoic anhydride. In the temperature range studied (0–80°) various lines of evidence, including uv and nmr spectra, point toward the presence of both the aroyl nitrate and dinitrogen pentoxide with a predominance of the former. With *o*-xylene seemingly the aroyl nitrate interacts directly with the aromatic, leading to benzoyloxylation in addition to nitration, a process which can be enhanced with boron trifluoride. Whether both substitution reactions proceed by way of a common intermediate was not ascertained. With toluene, on the other hand, only nitration occurred, and dinitrogen pentoxide appeared to be the crucial intermediate. At temperatures of 60° and less, nitration proceeded by an ionic pathway, and involved the nitronium ion as evidenced by (1) the similarity in relative rates and isomer distributions of this reaction to others in which the nitronium ion is responsible, (2) the invariance of substitution patterns from a series of para-substituted benzoyl nitrates and benzoyl nitrate with acid catalysts, and (3) the fact that dinitrogen pentoxide itself led to similar products under simulated reaction conditions. At 80° the decreased yield of nitrotoluenes is thought to arise from radical breakdown of dinitrogen pentoxide to dinitrogen tetroxide and oxygen. No evidence of homolytic cleavage of benzoyl nitrate itself was found. Addition of radical initiators to benzoyl nitrate did lead to a different type of nitration pattern, but it is suggested that intermediates from the peroxide–nitrate interaction may be responsible for this.

Experimental Section

Materials.—Toluene, *o*-xylene, benzene (AR grade), and acetonitrile (Mallinckrodt Nanograde) were used directly. The aroyl chlorides and benzoic anhydride (Aldrich) used came from freshly opened bottles and were not purified further. The diisopropyl peroxidicarbonate[27] was found to be about 95% pure by titration.

Stock Solution of Benzoyl Nitrate. General Procedure.—Basically the procedure of Francis[2] was used with slight modification. A solution of freshly dried, powdered silver nitrate in acetonitrile was loaded into a flask fitted with a drying tube, a dopping funnel, and a thermometer, and stirred mechanically while cooling in an acetone–Dry Ice bath. After being cooled to −20°, an equimolar amount of benzoyl chloride was slowly added since the reaction was somewhat exothermic. Immediate silver chloride precipitation occurred, the solution turned yellow, and a small amount of brown fumes evolved. The temperature was maintained at −15 to −20° for at least 3 hr. At the end of this time, the solid material was filtered off and the filtrate was kept below −40° in a tightly capped bottle. For many reactions (*e.g.*, acid-catalyzed decompositions) the appropriate amount of benzoyl nitrate solution was pipetted into a mixture containing a twofold molar excess of catalyst in either pure aromatic (aluminum chloride) or in aromatic with acetonitrile solvent (H_2SO_4, $HClO_4$, or BF_3) at the appropriate temperature.

In a similar fashion, stock solutions of various para-substituted benzoyl nitrates were also produced using the corresponding para-substituted benzoyl chloride.

Owing to the ready decomposition of benzoyl nitrate to benzoic acid in the presence of moisture, the stock solution of benzoyl nitrate generally deposited a white precipitate upon aging and the nmr indicated the presence of benzoic acid. This problem was particularly acute in the case of a number of the substituted benzoyl nitrates. Since the exact concentration of benzoyl nitrate in the stock solutions was hard to determine, an alternative method of making benzoyl nitrate was utilized in many cases.

Aromatic Nitration with Benzoyl Nitrate Prepared *in Situ*. General Procedure.—The appropriate benzoyl chloride (0.02 mol) in acetonitrile (10 ml) was added dropwise to a rapidly stirred solution of silver nitrate (3.4 g, 0.02 mol) in acetonitrile (50 ml) containing toluene (10 ml, 0.094 mol) at reflux. Silver chloride precipitated immediately, the solution turned yellow, and brown fumes of nitrogen dioxide were evolved. The reaction mixture was stirred for an additional 18–96 hr at this temperature until no fumes remained. At the end of this period of time, the heterogeneous mixture was filtered *in vacuo* and the silver chloride solid was dried and weighed to determine the completeness of the benzoyl nitrate formation (eq 4). In all cases examined, conversion of the benzoyl chloride to the nitrate was found to be 95–100% complete by this gravimetric silver chloride method.

Qualitative and quantitative analysis of the products was carried out directly on the organic phase by gas chromatography.

Yields were based on moles of product per mole of benzoyl nitrate, and in all cases the table entries represent an average of at least duplicate runs in close agreement.

For reactions under nitrogen or oxygen, an additional gas inlet bringing in a slow flow of the gas was provided. Reactions at temperatures other than 80° were performed in constant-temperature baths and occasional shaking was used instead of mechanical stirring. Control runs with and without stirring showed no difference in product yields.

The benzoyl nitrate–toluene runs with added diisopropyl peroxydicarbonate or acid catalysts were done according to the general procedure with the catalyst being added to the silver nitrate solution just prior to addition of benzoyl chloride.

Competitive Nitration. General Procedure.—A solution of toluene (0.094 mol) and benzene (0.112 mol) in 40 ml of acetonitrile containing silver nitrate (0.85 g, 0.005 mol) was preheated to 60°. The solution of acid chloride (0.005 mol) in acetonitrile was added with vigorous shaking. Upon completion, a sample of the reaction mixture was analyzed by gas chromatography to determine the relative amounts of nitrotoluenes and nitrobenzene as well as the isomer distribution of the former. Competitive runs were also carried out at benzene–toluene ratios of 4:1. The toluene–benzene product ratios corrected to equimolar reactant concentrations were used directly as a measure of the relative rate.[28]

Preparation of Dinitrogen Pentoxide.—A literature method[29] with some modification was used. Fuming nitric acid (50 g) was degassed with dry oxygen until colorless, and then frozen in a flask. Phosphorus pentoxide (62 g) was added all at once, and a flow of ozone in oxygen (P. S. I. Model LOA4 Corona) was continuously run into the flask. The solution was allowed to warm up with occasional stirring, and the dinitrogen pentoxide was distilled out into a preweighed receiver held at −75°. At the end this flask was reweighed (3 g) and then flushed out with the appropriate amount of acetonitrile. The resulting stock solution of dinitrogen pentoxide was used immediately in a variety of reactions.

Analytical Procedures. A. Gas Chromatography.—Glpc was used extensively for quantitative product yield determinations. Varian Models 1400 and 600D with flame ionization detectors were used with 10 ft × 0.125 in. 20% SE-30/Chromosorb W-DMCS columns. The inlet pressure for the nitrogen carrier gas was 50 psig for the 1400 and 20 psig for the 600D model, resulting in carrier gas flow rates of about 20 cc/min. The column temperature was 175–180°.

B. Product Identification.—From a thermal decomposition of benzoyl nitrate (25 mmol) in toluene, sodium carbonate extraction yielded benzoic acid (3.07 g, 25.1 mmol). The remaining organic solution was concentrated and products were separated by preparative glpc (Varian 90-P, thermal conductivity detector, 6 ft × 0.25 in. 20% SE-30/Chromosorb P). Benzaldehyde and *o*- and *p*-nitrotoluene were identified by their ir spectra.

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[27] We are grateful to the Pittsburg Plate Glass Co., Barberton, Ohio, and B. F. Goodrich Co., Henry, Ill., for samples of this compound.

[28] For a recent critical evaluation of competitive methods in aromatic nitration, see S. R. Hartshorn, R. B. Moodie, and K. Shofield, *J. Chem. Soc. B*, 1256 (1971).

[29] N. S. Gruenhut, M. Goldfrank, M. L. Cushing, and G. V. Caesar, *Inorg. Syn.*, **3**, 78 (1950).

The latter product was contaminated with the meta isomer, which was collected along with it. α-Nitrotoluene was identified by comparison of its retention time to that of an impure α-nitrotoluene sample prepared from benzyl bromide and silver nitrite.[30]

As a control, solutions of benzoyl nitrate in either acetonitrile or toluene were analyzed directly by glpc, with nitrobenzene (~1–2%) appearing as the only detectable pyrolysis product.

C. Quantitative Analysis.—Reaction product yields and isomer distributions were determined by adding a known quantity of a marker (*p*-chloroanisole) to a one-tenth portion (0.002 mol) of the reaction mixture and analyzing by glpc. The appropriate correction factors were used to convert area ratios to molar ratios and ultimately to product yields. To correct for detector response, mixtures containing known amounts of *p*-chloroanisole and nitrotoluenes were analyzed by glpc under the standard conditions. The slope of the straight line resulting from a plot of the relative area ratio against mole ratio for each product *vs.* the marker was the correction factor.

D. Relative Rates.—The reaction mixtures were analyzed directly by glpc. The molar ratio of isomeric nitrotoluenes to nitrobenzene was determined after correcting the peak areas for detector response.

E. Uv Spectroscopy.—A Beckman Model DK-2A spectrophotometer was used. Freshly prepared solutions were diluted to concentrations ranging from 0.00025 to 0.0015 *M* in acetonitrile for determination of their spectra.

F. Nmr Spectroscopy.—A Perkin-Elmer Model R-20 nmr spectrometer (60 MHz) was utilized, and spectra were determined in acetonitrile solvent.

Registry No.—Toluene, 108-88-3; benzoyl nitrate, 6786-32-9; dinitrogen pentoxide, 10102-03-1; diisopropyl peroxydicarbonate, 105-64-6; *o*-xylene, 95-47-6.

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[30] N. Kornblum and J. W. Powers, *J. Org. Chem.*, **22**, 455 (1957).

Benzoyl Nitrate Reduction with Halide Ions

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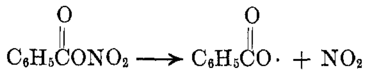
Benzoyl nitrate, prepared from benzoyl chloride and silver nitrate, was treated with a twofold excess of halide ions in the presence of aromatics. The normal nitrating action was altered as the acyl nitrate was rapidly reduced to nitrite ion and molecular halogen. In the chloride and bromide ion reactions halogenated aromatics subsequently resulted. The fact that nearly 2 mol of haloaromatic was produced/mol of benzoyl nitrate under optimum conditions was explained by the further interaction of nitrous acid with hydrogen halide to generate more molecular halogen. The chlorotoluene isomer distributions and cyclohexene products from this system when compared to those of other chlorinating agents indicated that nitryl chloride, and not benzoyl hypochlorite, was formed as an intermediate in the overall reduction process. This was capable of chlorinating directly or reacting further with more chloride ion to generate chlorine. Nitryl chloride arises either from direct displacement by chloride ion on benzoyl nitrate, or on dinitrogen pentoxide present in equilibrium with the nitrate.

Although acyl nitrates (*e.g.*, acetyl and benzoyl nitrate) have found considerable use as mild nitrating agents, relatively few other reactions of these reagents have been studied.[2,3] This may be due in part to the relative instability of this class of compounds, which are often prepared *in situ*. The nitrating action of these species appears to occur by way of the nitronium ion formed from a series of equilibria involving heterolytic acyl nitrate breakdown to dinitrogen pentoxide (eq 1).[3-6] Recently Barlow reported that benzoyl

$$2C_6H_5CONO_3 \rightleftharpoons (C_6H_5CO)_2O + N_2O_5 \qquad (1)$$

nitrate undergoes homolysis upon heating, giving rise to products best explained in terms of radical intermediates (eq 2).[7] The weakness of the O–N bond in the



$$C_6H_5\overset{\overset{O}{\|}}{C}ONO_2 \longrightarrow C_6H_5\overset{\overset{O}{\|}}{C}O\cdot + NO_2 \qquad (2)$$

acyl nitrate structure which allows for this homolysis reaction suggests that this class may behave analogously to peroxides. Consequently, we have set out to look at other "peroxide-type" reactions of these molecules. It is known that peroxides are readily reduced by halide ions;[8-10] indeed this reaction has proved quantitatively useful for analysis.[11] We would like to report here on the reaction between benzoyl nitrate and halide ions.

Results and Discussion

Benzoyl nitrate solutions in acetonitrile were prepared from benzoyl chloride and silver nitrate.[12] Appropriate amounts of the nitrate were pipetted from fresh stock solutions into acetonitrile containing toluene and the appropriate source of halide. Table I summarizes the results from such a study using hydrogen halides as well as aluminum chloride. The products (51% nitrotoluenes and quantitative benzoic acid) from the reaction of benzoyl nitrate with toluene in the absence of any additives[3] are included for comparison. This reaction, which generally required some 2–3 days to complete at room temperature, can be represented by the stoichiometry shown in eq 3.

$$C_6H_5CONO_3 + C_6H_5CH_3 \longrightarrow C_6H_5CO_2H + O_2NC_6H_4CH_3 \qquad (3)$$

Addition of aluminum chloride and the hydrogen halides caused a virtually instantaneous reaction at room temperature and below. With aluminum chloride, the nitrotoluene yield dropped off, and halotoluenes became evident in the product mixtures.

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[1] Presented at the 164th National Meeting of the American Chemical Society, New York, N. Y., Aug 31, 1972.

[2] G. A. Olah and S. J. Kuhn, "Friedel-Crafts and Related Reactions," Vol. III, G. A. Olah, Ed., Interscience, New York, N. Y., 1964, Chapter 43.

[3] See M. E. Kurz, L. T. A. Yang, E. P. Zahora, and R. C. Adams, J. *Org. Chem.*, **38**, 2271 (1973), and references cited therein.

[4] V. Gold, E. D. Hughes, and C. K. Ingold, *J. Chem. Soc.*, 2467 (1950).

[5] A. K. Sparks, *J. Org. Chem.*, **31**, 2299 (1966).

[6] R. O. C. Norman and G. K. Radda, *J. Chem. Soc.*, 3030 (1961); J. R. Knowles and R. O. C. Norman, *ibid.*, 3888 (1961).

[7] L. R. Barlow, *Tetrahedron*, **24**, 4913 (1968).

[8] C. H. Bamford and E. F. T. White, *J. Chem. Soc.*, 4490 (1960).

[9] J. K. Kochi, B. M. Graybill, and M. Kurz, *J. Amer. Chem. Soc.*, **86**, 5257 (1964).

[10] N. J. Bunce and D. D. Tanner, *ibid.*, **91**, 6096 (1969).

[11] *E.g.*, H. A. Flaschka, A. J. Barnard, Jr., and P. E. Sturrock, "Quantitative Analytical Chemistry," Vol. I, Barnes and Noble, New York, N. Y., 1969, p 325.

[12] F. E. Francis, *J. Chem. Soc.*, **89**, 1 (1906).