51834-39-0; 2-chlorosulfonyl-1-tetralone, 51834-37-8; *o*-aminophenol, 95-55-6; benzylsulfonyl chloride, 1939-99-7.

References and Notes

(1) Studies of α-Ketosulfenes. 8. Part 7 of this series: O. Tsuge and M. Noguchi, *Chem. Lett.*, 113 (1974).
(2) O. Tsuge and S. Iwanami, *Bull. Chem. Soc. Jpn.*, **43**, 3543 (1970).
(3) O. Tsuge and S. Iwanami, *Nippon Kagaku Zasshi*, **92**, 448 (1971).
(4) O. Tsuge and S. Iwanami, *Org. Prep. Proced. Int.*, **3**, 283 (1971).
(5) H. Ulrich, "Cycloaddition Reactions of Heterocumulenes", Academic Press, New York, N.Y., 1967, p 286. However, it has been recently reported that phenylsulfene reacted with benzylidenemethylamines to give 1,2-thiazetidine 1,1-dioxides: T. Hiraoka and T. Kobayashi, *Bull. Chem. Soc. Jpn.*, **48**, 480 (1975).
(6) O. Tsuge and M. Noguchi, *Chem. Lett.*, 113 (1974).
(7) W. E. Truce and J. R. Allison, *J. Org. Chem.*, **40**, 2260 (1975).
(8) W. E. Truce, J. W. Fieldhouse, D. J. Vrencur, J. R. Norell, R. W. Campbell, and D. G. Brady, *J. Org. Chem.*, **34**, 3097 (1969).
(9) W. E. Truce and J. F. Rach, *J. Org. Chem.*, **39**, 1109 (1974).
(10) All melting points are uncorrected. NMR spectra were recorded on a Hitachi R-20 NMR spectrometer with tetramethylsilane as internal standard. Mass spectra were obtained on a Hitachi RMS-4 mass spectrometer, using a direct inlet and an ionization energy of 70 eV.
(11) W. E. Truce and C. W. Vriesen, *J. Am. Chem. Soc.*, **75**, 2526 (1953).

Concurrent Nitration and Oxygenation of *o*-Xylene and Hemimellitene with Aroyl Nitrates

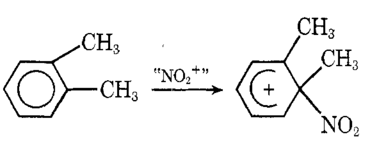
Michael E. Kurz* and Eugene Woodby

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

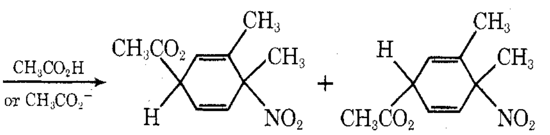
Received February 24, 1976

Upon reaction with a series of aroyl nitrates, *o*-xylene underwent not only nitration but also aroyloxylation to yield dimethylphenyl benzoates comprised primarily of the 3,4 isomer. Nitration ratios were little affected by the nature of the aroyl nitrate substituent suggesting a common nitrating species. The aryl ester product patterns were quite different than those resulting from reaction of *o*-xylene with aroyl peroxide and either cupric chloride or nitric acid where aroyloxy radical substitution is known to occur. The analogous product situation was observed for hemimellitene. This and other evidence was indicative of a mechanism involving nitronium ion attack at an ipso ring position followed by benzoate trapping of the resultant carbonium ion. The addition product so formed then rearomatized to an aryl benzoate by elimination of nitrous acid analogous to the addition–elimination scheme proposed earlier for acetyl nitrate.

The observation by Fischer and co-workers that *o*-xylene undergoes not only nitration but also acetoxylation when treated with nitric acid–acetic anhydride[1] has spurred a considerable amount of further investigation into this dual substitution process.[2] The acetate esters have been accounted for by an electrophilic addition–elimination process involving initial nitronium ion attack at the 1 position (ipso attack) to give a phenonium ion (**1**). This species, which is reluctant to lose either a nitro or methyl group, instead adds a nucleophilic acetate to form a cis–trans pair of 1,4-cyclohexadienes (**2** and **3**, eq 1), which have been isolated upon careful quenching of the reaction.[3] Upon workup **2** and **3** rearomatize to produce primarily 3,4-dimethylphenyl acetate (eq 2).[3,4]

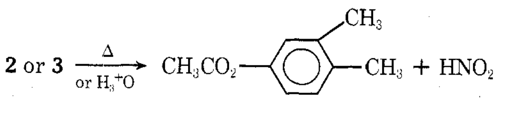


1



(1)

2 **3**



$$2 \text{ or } 3 \xrightarrow[\text{or } H_3^+O]{\Delta} CH_3CO_2\text{–}C_6H_3(CH_3)\text{–}CH_3 + HNO_2 \qquad (2)$$

Analogous cyclohexadiene intermediates and the subsequent aryl acetates have been observed in the reactions of acetyl nitrate with hemimellitene,[5] *p*-xylene,[5] pseudocumene,[2a] toluene,[6] and others.[7] The demonstration of the occurrence of ipso attack has led to critical reinvestigations of previously reported substitution patterns in the nitration of polyalkylbenzenes.[4,8]

Previous work in this laboratory had demonstrated that dimethylphenyl benzoates are produced in yields ranging from 3 to 14% upon treating *o*-xylene with benzoyl nitrate under a variety of conditions.[9] However, radical breakdown of benzoyl nitrate to the benzoyloxy and ultimately phenyl radicals (eq 3) had been reported[10] and the former radical is known to substitute on aromatic rings to form aryl benzoates (eq 4) in the presence of suitable oxidants.[11]

$$C_6H_5CO_2NO_2 \longrightarrow NO_2 + C_6H_5CO_2\cdot \longrightarrow C_6H_5\cdot + CO_2 \qquad (3)$$

$$C_6H_5CO_2\cdot + ArH \xrightarrow[-H^+]{\text{oxidant}} C_6H_5CO_2Ar \qquad (4)$$

Since either a scheme involving benzoyloxy radicals (eq 3 and 4) or an electrophilic ipso nitration process as proposed for acetyl nitrate (eq 1 and 2) seemed to be feasible, we set out to determine which mechanism of benzoate ester formation was applicable in the interaction of a series of para-substituted benzoyl nitrates with *o*-xylene. The reaction of benzoyl nitrate with hemimellitene was also examined.

Results and Discussion

All of the para-substituted benzoyl nitrates were prepared and used in situ both to ensure a known concentration of the nitrate ester and to reduce the possibility of their hydrolysis. They were prepared from the reaction of silver nitrate and the appropriate para-substituted benzoyl chloride in accordance with the following stoichiometry (eq 5).

$$XC_6H_4COCl + AgNO_3 \xrightarrow[25\,^{\circ}C]{CH_3CN} XC_6H_4CO_2NO_2 + AgCl \qquad (5)$$

The organic products from the reaction of benzoyl nitrate with *o*-xylene at room temperature are listed in Table I. Nitration and benzoyloxylation products (nitro-*o*-xylenes and

Table I. Reaction of Para-Substituted Benzoyl Nitrates with *o*-Xylene

		Products[a]					
		Nitroxylenes		Dimethylphenyl benzoates			
Registry no.	*p*-X-$C_6H_4CO_2NO_2$ X =	Yield	3-/4-	Yield	3-/4-[b]	*o*-Methylbenzyl nitrate[c]	$C_{16}H_{18}$[d]
39835-12-2	CH_3O	20	31/69	5	0/100[e]	4	5
39247-26-2	CH_3	23	27/73	17	1/99	5	6
6786-32-9	H[f]	28	32/68	16	5/95[g]	6	5
39835-17-1	Cl	21	36/64	1	0/100[e]	6	5
59104-70-9	F	26	28/72	18	4/96	5	7
39835-16-0	NO_2[h]	23	31/69	2	0/100[e]	4	5

[a] Yields are based on moles of product per mole of benzoyl nitrate; other products formed in varying but small amounts (>) included benzyl alcohol, *o*-tolualdehyde, α-nitroxylene, and dinitroxylene. [b] Some fluctuation in duplicate runs, ±3%, due to small overall yield. [c] Determined by difference in analysis on two columns: the UCW-982 where this product superimposed on 3-nitro-*o*-xylene and on the OV-225 column on which this product was not eluted. [d] Mixture of suspected trimethyldiphenylmethane isomers; see Experimental Section. [e] No 3 isomer was detected, although owing to the low benzoate yield, a small amount could have gone undetected. [f] Benzoic acid, 70% isolated yield. [g] Average of seven runs with variable (1–16%) ratios of 3 isomer. [h] *p*-Nitrobenzoic acid, 93% isolated yield.

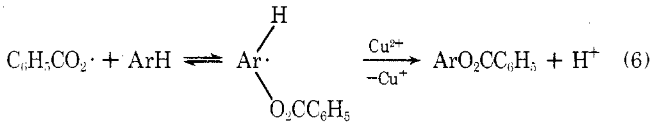
dimethylphenyl benzoates) were found along with various side products: *o*-methylbenzyl nitrate, isomeric *o*-xylene dimers, benzoic acids, and small amounts of *o*-methylbenzaldehyde and dinitro-*o*-xylenes. The substituted benzoic acids were by-products of the aroyl nitrate decomposition and were not analyzed quantitatively. The presence of dimers (thought to be isomeric trimethyldiphenylmethanes) along with *o*-methylbenzyl nitrate suggested possible benzylic cation involvement, the origin of which is not clear.

Relatively similar yields and consistent orientation was observed for the nitroxylenes obtained from the variously substituted benzoyl nitrates. A likely common intermediate is the nitronium ion or incipient nitronium ion formed from dinitrogen pentoxide.[9,12]

The products of most significance to our investigation were the dimethylphenyl benzoates. It is not known why there were rather poor yields of these esters with certain of the aroyl nitrates, but there did not appear to be a trend relating aroyl nitrate structure to dimethylphenyl benzoate production. In all reactions nitrogen dioxide fumes were evident above the reaction mixture, and their escape could account for the poor and variable material balance for the nitro entity in the aroyl nitrate.

To try to determine the exact nature of the aroyloxylating species, several systems known to involve aromatic substitution by aroyloxy radicals were studied with *o*-xylene. Product yields and patterns were compared to those from the aroyl nitrate-*o*-xylene system.

It had been shown that toluene reacts with benzoyl peroxide in the presence of cupric chloride at 60–80 °C to produce tolyl benzoates.[11b,13] Benzoyloxy radicals from peroxide thermolysis or cuprous ion induced breakdown reversibly add to toluene and the resulting σ radical **4** is oxidized to the aryl benzoate by way of a σ carbonium ion (eq 6). A Hammett ρσ treatment indicated that the benzoyloxy, *p*-methylbenzoyloxy, and *p*-nitrobenzoyloxy radicals possessed electrophilic properties in this process. The reaction by-products, benzyl chloride, benzyl alcohol, and methylbiphenyls, were attributed to other radicals produced from chain transfer or decomposition of benzoyloxy radicals.[13]

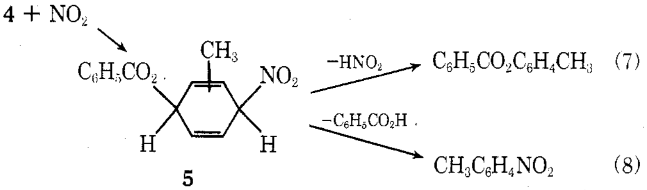


$$C_6H_5CO_2\cdot + ArH \rightleftharpoons Ar\cdot(H)(O_2CC_6H_5) \xrightarrow[-Cu^+]{Cu^{2+}} ArO_2CC_6H_5 + H^+ \quad (6)$$

4

Our general procedure consisted of treating benzoyl peroxide or the para-substituted benzoyl peroxide (nitro-, methyl-) with *o*-xylene at reflux in acetonitrile using cupric chloride as catalyst. The products of most significance to this study, the dimethylphenyl benzoates, were formed in yields ranging from 31 to 63% with the three peroxides. Side products resulting from schemes analogous to those reported for toluene[11b,13] included *o*-methylbenzyl chloride (15–25%), dimethylbiphenyls (10–12%), and small amounts of *o*-methylbenzyl alcohol and phenyl benzoates.

Previously[11a] the reaction of benzoyl peroxide with toluene in the presence of nitric acid had led to both tolyl benzoates and nitrotoluenes in moderate amounts. Various lines of evidence including an unusual nitrotoluene isomer composition (*o*-/*m*-/*p* = 20/70/10) had led to the proposal of a common intermediate leading to both substitution products. Aroyloxy radical attack onto toluene was suggested as the initial step followed by nitrogen dioxide trapping of the radical intermediate **4** (eq 7, 8) to give a dihydroaromatic derivative **5**. This in turn rearomatized by loss of nitrous acid (eq 7) or benzoic acid (eq 8) to give an ester or nitroaromatic, respectively. Previously reported[11a] by-products from toluene included benzaldehyde, benzyl alcohol, benzyl nitrate, and methylbiphenyls.



5

Our general procedure consisted of treating benzoyl peroxide or the para-substituted benzoyl peroxide with *o*-xylene at reflux in acetonitrile using nitric acid as a promoter. Dimethylphenyl benzoates (10–22%) and nitroxylenes (19–24%) were produced presumably by schemes analogous to eq 7 and 8, respectively. Also found with all three peroxide systems were the side products *o*-methylbenzaldehyde (13–28%), *o*-methylbenzyl alcohol (10–35%), *o*-methylbenzyl nitrate (37–71%), *o*-xylene dimers (6–15%), and dimethylbiphenyls (25–34%) analogous to the earlier reported by-products in the nitric acid–benzoyl peroxide–toluene reaction.[11b]

The nitration and oxygenation products obtained from benzoyl nitrate are compared to those found from benzoyl peroxide with cupric chloride or nitric acid in Table II. Also, included are literature results of the analogous products from acetyl nitrate.[1,4]

It is evident from inspection of the ester product ratios from the various systems that the benzoyloxylating species from benzoyl nitrate possesses considerably more selectivity than

Table II. Comparison of *o*-Xylene Products from Various Oxygenation Systems

	Products			
	Dimethylphenyl benzoates		Nitroxylenes	
System	Yield	3-/4-	Yield	3-/4-
$C_6H_5CO_2NO_2$	16	5/95	28	32/68
$(C_6H_5CO_2)_2$–$CuCl_2$	31	59/41	—	—
$(C_6H_5CO_2)_2$–HNO_3	17	61/39	19	21/79
$CH_3CO_2NO_2$	36[b]	0/100	37	39/61
$CH_3CO_2NO_2$[a]	39[b]	0/100	34	32/68

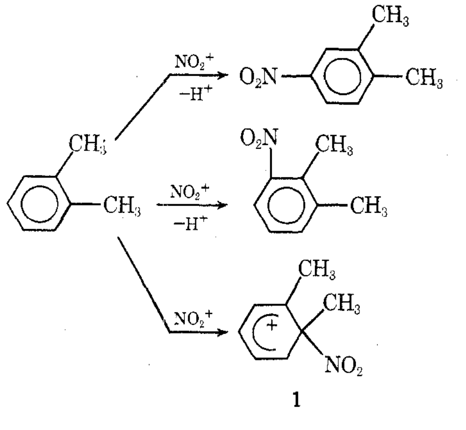
[a] See ref 1 and 4. [b] Dimethylphenyl acetates.

Table III. Comparison of *o*-Xylene Reaction with Substituted Benzoyloxylation Systems

	p-$XC_6H_4CO_2C_6H_3(CH_3)_2$, X =			
	CH_3		NO_2	
System	Yield	3-/4-	Yield	3-/4-
p-$XC_6H_4CO_2NO_2$	17	0/100	2	0/100
$(p$-$XC_6H_4CO_2)_2$–$CuCl_2$	36	58/42	63	56/44
$(p$-$XC_6H_4CO_2)_2$–HNO_3	22	61/39	8	56/44

the benzoyloxy radical involved in the benzoyl peroxide systems. The close similarity (nearly exclusive 4-benzoyloxylation) to the dimethylphenyl acetate pattern observed from acetyl nitrate strongly suggests an analogous reaction pathway to that proposed by Fischer.[3] Initial nitronium ion attack at the 3 or 4 position of *o*-xylene results in a straightforward nitration product (eq 9, 10). However, ipso nitration (at position 1) forms a σ carbonium ion (1) that is apparently capable of being trapped by benzoate (eq 11) in the same manner noted previously for acetate (eq 1). The cyclohexadiene (**6**) so produced loses nitrous acid leading to the nearly exclusive production of the 3,4-dimethylphenyl benzoate. The nitration pattern from benzoyl nitrate is virtually identical with that noted previously[1,3,4] for acetyl nitrate with *o*-xylene lending further support to this mechanism. However, the presence of small and somewhat variable amounts of 2,3-dimethylphenyl benzoates from three of the aroyl nitrate reactions may be indicative of slight competition from radical substitution.

Table III compares aryl esters from the *p*-methyl- and *p*-nitrobenzoyl nitrate–*o*-xylene reactions to the *p*-methyl- and *p*-nitrobenzoyl peroxide–*o*-xylene studies. Again, it is clear that each of these nitrates gives rise to substituted dimethylphenyl benzoates in a manner not involving para-substituted benzoyloxy radical attack, but rather trapping of an initially formed ipso nitration adduct (eq 11).



(9)

(10)

(11a)

1

Table IV. Comparison of Hemimellitene Products from Various Oxygenation Systems

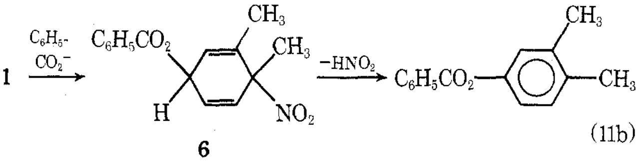
	Trimethylphenyl benzoates		Nitrohemimellitenes	
System	Yield	4-/5-	Yield	4-/5-
$C_6H_5CO_2NO_2$	11	17/83	26	78/22
$(C_6H_5CO_2)_2$–$CuCl_2$	63	85/15		
$(C_6H_5CO_2)_2$–HNO_3	4	>98/2	58	45/55
$CH_3CO_2NO_2$[a]	45[b]	21/79	55	84/16

[a] See ref 5. [b] Trimethylphenyl acetates.

Table V. Product Distribution before and after Solvolysis

Products	Direct analysis[a]	After solvolysis with 70% H_2SO_4[b]
3-Nitro-*o*-xylene	8.9	14.5
4-Nitro-*o*-xylene	21.6	21.3
3,4-Dimethylphenyl benzoate	10.1	9.3

[a] Benzoyl nitrate and *o*-xylene reacted in acetonitrile at 25 °C for 48 h; direct GC analysis. [b] Same reaction mixture treated for 10 min at 25 °C with acid, then analyzed by GC.



6

(11b)

Hemimellitene was also treated with benzoyl nitrate and the resulting benzoyloxylation and nitration products compared to those obtained from benzoyl peroxide–cupric chloride and benzoyl peroxide–nitric acid (Table IV). In this case the major trimethylphenyl benzoate was the 5 isomer, in good agreement with what had been noted previously from acetyl nitrate.[5] This predominance of the 5 isomer stood in marked contrast to the pattern observed in the benzoyloxy radical systems[11] where primarily the 4-substituted aryl ester was found. The nitration pattern with benzoyl nitrate was also more consistent with that noted previously for acetyl nitrate.[5]

To date efforts to actually isolate cyclohexadiene intermediates **6** from either *o*-xylene or hemimellitene by chromatographic workup have been fruitless. However, further indirect evidence for their presence as initial reaction products was indicated by treating the crude reaction mixture from *o*-xylene–benzoyl nitrate with 70% sulfuric acid. An increase in the proportion of 3-nitro-*o*-xylene and an accompanying slight decrease in 3,4-dimethylphenyl benzoate was noted compared to directly analyzed reaction product (Table V).[14] This suggested the probable diversion of **6** to the rearranged 3-nitro-*o*-xylene as was observed previously in the acetyl nitrate system.[4,15]

That the trapping of the initial phenonium ion **1** from ipso attack by carboxylate species appears to be an intermolecular process was demonstrated by a series of competition experiments (Table VI). When equimolar amounts of *p*-methylbenzoyl nitrate and benzoyl nitrate were treated with *o*-xylene virtually equal amounts of *p*-methylbenzoate and benzoate esters were produced. Addition of cupric benzoate to the *p*-methylbenzoyl nitrate–*o*-xylene system also led to approximately equal amounts of the two types of benzoates though in much lower yields. Benzoyl nitrate reactions with *o*-xylene in the presence of excess acetic or trifluoroacetic acid resulted in the repression of the benzoate ester products. In the former

Table VI. Competition Experiments Aroyl Nitrate–*o*-Xylene

p-X-$C_6H_4CO_2NO_2$ X =	Added nucleophile or solvent	Aryl esters, % $C_6H_5CO_2C_6H_3(CH_3)_2$	Other
CH_3 and H[a]		7.2	7.3 [*p*-$CH_3C_6H_4CO_2C_6H_3(CH_3)_2$]
CH_3	$Cu(O_2CC_6H_5)_2$[b]	1.4	1.3 [*p*-$CH_3C_6H_4CO_2C_6H_3(CH_3)_2$]
H	CH_3CO_2H[c]	0.3	19 [4-$CH_3CO_2C_6H_3(CH_3)_2$]
H	CF_3CO_2H[c]	1.1	

[a] Equimolar (0.005 mol) ratios. [b] Aroyl nitrate (0.010 mol), cupric benzoate (0.005 mol). [c] Present in approximately a 20-fold molar excess compared to the aroyl nitrate.

Table VII. Authentic Dimethylphenyl Benzoates

Registry no.	3,4-$(CH_3)_2C_6H_3O_2CC_6H_4X$-*p* X =	Mp, °C	Mass spectrum: Molecular ion, *m/e*	Mass spectrum: Base peak, *m/e*
3845-63-4	H	55–57[a]	226	105
59014-71-0	CH_3	99–103	240	119
59014-72-1	OCH_3	87–89	256	135
59014-73-2	NO_2	124–127[b]	271	150
59014-74-3	Cl	79–83	260 (262)[c]	139 (141)[c]
59014-75-4	F	65–67	244	125
	2,3-$(CH_3)_2C_6H_3O_2CC_6H_4X$-*p* X =			
5554-27-8	H	55–57[d]	226	105
59014-76-5	CH_3	92–93	240	119
59014-77-6	OCH_3	61–62	256	135
59014-78-7	NO_2	123–125	271	150
59014-79-8	Cl	105–106	260 (262)[c]	139 (141)[c]

[a] Lit. mp 58.5 °C: R. Granger, H. Orzalesi, and P. Joyeux, *C. R. Acad. Sci.*, **260,** 923–925 (1965). [b] Lit. mp 128 °C, G. Harris, J. R. A. Pollock, and R. Stevens, "Dictionary of Organic Compounds", Vol. 1, Oxford University Press, London, 1965. [c] Isotopic peak. [d] Mixture melting point depression (15 °C) noted upon admixture with the 3,4 isomer.

case the acetate addition–elimination product was formed instead.[16]

The acyl nitrate precursor seemed to be necessary to obtain aryl esters. An attempt to nitrate *o*-xylene at room temperature in the presence of benzoic acid led to no reaction. At elevated temperatures (80 °C) nitration did occur (23% yield, 3-/4- ratio 22/78) but no benzoate esters were detected.

Conclusions

Aroyl nitrates react with certain polymethylbenzenes in a manner analogous to acetyl nitrate resulting in both nitration and aroyloxylation products.

Experimental Section

The chemical reagents used were analyzed by GC where possible and used directly without further purification. The substituted peroxides were synthesized from sodium peroxide and the appropriate acid chloride[17] and analyzed for purity by standard procedures.[18] Authentic 2,3- and 3,4-dimethylphenyl benzoates were prepared from 2,3- and 3,4-dimethylphenol and the appropriate para-substituted benzoyl chloride according to a literature procedure.[19] The esters, most of which have not been reported in the literature, are listed in Table VII.

Synthesis and in Situ Reactions of Aroyl Nitrates with Polymethylbenzenes. General Procedure. The appropriate para-substituted benzoyl chloride (0.020 mol) in acetonitrile (10 ml) was added dropwise to a rapidly stirred solution of silver nitrate (3.4 g, 0.020 mol) in 50 ml of acetonitrile containing *o*-xylene (10 ml, 0.094 mol) or hemimellitene (0.075 mol) at room temperature (25 °C).[7] Silver chloride precipitated immediately, the solution turned yellow, and brown fumes of nitrogen dioxide were evolved. The reaction mixture was stirred for an additional 48 h at this temperature. Iodometric analysis of aliquots from representative reaction mixtures from each aroyl nitrate indicated that less than 10% active oxidizing species (unreacted nitrate or nitrogen oxide species therefrom) remained. The heterogeneous mixture was then filtered in vacuo and the silver chloride dried and weighed to determine the completeness of the benzoyl nitrate formation. Silver chloride recovery ranged from 88 to 96% based on eq 5. Product analyses were made by GC and GC–MS carried out on the filtrate.

On a number of benzoyl nitrate reactions with both *o*-xylene and hemimellitene the acetonitrile solvent was stripped away and the residue containing unreacted aromatic and products was subjected to liquid and column chromatography using silica gel and alumina, respectively. No evidence (NMR, ir, or physical data) could be garnered for the presence of adducts such as **6** among the reaction products.

Reactions of acetyl nitrate with *o*-xylene were performed according to a literature method.[3,4] Careful quenching at −50 °C with anhydrous ammonia followed by workup[6] led to a product mixture which contained the 1,4-cyclohexadienes, **2** and **3**. When a few drops of this mixture were heated in aqueous acetic acid the evolution of brown nitrogen dioxide fumes was clearly evident due to the breakdown of **2** and **3** (eq 2). Similar testing of direct aliquots from various benzoyl nitrate–*o*-xylene reaction mixtures and an acetyl nitrate–*o*-xylene reaction which had been subjected directly to an aqueous wash indicated no nitrogen oxide fumes. Thus it appears that the suspected cyclohexadiene intermediates from benzoyl nitrate systems (**6**) are not very stable, but break down under reaction conditions.

Reactions of Benzoyl Peroxide–Polymethylbenzenes. General Procedure. Cupric chloride (0.2 g, 0.0015 mol) was dissolved with heat and stirring in acetonitrile (50 ml) and the solution transferred to a boiling flask (250 ml) equipped with a condenser. The appropriate para-substituted benzoyl peroxide (0.005 mol) was dissolved in *o*-xylene or hemimellitene (10 ml) and acetonitrile (25 ml) and added to the flask. The solution was then refluxed (~80 °C) for 48 h during which time the mixtures turned green. After cooling, product analysis was performed by GC and GC–MS.

The nitric acid promoted reactions were carried out in similar manner except that the nitric acid (0.010 M, twofold molar excess to the peroxide) was added last and after a 48-h reflux period the reaction mixture had turned a red-brown.

Identification of Products. Most reaction product mixtures were analyzed on a Finnegan Model 3000 GC peak identifier with a quadrupole mass filter. Mass spectra were obtained at 70 eV for the reaction products eluted from a 6 ft × 0.125 in. stainless steel, 3% OV-1/Chromosorb W column.

GC analyses for the reaction mixtures were made on two dual column instruments (Hewlett-Packard Models 5700A and 5830A) equipped with hydrogen flame ionization detectors. The following 0.125-in. stainless steel columns were used: 2% OV-17/Chromosorb W, 3% UCW-982/Chromosorb W, and 3% OV-225/Chromosorb W.

For all of the systems studied, comparisons between the relative retention times of reaction products and authentic materials on two different columns, and noting peak enhancement upon "spiking" reaction mixtures with authentics comprised one approach for product identification. The mass spectra were used to determine the identities of many of the products (comparison to mass spectra of authentic available products was performed where possible). In this manner 3- and 4-nitro-*o*-xylene and all the benzoic acids and dimethylphenyl benzoates (Table VII) were identified.

o-Methylbenzyl nitrate was determined on the basis of its mass spectrum (molecular ion at *m/e* 167, base peak at *m/e* 91). The product identified as *o*-xylene dimers consisted of three closely spaced peaks all with similar mass spectra (molecular ion at *m/e* 210, base peak at *m/e* 77). None had the exact retention time of 2,2′-dimethylbibenzyl (mp 57–58 °C, mass spectrum molecular ion at *m/e* 210, base peak at *m/e* 105) synthesized by refluxing di-*tert*-butyl peroxide in excess *o*-xylene and removing unreacted monomer by distillation under reduced pressure.

To demonstrate unequivocally that the aroyloxy groups were attached to *o*-xylene at a nuclear position rather than at a side chain in the aryl ester products a concentrated product mixture from a *p*-methylbenzoyl nitrate–*o*-xylene run was hydrolyzed with 5% methanolic potassium hydroxide. The basic aqueous extract of the resulting mixture yielded *p*-methylbenzoic acid and 3,4-xylenol upon acidification (GC analysis), while the original organic portion no longer contained any aryl ester product or any new alcohol product.

All of the hemimellitene products were identified on the basis of their mass spectra and relative GC retention times. 2,3,4-Trimethylphenyl benzoate (mass spectrum molecular ion at *m/e* 240, base peak at *m/e* 105) eluted before 3,4,5-trimethylphenyl benzoate (mass spectrum molecular ion at *m/e* 240, base peak at *m/e* 105). Other products included a chlorohemimellitene (mass spectrum molecular ion at *m/e* 154, M + 2 at *m/e* 156) (structure not determined, but likely an α-chloro isomer[13]) from the cupric chloride–benzoyl peroxide reaction and 4-nitrohemimellitene (mass spectrum molecular ion at *m/e* 165, base peak at *m/e* 119) and 5-nitrohemimellitene (mass spectrum molecular ion at *m/e* 165, base peak at *m/e* 119) from both the benzoyl nitrate and benzoyl peroxide–nitric acid reactions. Also observed from this latter system were a dimethylbenzaldehyde isomer (mass spectrum molecular ion at *m/e* 134), a dimethylbenzyl alcohol isomer (mass spectrum molecular ion at *m/e* 136) and a trimethylbiphenyl isomer (mass spectrum molecular ion at *m/e* 196).

Reaction product yields were determined using phenyl benzoate or carbazole as an internal standard, and comparing product areas to that of the marker added in known amount. The mean of duplicate analyses in good agreement was used, and response factors were calculated for mixtures of authentic vs. the internal standard and used to correct area ratios to mole ratios. The benzoic acid by-product yields were determined in two cases (Table I) by aqueous base extraction and isolation. Together with the aryl ester products in these two runs the benzoyloxy moiety material balance from the *p*-nitrobenzoyl nitrate and benzoyl nitrate reactions was 95 and 86%, respectively.

Registry No.—$AgNO_3$, 7761-88-8; *p*-methoxybenzyl chloride, 100-07-2; *p*-methylbenzoyl chloride, 874-60-2; benzoyl chloride, 98-88-4; *p*-chlorobenzoyl chloride, 122-01-0; *p*-fluorobenzoyl chloride, 403-43-0; *p*-nitrobenzoyl chloride, 122-04-3; *o*-xylene, 95-47-6; hemimellitene, 526-73-8.

References and Notes

(1) (a) A. Fischer, J. Packer, J. Vaughan, and G. J. Wright, *J. Chem. Soc.*, 3687–3690 (1964); (b) A. Fischer, A. J. Read, and J. Vaughan, *ibid.*, 3691–3701 (1964).

(2) (a) A. Fischer and J. N. Ramsay, *J. Am. Chem. Soc.*, **96,** 1614–1616 (1974); (b) R. C. Hahn and D. L. Strack, *ibid.*, **96,** 4335–4337 (1974); (c) M. W. Galley and R. C. Hahn, *ibid.*, **96,** 4337–4339 (1974).

(3) D. J. Blackstock, A. Fischer, K. E. Richards, J. Vaughan, and G. J. Wright, *Chem. Commun.*, 641 (1970).

(4) P. C. Myhre, *J. Am. Chem. Soc.*, **94,** 7921–7923 (1972).

(5) D. J. Blackstock, J. Cretney, A. Fischer, M. P. Hartshorn, K. E. Richards, J. Vaughan, and G. J. Wright, *Tetrahedron Lett.*, 2793–2796 (1970).

(6) A. Fischer and J. N. Ramsay, *J. Chem. Soc., Perkin Trans. 2*, 237–240 (1973).

(7) (a) A. Fischer and A. L. Wilkinson, *Can. J. Chem.*, **50,** 3988–3992 (1972); (b) A. Fischer and D. R. A. Leonard, *ibid.*, **50,** 3367–3372 (1972); (c) A. Fischer, C. C. Greig, A. L. Wilkinson, and D. R. A. Leonard, *ibid.*, **50,** 2211–2216 (1972); (d) A. Fischer and C. C. Greig, *J. Chem. Soc., Chem. Commun.*, 396 (1973); (e) D. J. Blackstock, M. P. Hartshorn, A. J. Lewis, K. E. Richards, J. Vaughan, and G. J. Wright, *J. Chem. Soc. B*, 1212–1213 (1972).

(8) (a) C. L. Perrin and G. A. Skinner, *J. Am. Chem. Soc.*, **93,** 3389–3394 (1971); (b) S. R. Hartshorn, R. B. Moodie, and K. Schofield, *J. Chem. Soc. B*, 1256–1261 (1971); (c) J. W. Barnett, R. B. Moodie, K. Schofield, and J. B. Weston, *J. Chem. Soc., Perkin Trans. 2*, 648–654 (1975).

(9) M. E. Kurz, L. T. A. Yang, E. P. Zahora, and R. C. Adams, *J. Org. Chem.*, **38,** 2271–2277 (1973).

(10) L. R. Barlow, *Tetrahedron*, **24,** 4913–4915 (1968).

(11) (a) M. E. Kurz, R. L. Fozdar, and S. S. Schultz, *J. Org. Chem.*, **39,** 3336–3342 (1974); (b) M. E. Kurz and M. Pellegrini, *ibid.*, **35,** 990–992 (1970).

(12) (a) V. Gold, E. D. Hughes, and C. K. Ingold, *J. Chem. Soc.*, 2467–2473 (1950); (b) S. R. Hartshorn, R. B. Moodie, and K. Schofield, *J. Chem. Soc. B*, 2454–2461 (1971).

(13) M. E. Kurz and P. Kovacic, *J. Org. Chem.*, **33,** 1950–1956 (1968).

(14) Addition products such as **2** and **3** break down to aryl esters upon GC analysis (see ref 3 and 4). The corresponding cyclohexadienes (**6**) would be expected to do the same, and appear to be even less stable than **2** or **3** (see Experimental Section).

(15) R. J. Coombes and L. W. Russell, *J. Chem. Soc. B*, 2443–2447 (1971).

(16) Because of the complex equilibria known to exist for acyl nitrate systems (see ref 9, 12a), it is possible that this combination of reagents formed acetyl nitrate which could have been responsible for the products.

(17) C. C. Price and E. Krebs, "Organic Syntheses", Collect. Vol. III, Wiley, New York, N.Y. 1955, pp 649–650.

(18) L. S. Silbert and D. Swern, *J. Am. Chem. Soc.*, **81,** 2364–2367 (1959).

(19) M. E. Kurz, E. M. Steele, and R. L. Vecchio, *J. Org. Chem.*, **39,** 3331–3336 (1974).

Biosynthetic Oxidation and Rearrangement of Vittatine and Its Derivatives[1]

A. I. Feinstein and W. C. Wildman*

Department of Chemistry, Iowa State University of Science and Technology, Ames, Iowa 50011

Received January 5, 1976

By the use of appropriately labeled radioactive precursors it is demonstrated that vittatine (**2d**) is a precursor of haemanthamine (**2e**) and montanine (**4a**) in *Rhodophiala bifida*. Evidence is presented to show there is no equilibration of the enantiomeric (−)- and (+)-crinine ring systems in the plants.

Although the Amaryllidaceae alkaloids are almost invariably isolated in optically active form, the family is unique because a given plant may produce two very similar alkaloids possessing enantiomeric nuclei. Thus *Nerine bowdenii* W. Wats. contains both crinine (**1**) and (+)-epicrinine (**2a**).[2,3] Several plants contain the optical antipode of **1**, vittatine (**2d**),[4–9] but racemic crinine has never been isolated. Because more oxygenated derivatives of **1** and **2a** have been