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.

---

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

Benzoyl Nitrate Reduction with Halide Ions

MICHAEL E. KURZ,* EDWARD P. ZAHORA,[1] AND DONALD LAYMAN

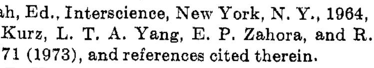
Department of Chemistry, Illinois State University, Normal, Illinois 61761

Received June 22, 1972

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 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 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.

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



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

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.

---

[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).

TABLE I

BENZOYL NITRATE–HALO ACIDS–TOLUENE IN ACETONITRILE[a]

Catalyst	Temp, °C	Nitrotoluenes Yield, %	o-	m-	p-	PhCHO	$PhCH_2X$	Other
None	25	51	62	4	34	0	0	
$AlCl_3$	0	16	61	3	36	Trace	Trace	60[b]
HBr (aq)	25	0				2	6[c]	190[d]
HCl (aq)	25	0				0	Trace[e]	170[b]
HI (aq)	25	0				0	0	6[f]

[a] Toluene:acid catalyst:$C_6H_5CONO_3$ = 7.5:2:1 in acetonitrile (50 ml); see Experimental Section. [b] Chlorotoluenes. [c] Benzyl alcohol. [d] Bromotoluenes. [e] Benzyl chloride. [f] Unidentified.

TABLE II

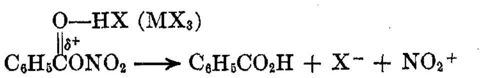
BENZOYL NITRATE–TOLUENE–BROMIDE IN ACETONITRILE[a]

Catalyst	Molar ratio catalyst: nitrate	Temp, °C	Days	$BrC_6H_4CH_3$ Yield, %	o-/p-	C_6H_5-CH_2Br	Total bromotoluenes	$O_2NC_6H_4CH_3$	C_6H_5CHO	$C_6H_5CH_2OH$	Other
HBr (aq)[b]	2	25	4	190	33/67	0	190	0	2	6	1[c,d]
HBr (aq)	2	60	1	136	33/67	31	167	0	10	10	
HBr (aq)	2	80	3	62		19	81		13	46	6[c,d]
HBr (aq)[e]	2	25	6	190	33/67	0	190	0	Trace	Trace	
HBr (g)[f]	2	60	1	82	38/62	35	117	5	10	12	4
HBr (g)	1	60	1	83	41/59	24	107	5	3	7	
HBr (g)	2	25	10	155	36/64	15	170	0	0	12	3
HBr (g)	1	25	12	65	37/63	7	72	3[g]	1	1	6[c]
HBr (g)[h]		60	1	0		0		0	0	0	d
LiBr[e]	2	60	1	40	49/51	8	48	Trace	4	18	27[k]
LiBr[e,i]	2	60	1	37	49/51	17	54	Trace	2	7	
LiBr[e,j]	2	60	1	10	41/59	5	15	Trace	1	12	4[k]
Br_2[l]		25	10	48	34/66	16	64				
Br_2[l]		60	1	37	34/66	8	45				
HBr(g)–$NaNO_2$[m]	2	60	1	5	37/63	24	29		13	8	
HBr(aq)–HNO_2[n,o]	2	60	1	107	34/66	11	118	0	26	10	
HBr(aq)–HNO_2[n,o]	2	25	7	14		0	14	0	1	3	
HBr(aq)–N_2O_5[o]	2	60	2	163	32/68	10	173	0	5	8	
HBr(aq)–HNO_3[o]	2	60	2	147	32/68	37	184	0	9	1	

[a] Toluene (0.094 mol), $C_6H_5CONO_3$ (0.0125 mol) in acetonitrile (50 ml); see Experimental Section. [b] 48% aqueous HBr. [c] Benzyl benzoate. [d] NH_4Br precipitated from the reaction mixture but was not determined quantitatively. [e] Mixed solvent of acetonitrile (25 ml) and acetic acid (25 ml) was used. [f] Reaction was run in acetonitrile (25 ml) and excess toluene (30–40 ml) solvent. [g] Ortho:meta:para = 65:5:30. [h] Control run, no $C_6H_5CONO_3$. [i] Run under nitrogen. [j] H_2O (0.09 mol) added. [k] Benzyl acetate. [l] Bromine (0.0125 mol), no $C_6H_5CONO_3$. [m] $NaNO_2$ (0.0125 mol) in H_2O (5 ml), no $C_6H_5CONO_3$. [n] From equimolar $NaNO_2$–$HClO_4$. [o] No $C_6H_5CONO_3$.

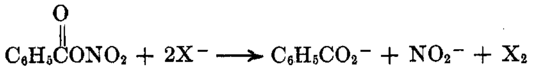
Hydrogen halides were immediately oxidized to molecular halogens, as evidenced by the yellow to dark red solutions formed upon mixing. The hydrochloric and hydrobromic acid reaction mixtures were allowed to stand until the halogen color disappeared, and analysis then showed chloro- and bromotoluenes to be produced in large amounts with virtually no nitrotoluenes found. No aromatic substitution products resulted in the hydriodic acid system.

With the acid catalysts being used, two competing benzoyl nitrate decomposition pathways seem possible: acid-catalyzed heterolysis of the benzoyl nitrate or dinitrogen pentoxide[3] yielding the nitronium ion



$$C_6H_5\overset{\overset{O—HX\ (MX_3)}{\|\delta+}}{C}ONO_2 \longrightarrow C_6H_5CO_2H + X^- + NO_2^+ \qquad (4)$$

(eq 4), and nitrate reduction by halide ion resulting in molecular halogen (eq 5).



$$C_6H_5\overset{\overset{O}{\|}}{C}ONO_2 + 2X^- \longrightarrow C_6H_5CO_2^- + NO_2^- + X_2 \qquad (5)$$

With aluminum chloride, both pathways were apparently operative, whereas the ionized Brønsted acids reacted preferentially by halide ion reduction (eq 5).

The bromide ion–benzoyl nitrate system was scrutinized in more detail using both hydrobromic acid and LiBr as halide ion sources (Table II). In all cases studied, the deep red coloration of bromine occurred immediately upon mixing, and the reactions were subsequently allowed to react until the bromine was consumed. Bromotoluenes were the major organic products of all runs involving benzoyl nitrate with hydrobromic acid in both the aqueous and gaseous form. Other products besides stoichiometric quantities of benzoic acid were varying amounts of benzaldehyde and benzyl alcohol and in a few of the reactions some nitrotoluenes. The following observations concerning the HBr–benzoyl nitrate system can be gleaned from Table II: (1) a 2:1 ratio of acid to nitrate led to bromotoluene yields approaching 200% based on benzoyl nitrate as the limiting reagent; (2) the ring bromination yield fell off at higher reaction temperatures and increased amounts of benzyl bromide and other products from the side chain of toluene were formed; (3) no change in the reaction path occurred when a mixed acetic acid–acetonitrile solvent was utilized; (4) the isomeric composition of bromotoluenes in aqueous HBr was the same as that obtained from molecular bromine under the same conditions and the ortho–para distribution in the gaseous HBr system was more erratic; (5) a control run with HBr in the absence of benzoyl nitrate led to no aromatic substitution products.

Similar reactions performed with LiBr–benzoyl nitrate also produced bromotoluenes, albeit in lower yield. In these cases which were run in mixed acetic acid–acetonitrile solvent, benzyl acetate was also produced as by-product. Although the product mixture from reactions run under nitrogen or air showed little difference, the addition of water to the system caused a marked decrease in bromotoluenes from about 40% to 10%. The ortho:para ratio of the substitution product showed a higher percentage of ortho than that formed from bromine.

The mechanism suggested for the bromination reaction is shown below for the HBr–benzoyl nitrate system. Stoichiometrically 2 mol of HBr are required to generate 1 mol of bromine (eq 6), which in turn can

$$C_6H_5CONO_3 + 2HBr \longrightarrow C_6H_5CO_2H + HONO + Br_2 \qquad (6)$$

react with toluene to form 1 mol of bromotoluenes (eq 7). To explain the nearly 200% yield of the

$$Br_2 + C_6H_5CH_3 \longrightarrow BrC_6H_4CH_3 + HBr \qquad (7)$$

brominated aromatic under optimum conditions it is suggested that nitrous acid arising from the nitrate reduction (eq 6) can interact with HBr from eq 7 to generate more bromine (eq 8). The reactions (eq 7 and

$$2HBr + 2HONO \longrightarrow Br_2 + 2H_2O + 2NO \qquad (8)$$

8) can then reoccur until all the nitrous acid and/or hydrobromic acid are consumed. This could theoretically lead to 2 mol of brominated product/mol of benzoyl nitrate. Reduction by iodide is a known quantitative method for determining nitrous acid;[10,11] so the analogous reactions (eq 8) with other halide ions seem reasonable. Similar reductions have been proposed as steps in the gas-phase reduction of nitrogen dioxide with HBr[13] and HCl.[14] To actually test this theory, a 2:1 mixture of HBr:HONO was mixed with toluene in acetonitrile at 60° under simulated reaction conditions and led to a good yield of bromotoluenes having the characteristic isomer distribution as from molecular bromine (Table II). The brominated products were also produced, although in much lower yield, from a similar reaction at 25° and a gaseous HBr–NaNO$_2$ run at 60°. These experiments verified the feasibility of eq 8.

The lower yields of bromotoluenes from benzoyl nitrate–HBr at higher temperatures may well result from loss of HBr from the reaction mixtures. Radical process also began to occur, as attested to by the formation of benzyl bromide and other products of the benzyl radical. One can also attribute the lower yield in the lithium bromide runs to the fact that the nitrite ion is much less susceptible to reduction than nitrous acid.

Subjection of N$_2$O$_5$ with a twofold molar excess of HBr to similar conditions in the presence of toluene led to results still consistent with 2 mol of halotoluenes/mol of oxidant. Nitric acid–hydrochloric acid under standard reaction conditions also produced nearly 2 mol of halotoluene/mol of nitric acid as had been previously reported.[15]

A more detailed study (Table III) of benzoyl nitrate with chloride ion led to similar results. Chlorotoluenes were the major aromatic substitution products, again accompanied by varying amounts of benzyl radical products and in some cases nitrotoluenes. As in the bromide ion study, use of HCl at lower temperatures gave higher yields of chlorotoluenes than did the higher temperature HCl and all of the LiCl runs. Control reactions also demonstrated that chlorine could be formed from nitrous acid, nitric acid, or dinitrogen pentoxide in the presence of HCl (Table III).

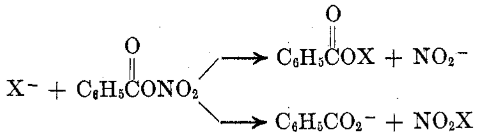
TABLE III

TOLUENE CHLORINATION WITH BENZOYL NITRATE–CHLORIDE[a]

	Products			
	ClC$_6$H$_4$CH$_3$[b]			O$_2$NC$_6$H$_4$CH$_3$
Catalyst	Yield,[c] %	*o*-	*p*-	
HCl (g)[d]	104	54	46	22[e]
HCl (aq)[d]	69	52	48	0
HCl (aq)[d,f]	170			0
LiCl	60	56	44	8
LiCl[g]	34	56	44	13
HCl–HONO[h,i]	44	55	45	0
HCl–HNO$_3$[d,i]	48	53	47	0
HCl–N$_2$O$_5$[d,i]	137	52	48	0

[a] Toluene (0.094 mol), C$_6$H$_5$CONO$_3$ (0.0125 mol), catalyst (0.025 mol) in acetonitrile (25 ml)–acetic acid (25 ml) solvent, 60°, 1 day. [b] Small amounts of benzyl chloride (up to 2%) were noted in many cases. [c] Based on 1 mol of product/mol of nitrate. [d] Acetonitrile solvent (50 ml). [e] Ortho:meta:para = 60:5:35. [f] 25°, 7 days. [g] Run under nitrogen or with added water (0.09 mol). [h] From equimolar NaNO$_2$–HClO$_4$. [i] No C$_6$H$_5$CONO$_3$.

Although it is clear that halide ions are capable of reducing benzoyl nitrate, it is of interest to determine the actual stepwise breakdown of the oxidant. With the aroyl nitrate, theoretically, two pathways are conceivable, leading to the possible reactive intermediates benzoyl hypohalite (eq 9) or nitryl halide (eq 10).



$$X^- + C_6H_5\overset{\overset{O}{\|}}{C}ONO_2 \longrightarrow C_6H_5\overset{\overset{O}{\|}}{C}OX + NO_2^- \qquad (9)$$

$$X^- + C_6H_5\overset{\overset{O}{\|}}{C}ONO_2 \longrightarrow C_6H_5CO_2^- + NO_2X \qquad (10)$$

In addition, if dinitrogen pentoxide, in equilibrium with benzoyl nitrate,[3,4] reacts with the halide, nitryl halide would be expected to be formed (eq 11). We

$$X^- + O_2NONO_2 \longrightarrow O_2NX + NO_3^- \qquad (11)$$

attempted to determine whether benzoyl hypohalite or nitryl halide was involved as an intermediate in the toluene–benzoyl nitrate–chloride ion case by carefully determining the isomer distribution of chlorotoluenes and comparing them to known halogenating agents (Table IV).

The isomer composition from benzoyl nitrate with a twofold excess of chloride ion was the same as that from molecular chlorine under the same conditions. However, as the amount of halide:nitrate was lowered gradually to 0.25:1, the ortho:para ratio changed slightly to 55:45. Benzoyl hypochlorite has been

---

(13) K. S. B. Addecott and J. H. Thomas, *Trans. Faraday Soc.*, **57**, 664 (1961).

(14) J. R. Gilbert and J. H. Thomas, *ibid.*, **59**, 1600 (1963).

(15) S. Bursa and J. Straszko, *Przem. Chem.*, **41**, 133, 185 (1962); C. M. Selwitz and V. A. Notaro, *Amer. Chem. Soc., Div. Petrol. Chem., Prepr.*, **17**, E37 (1972).

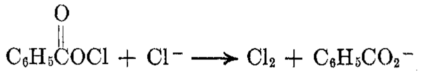
TABLE IV

CHLORINATION OF TOLUENE WITH VARIOUS CHLORINATING AGENTS

Chlorinating agent[a]	Molar ratio	Chlorotoluenes Yield, %	o-	p-	Benzyl chloride
$HCl(g)-C_6H_5CONO_3$[b]	2:1	104	54.0	46.0	
$LiCl-C_6H_5CONO_3$	2:1	60	56.7	43.3	
$LiCl-C_6H_5CONO_3$	0.97:1	41	56.0	44.0	10[c]
$LiCl-C_6H_5CONO_3$	0.51:1	26	55.2	44.8	10[c]
$LiCl-C_6H_5CONO_3$	0.25:1	[i]	54.7	45.3	[i]
$LiCl-Cl_2$	2:1	83	56.7	43.3	
$LiCl-(C_6H_5CO_2)_2$[d]	2:1	15	57.5	42.5	22[e]
$LiCl-(C_6H_5CO_2)_2$	0.5:1	5	[i]	[i]	9[e]
NO_2Cl		41	55.3	44.7	
NO_2Cl[b]		31	54.6	45.4	5
$LiCl-NO_2Cl$	0.85:1	47	55.6	44.4	
$HCl-N_2O_5$[b]	2:1	137	52.1	47.9	
$HCl-HNO_3$	2:1	78	57.9	42.1	
$HBr-NO_2Cl$	1:1	2[f]			
$HBr-NO_2Cl$[g]	1:1	1[h]			

[a] Generally 0.0125 mol of chlorinating agent was used with toluene (0.094 mol) in acetonitrile (25 ml)–acetic acid (25 ml) solvent at 60°; see Experimental Section. [b] Acetonitrile solvent (50 ml). [c] Trace of benzyl acetate was also formed. [d] Air was bubbled through reacting mixture. [e] Other products (methylbiphenyls, bibenzyl, and benzyl benzoate) were produced. [f] Bromotoluenes, 28%, benzyl alcohol, 8%. [g] 25°. [h] Bromotoluenes, 51%. [i] Not determined.

demonstrated to be an intermediate in the reaction between benzoyl peroxide and chloride ion.[8–10] Two lithium chloride–peroxide runs were performed in an attempt to make benzoyl hypochlorite,[9] but the isomer distribution of the chlorotoluenes resulting indicated that either the hypochlorite had a similar selectivity in aromatic substitution to chlorine or that under the conditions used (even at low chloride:peroxide ratios) it reacted further with more chloride (eq 12) before it



$$C_6H_5\overset{O}{\overset{\|}{C}}OCl + Cl^- \longrightarrow Cl_2 + C_6H_5CO_2^- \qquad (12)$$

could react with the aromatic. Nitryl chloride proved to be an effective chlorinating agent under similar conditions and gave an isomeric composition of around 55% ortho and 45% para. Addition of lithium chloride to the nitryl chloride caused a slight shift in isomers toward that of molecular chlorine, indicating the probability of halogen formation as in eq 13. The

$$NO_2Cl + Cl^- \longrightarrow Cl_2 + NO_2^- \qquad (13)$$

chlorination isomer distribution from dinitrogen pentoxide–HCl was actually lower in ortho content than nitryl chloride, perhaps owing partly to the difference in the solvent utilized. Even though nitryl chloride, molecular chlorine, and benzoyl hypochlorite generated *in situ* do not differ too much in their selectivity toward toluene, the closer similarity of the benzoyl nitrate–chloride ion isomer distribution under optimum conditions to that of nitryl chloride suggests that this species is generated initially (eq 10 or 11). Nitryl chloride is known to preferentially chlorinate rather than nitrate aromatics.[16] In many instances at which higher lithium chloride:benzoyl nitrate ratios were used, molecular chlorine, formed subsequently (eq 13), probably served as the actual halogenating agent.

To determine how readily nitryl chloride can react with halide ion, equimolar amounts of hydrobromic acid and nitryl chloride were treated with toluene, and virtually only bromotoluenes resulted. This indicated that with bromide at least nitryl chloride reduction very favorably competed with aromatic chlorination.

It is interesting to note that with hydrochloric acid–benzoyl nitrate reactions the isomer distribution even at high acid:nitrate ratios was quite similar to that from nitryl chloride.

In a further attempt to distinguish between nitryl chloride and benzoyl hypochlorite as the initially formed reduction product, the benzoyl nitrate–chloride ion system was treated with cyclohexene. Previously, nitryl chloride had been reported to yield 2-chloro-1-nitrocyclohexane, 1,2-dichlorocyclohexane, 2-chlorocyclohexanol, and cyclohexen-3-ol as well as other minor products.[17,18] Presumably, radicals from homolysis of the nitryl halide add to the double bond or abstract an allylic hydrogen to account for these products,[17–20] although ionic intermediates have also been proposed.[21] In contrast, the major products recorded from cyclohexene–benzoyl hypochlorite (from tetramethylammonium chloride and benzoyl peroxide) were 2-chlorocyclohexyl benzoate (34%) and 1,2-dichlorocyclohexane (27%).[10] The former product is characteristic of the Prevost reaction.[22]

In the present study, the products from benzoyl nitrate and cyclohexene with both an excess and deficiency of chloride ions in mixed acetic acid–acetonitrile solvent were compared to those from cyclohexene with nitryl chloride–lithium chloride and benzoyl peroxide–lithium chloride under analogous conditions (Table V). The complex product mixture from benzoyl nitrate (which contained cyclohexen-3-ol acetate, 1,2-dichlorocyclohexane, 2-chlorocyclohexyl acetate, and 2-chloro-1-nitrocyclohexane as major products) very much resembled that from nitryl chloride, suggesting the intermediacy of nitryl chloride as the initial reduction product from the nitrate with

---

[16] F. P. Gintz, D. R. Goddard, and M. J. Collis, *J. Chem. Soc.*, 445 (1958).

[17] J. C. D. Brand and J. D. R. Stevens, *J. Chem. Soc.*, 629 (1958).

[18] C. C. Price and C. A. Sears, *J. Amer. Chem. Soc.*, **75**, 3275 (1953).

[19] H. Shechter, F. Conrad, A. L. Daulton, and R. E. Kaplin, *ibid.*, **74**, 3052 (1952).

[20] A. Hassner, J. E. Kropp, and G. J. Kent, *J. Org. Chem.*, **34**, 2628 (1969).

[21] G. B. Bachman and T. J. Logan, *ibid.*, **21**, 1467 (1956).

[22] K. B. Wiberg and K. A. Saegebarth, *J. Amer. Chem. Soc.*, **79**, 6256 (1957).

TABLE V

CYCLOHEXENE TRAPPING REACTIONS[a]

Products	Retention time[b]	Reactants $C_6H_5CONO_3$ + LiCl[c]	 NO_2Cl[d]	 $C_6H_5CO_2Cl$[e]
f	4.0	m[g]	m	m
f	4.3	m	m	m
Cyclohexen-3-ol acetate	6.6	M[g]	M	M
1,2-Dichlorocyclohexane[h]	7.8 + 8.8	M	M	<1
1-Nitrocyclohexene	9.9	m	m	
2-Chlorocyclohexyl acetate	12.8	M	M	M
2-Chloro-1-nitrocyclohexane	13.6	M	M	
f	17.4	m	m	<1
2-Chlorocyclohexyl benzoate	23.3[i]	*j*	*j*	M

[a] Cyclohexene:LiCl:oxidizing agent = 10:0.3–2:1, acetonitrile (25 ml)–acetic acid (25 ml) solvent, 60°, 24 hr. [b] On glpc column A, 160°; see Experimental Section. [c] Similar results with LiCl:nitrate ratios of 0.67 and 1.95. [d] Similar results with LiCl:NO_2Cl = 0.38 or NO_2Cl alone. [e] Similar results with LiCl:$(C_6H_5CO_2)_2$ = 0.63 and 2.02. [f] Not identified. [g] m = minor product (<10%); M = major product (>10%). [h] Mixture of cis and trans. [i] Programmed at 170–250° at 10°/min. [j] No higher boilers noted upon programming to 250°.

chloride. Apparently, benzoyl hypochlorite is not formed in the nitrate reduction; if it had been produced, 2-chlorocyclohexyl benzoate (a major product from the benzoyl hypochlorite–cyclohexene control, Table V) would have been noted.

Experimental Section

Reactions involving benzoyl nitrate were carried out using freshly prepared stock solutions in acetonitrile as described elsewhere.[3,12] Nitryl chloride was prepared according to a published procedure,[23] and also used as a stock solution in acetonitrile as was dinitrogen pentoxide.[3] In all reactions, the oxidant solution was added last to a solution of all the other components at the temperature desired. Although all reactions involving benzoyl nitrate–halide ion gave instantaneous indication of molecular halogen formation, they were allowed to react at the designated temperature until halogen decomposition was complete. At the end of the reactions the mixtures were analyzed directly by gas chromatography.

Varian Models 1400 and 600D (with flame ionization detectors) were used with the following columns: (A) 10 ft × 0.125 in. 20% SE-30/Chromosorb W-DMCS, 60/80 mesh; (B) 10 ft × 0.125 in. 10% OV-225/Suprelcoport, 80/100 mesh; (C) 6 ft × 0.125 in. 20% DEGS/Chromosorb W, 60/80 mesh.

Reaction product yields were determined by adding a known quantity of marker (*p*-chloroanisole, *p*-bromoanisole, or *p*-bromotoluene) to a one-tenth portion of the reaction mixture and analyzing by glpc (column A, 160–180°). The appropriate correction factors were used to convert area ratios to molar ratios and ultimately to product yields.[3] Yields were based on moles of product/mole of benzoyl nitrate (benzoyl peroxide, halogen, or nitryl chloride), and in all cases the table entries represent an average of at least duplicated runs in close agreement. Benzoic acid yields were determined in a number of representative reactions by titration, and were found to be quantitative based on starting aroyl nitrate.

Bromo- and chlorotoluene isomers were analyzed on glpc column B (100–150°) and column C (100°).

The products from the cyclohexene reactions were collected by way of preparative glpc (Varian Model 90-P, thermal conductivity detector, 6 ft × 0.25 in. 3% SE-30/Chromosorb W, 60/80 mesh) on concentrated reaction mixtures. Ir and nmr spectra were used to identify the products with comparison to authentic spectra performed where available. Semiquantitative amounts of each product (Table V) were obtained using glpc column A at 160°, with programming to higher temperatures in some cases.

Registry No.—Benzoyl nitrate, 6786-32-9; chloride ion, 16887-00-6; bromide ion, 24959-67-9; nitryl chloride, 13444-90-1.

---

[23] M. J. Collis, F. P. Gintz, D. R. Goddard, E. A. Hebron, and G. J. Minkoff, *J. Chem. Soc.*, 438 (1958).

The Stereochemistry and Ultraviolet Spectra of Simple Nitrate Esters[1a]

V. M. CSIZMADIA, S. A. HOULDEN, G. J. KOVES, J. M. BOGGS, AND I. G. CSIZMADIA*[1b]

Lash Miller Chemical Laboratory, Department of Chemistry, University of Toronto, Toronto 5, Ontario

Received November 13, 1972

Eight simple representative nitrate esters (methyl nitrate, ethyl nitrate, *n*-propyl nitrate, isopropyl nitrate, *n*-butyl nitrate, *tert*-butyl nitrate, benzyl nitrate, and β-phenethyl nitrate) have been investigated by the extended Hückel molecular orbital (EHMO) method. The uv spectra of this set of compounds were recorded in heptane and resolved into a number of component bands as suggested by the EHMO calculations. The charge distributions of these molecules were calculated by an iterative charge consistency method.

Nitrate esters are used as propellants and explosives and as drugs for the relief of hypertension and *angina pectoris*. In synthetic work, the nitrato group (ONO_2) is frequently employed for blocking hydroxyl groups in molecules while the manipulation of other functional groups is carried out.

The physical and chemical properties of this interesting π-electron system have so far, however, received only brief attention in the literature.[2] We report here theoretical and experimental investigations of the stereochemistry and uv spectra of methyl, ethyl, *n*-propyl, isopropyl, *n*-butyl, *tert*-butyl, benzyl-, and β-phenethyl nitrates.

---

[1] (a) Presented in part at the 50th Canadian Chemical Conference of the Chemical Institute of Canada, June 4–7, 1967, Toronto. (b) On leave during 1971–1972 at the Department of Chemistry, University of York, Heslington, York, England.

[2] L. D. Hayward, "The Chemistry of Nitrate Esters," in preparation; J. Honeyman and J. W. W. Morgan, *Advan. Carbohyd. Chem.*, **12**, 117 (1957).