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Preparation and Thermal Decomposition of Acyl Carbamoyl Peroxides

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Thirteen acyl carbamoyl peroxides, a new class of peroxides, were prepared by addition of peroxy-acids to organic isocyanates and their properties were examined. The thermal decompositions, especially of benzoyl *N*-(*p*-nitrophenyl)carbamoyl peroxide and benzoyl *N*-benzoylcarbamoyl peroxide, were studied in crystalline state and in solution, and it was shown that they decompose via three different mechanisms, involving either an amino-radical, a nitrene or a protonated nitrene, depending on reaction conditions.

Peroxides having active hydrogens, such as hydrogen peroxide and alkyl hydroperoxides are known to undergo addition reaction with isocyanates; hydrogen peroxide produces azo-compounds *via* dicarbamoyl peroxides which are too unstable to be isolated,[1] whereas hydroperoxides form considerably stable peroxycarbamates.[2,3] We have preliminarily communicated elsewhere[4] that peroxy-acids also react with isocyanates to give acyl carbamoyl peroxides, a new class of peroxides:

$$RN{=}C{=}O + R'C({=}O)OOH \rightarrow RNHC({=}O)OOC({=}O)R'$$

The present paper presents detailed accounts of the preparation and thermal decomposition of these peroxides.

Results and Discussion

Acyl carbamoyl peroxides were prepared at −10∼−15 °C by adding a peroxy-acid in ether to an ethereal solution of an isocyanate containing a trace of pyridine as catalyst. The peroxides thus obtained and their characteristic infrared absorption bands are listed in Tables 1 and 2, respectively.

Reaction between *N*-methyl-*N*-(*p*-nitrophenyl)carbamoyl chloride and peroxybenzoic acid with 30% potassium hydroxide as a base gave benzoyl *N*-methyl-*N*-(*p*-nitrophenyl)carbamoyl peroxide, which was found so unstable as to decompose readily at room temperature yielding carbon dioxide. In Table 3 are summarized attempted syntheses which did not give the peroxides expected.

Tables 1 and 3 show that in order for acyl carbamoyl peroxides to be prepared isocyanates must carry an electronegative substituent. With *p*-nitrophenyl isocyanate, all the peroxy-acids examined gave the corresponding peroxides irrespective of the nature of their substituents and the substituent in isocyanates appears to have to be more electronegative than, say, a *m*-chloro substituent. This trend is similar to that observed in the preparation of substituted *N*-phenylperoxycarbamates, of which the *p*-methyl and *p*-methoxy derivatives were not prepared.[3] The aliphatic isocyanate does not seem to give peroxides with peroxy-acids, although the aliphatic peroxy-acid reacts with appropriate aromatic isocyanates to yield peroxides. Replacement of a hydrogen on the nitrogen of the carbamoyl group by a methyl group makes the peroxide remarkably unstable.

The effect of an electron-withdrawing substituent in the isocyanate is explained because it increases the reactivity of an isocyanate towards addition[5] and at the same time seems to make it less vulnerable to oxidative attack by peroxy-acids. Further, an electro-

TABLE 1. PREPARATION AND PROPERTIES OF ACYL CARBAMOYL PEROXIDES $RNHC({=}O)OOC({=}O)R'$

Compd.	R	R'	Yield (%)	Solvent[a]	Dp (°C)[b]	Purity[c] (%)	Analyses					
							Found			Calcd		
							C	H	N	C	H	N
I	p-$O_2NC_6H_4$	C_6H_5	55	A	63	98	55.77	3.46	9.57	55.62	3.34	9.27
II	p-NCC_6H_4	C_6H_5	57	A	51	93	61.60	4.60	4.66	62.00	4.59	4.25
III	p-$EtO_2CC_6H_4$	C_6H_5	56	A	55	96	63.15	4.16	9.39	63.84	3.57	9.93
IV	m-ClC_6H_4	C_6H_5	55	B		[d]						
V	o-$O_2NC_6H_4$	C_6H_5	69	A	64	94	55.34	3.60	9.09	55.62	3.34	9.27
VI	p-$O_2NC_6H_4$	p-$CH_3OC_6H_4$	68	A	68	100	53.78	3.93	8.27	54.22	3.64	8.43
VII	p-$O_2NC_6H_4$	p-$CH_3C_6H_4$	86	A	64	94	57.12	4.22	9.02	56.96	3.82	8.86
VIII	p-$O_2NC_6H_4$	m-ClC_6H_4	40	C	60	97	49.42	2.85	8.66	49.94	2.69	8.32
IX	p-$O_2NC_6H_4$	p-$O_2NC_6H_4$	19	D	55	84	47.91	3.19	12.02	48.42	2.61	12.10
X	p-$O_2NC_6H_4$	n-$C_{11}H_{23}$	47	D	49	95	59.82	7.62	7.30	59.98	7.42	7.36
XI	C_6H_5CO	C_6H_5	75	D	60	97	62.59	3.92	4.97	63.19	3.89	4.91
XII	$C_6H_5SO_2$	C_6H_5	74	D	80	82	51.97	3.63	4.76	52.33	3.45	4.36

a) Solvent for recrystallization: A, dichloromethane; B, ether-petroleum ether; C, dichloromethane-petroleum ether; D, ether. b) Decomposition point; all peroxides decompose explosively at these temperatures except compound XII. c) Active oxygen estimated by iodometry in acetic acid (A.T. Blomquist and A.F. Ferris, *J. Amer. Chem. Soc.*, **73**, 3408 (1951)). d) Too unstable to be analyzed correctly (see Experimental).

TABLE 2. INFRARED SPECTRA OF ACYL CARBAMOYL PEROXIDES[a)]

Compound	$\nu_{\mathrm{N-H}}$ (cm^{-1})	$\nu_{\mathrm{C=O}}$ (cm^{-1})		
I	3412[b)]	1807	1777	
II	3410	1803	1780	
III	3415	1806	1783	1770
V	3321	1810	1780	
VI	3414	1806	1773	
VII	3412	1810	1787	
X	3417	1814	1789	
XI	3413	1835	1781	1728
XII	3385	1811	1781	

a) In chloroform in concentration of about 0.01 mol/l.
b) In carbon tetrachloride, 3420 cm^{-1}.

negative substituent seems to stabilize acyl carbamoyl peroxides as is observed with various types of peroxides, such as substituted benzoyl peroxides,[6)] *t*-butyl *N*-phenylperoxycarbamates,[3)] *t*-butyl peroxybenzoates[7)] and *t*-butyl peroxyphenylacetates.[8)] The destabilizing effect of a methyl group mentioned above seems to be due to its electron-releasing effect. Aliphatic isocyanates, which have low reactivity compared with aromatic ones,[5)] do not yield acyl carbamoyl peroxides; on the other hand, benzoyl[9)] and benzenesulfonyl[10)] isocyanates, which are known for high reactivity, gave the corresponding peroxides in high yields.

The results of the thermal decompositions of benzoyl *N*-(*p*-nitrophenyl)carbamoyl peroxide in solutions as well as in crystalline state are summarized in Table 4. The yield of carbon dioxide exceeded 100 mol% by about 20% or more in benzene, chloroform and acetic acid, but it was about 100 mol% in the decomposition in crystalline state and in ethanol. Benzoic acid was produced in a relatively large amount in each case, but there was a definite difference in its yield between the decomposition in benzene, chloroform or acetic acid (about 50 mol%) on the one hand and that in crystalline state or in ethanol (70—80 mol%) on the other. Some products which appear to have been derived from phenyl radicals, such as biphenyl and benzene were formed in benzene, chloroform and acetic acid. The following nitrogen containing products were identified: *p,p'*-dinitroazobenzene in the decomposition in crystalline state; *p,p'*-dinitroazobenzene and *p*-nitroaniline in benzene and chloroform; *p*-nitroacetanilide in acetic acid; and 5-nitro-2-aminophenetole and 5-nitro-2-benzamidophenol in ethanol. Some of these findings strongly suggest a homolytic nature of the decomposition, but the concurrence of an ionic mechanism is very likely in view of the production of 5-nitro-2-aminophenetole and 5-nitro-2-benzamidophenol in ethanol.

The homolytic fission of the peroxidic linkage of benzoyl *N*-(*p*-nitrophenyl)carbamoyl peroxide would primarily produce an *N*-(*p*-nitrophenyl)-carbamoyloxy p-$\mathrm{O_2NC_6H_4NHCOO}\cdot$ and a benzoyloxy $\mathrm{C_6H_5COO}\cdot$ radicals. In order to know the behavior, under the prevailing conditions, of these radicals, *t*-butyl *N*-(*p*-nitrophenyl)peroxycarbamate[2,3)] and benzoyl peroxide,[11)] which are known to generate these radicals respectively, were separately decomposed in benzene and in ethanol and the products were examined. The results are summarized in Table 5. They show that the

TABLE 3. ATTEMPTED REACTIONS[a)] WHICH GAVE NO PEROXIDES

Isocyanates	Peroxy-acids	Products isolated
p-$\mathrm{ClC_6H_4NCO}$	$\mathrm{C_6H_5CO_3H}$	*p,p'*-Dichloroazobenzene(10%) *p,p'*-Dichloroazoxybenzene(2%)
$\mathrm{C_6H_5NCO}$	$\mathrm{C_6H_5CO_3H}$	Nitrobenzene(1%), azobenzene(trace)
p-$\mathrm{O_2NC_6H_4NCO}$	o-$\mathrm{HOOCC_6H_4CO_3H}$	No reaction
$\mathrm{C_{11}H_{23}NCO}$	$\mathrm{C_6H_5CO_3H}$	No reaction
$\mathrm{C_{11}H_{23}NCO}$	$\mathrm{C_{11}H_{23}CO_3H}$	No reaction
p-$\mathrm{O_2NC_6H_4NCO}$	$\mathrm{H_2O_2}$	*p,p'*-Dinitroazobenzene(30%)
p-$\mathrm{OCNC_6H_4NCO}$	$\mathrm{C_6H_5CO_3H}$	Tarry material

a) Reactions were carried out by essentially the same procedure as described for the preparation of benzoyl *N*-(*p*-nitrophenyl)carbamoyl peroxide.

TABLE 4. PRODUCTS OF DECOMPOSITION OF BENZOYL *N*-(*p*-NITROPHENYL)CARBAMOYL PEROXIDE

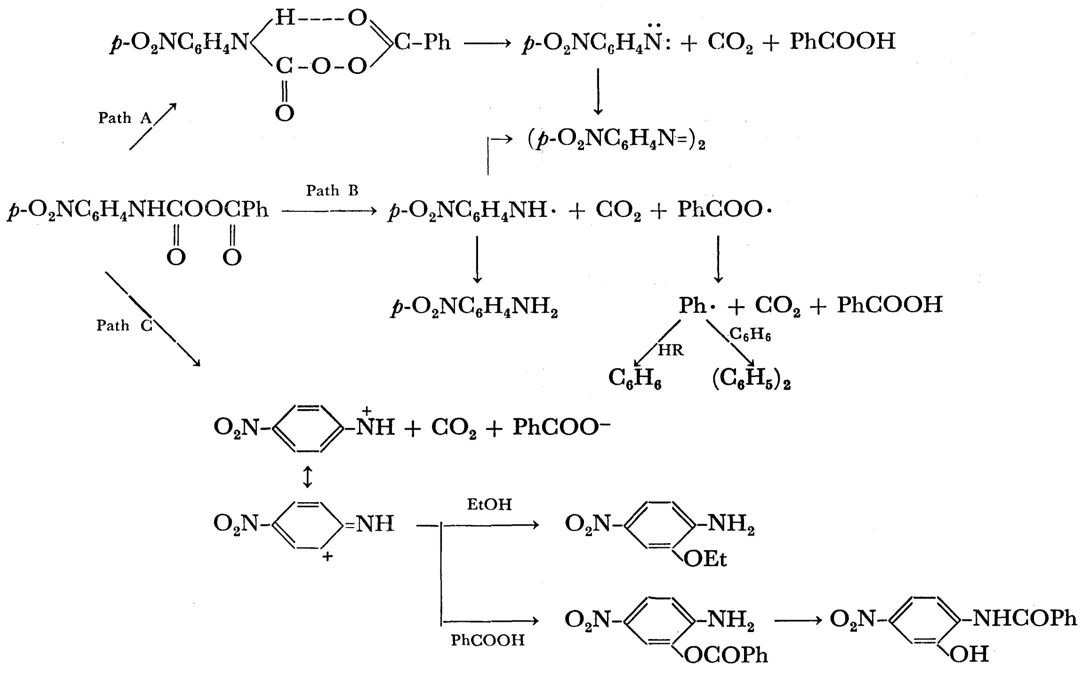
Reaction conditions		Products (yield in mol% of peroxide)[a)]								
Solvent	Temp. °C	Carbon dioxide	Benzoic acid	Benzene	Biphenyl	*p*-Nitroaniline	*p,p'*-Dinitroazobenzene	*p*-Nitroacetanilide	5-Nitro-2-benzamidophenol	5-Nitro-2-aminophenetole
None	20	98	80			trace	15			
Benzene	80	117	48		20	15	12			
Chloroform	61	127	45	33		17	14			
Acetic acid	50	118	47	9				59		
Ethanol	78	96	68						10	63

a) The decomposition of benzoyl *N*-(*p*-nitrophenyl)carbamoyl peroxide usually gave a dark brown polymeric substance besides the compounds listed in this table.

TABLE 5. PRODUCTS OF DECOMPOSITION OF *t*-BUTYL *N*-(*p*-NITROPHENYL)PEROXYCARBAMATE AND BENZOYL PEROXIDE

Peroxide	Reaction conditions		Products (yield in mol% of peroxide)				
	Solvent	Temp. °C	Carbon dioxide	Benzoic acid	Biphenyl	*p,p'*-Dinitroazobenzene	*p*-Nitroaniline
Peroxycarbamate	Benzene	80	96		4	8	77
Peroxycarbamate	Ethanol	78	98			1	90
Benzoyl peroxide	Benzene	80	178	7	126[a)]		

a) Biphenyl 90% and dihydrobiphenyl 36%.



Scheme 1.

carbamoyloxy radical, when generated in benzene or in ethanol, gives mainly carbon dioxide (96—98%) and *p*-nitroaniline (77—90%) with *p,p'*-dinitroazobenzene as a minor product, and that 89% of the benzoyloxy radical generated in benzene loses carbon dioxide before it engages in other reactions, finally to form 63% of biphenyl, and only 3.5% of benzoic acid was obtained. No trace of 5-nitro-2-aminophenetole was detected in the decomposition in ethanol.

On the basis of the results presented above, three pathways are proposed as shown in Scheme 1 for the thermal decomposition of benzoyl *N*-(*p*-nitrophenyl) carbamoyl peroxide. Path A is a concerted mechanism via a seven-membered cyclic transition state giving rise to *p*-nitrophenylnitrene; path B is a radical mechanism beginning with the homolysis of the oxygen-oxygen bond usually observed in the thermal decomposition of peroxides; and path C is an ionic mechanism. The extent to which each of these mechanisms is operative depends on the experimental conditions under which the peroxide is decomposed.

Path A is straightforward and best explains the decomposition in crystalline state, since carbon dioxide and benzoic acid were obtained in nearly 100% yield and the fact that 30% of the *p*-nitrophenylcarbamoyloxy moiety was accounted for as *p,p'*-dinitroazobenzene strongly suggests the intermediacy of *p*-nitrophenylnitrene.[12)]

Since the *p*-nitrophenylcarbamoyloxy moiety will liberate 100% of carbon dioxide in any of the postulated pathways, the fact that the carbon dioxide was evolved in excess of 100% in the decomposition in benzene, chloroform or acetic acid indicates the involvement of path B, in which the benzoyloxy radical generated decomposes also to give carbon dioxide at the expense of benzoic acid. However, if path B were the only mechanism operative in these solvents, the yield of benzoic acid would have been much less than actually found and as much as 180% or more of carbon dioxide would have been obtained, since benzoyloxy radicals extensively decompose to give phenyl radicals and carbon dioxide (cf. Table 5). Thus, the results of product analyses indicate that the decomposition in benzene proceeds via both paths A and B to the exclusion of path C, *viz.*, about 25%[13)] through path B and consequently about 75% through path A.

The mode of decomposition in chloroform appears to be similar to that in benzene, but benzene was formed instead of biphenyl, the intermediate phenyl radical abstracting a hydrogen atom from chloroform.

Some of the *p*-nitrophenylamino radical produced in path B may undergo dimerization followed by dehydrogenation under the prevailing oxidizing conditions finally to give *p,p'*-dinitroazobenzene; but obviously its chief reaction is abstraction of a hydrogen atom from an appropriate hydrogen-donating species to give *p*-nitroaniline (cf. Table 5 and Ref. 2). It can also arise, however, from *p*-nitrophenylnitrene,[14] although this mode of formation seems to be a remote possibility in benzene.

As regards the decomposition in ethanol, product analysis suggests that it proceeds chiefly by path C, in which a protonated *p*-nitrophenylnitrene or a *p*-nitrophenylnitrenium ion[15] is postulated; a polar protic solvent such as ethanol is likely to favor such an ionic process. The production of 5-nitro-2-aminophenetole in a yield of as high as 63% supports this view and is best explained by nucleophilic attack on a mesomeric form of the nitrenium ion *p*-$O_2NC_6H_4NH^+$ by a molecule of ethanol as shown in Scheme 1. The formation of 5-nitro-2-benzamidophenol is similarly explained in terms of nucleophilic attack on the ring by benzoic acid or benzoate ion followed by migration of the benzoyl group to the nitrogen.[16] If path B were also operative to any perceptible extent, benzene and *p*-nitroaniline would have been detected. The intermediacy of *p*-nitrophenylnitrene is excluded because neither nitrogen-containing products expected from it nor products of dehydrogenation of ethanol such as acetaldehyde[17] were found.

The decomposition pattern in acetic acid is different from that in ethanol, especially in that such a product as 5-nitro-2-acetamidophenol, which would have readily arisen by way of path C was not detected; the intermediacy of protonated nitrene (path C) is thus ruled out. It is similar to that in benzene or chloroform as far as the yields of carbon dioxide and benzoic acid concerned; accordingly, path B is undoubtedly operating in some measure, and path A must be the major one, although *p,p'*-dinitroazobenzene and *p*-nitroaniline were absent from the reaction mixture. It is worth noting that 59% of *p*-nitroacetanilide was obtained as the sole product which accounts for the *p*-nitrophenylcarbamoyl group. A small part of the anilide may have been produced by prolonged contact of the *p*-nitroaniline initially formed with hot acetic acid solvent during the period of the reaction and the subsequent work-up, as was shown to be the case by separate experiments. The mechanism by which most of the *p*-nitroacetanilide was formed from *p*-nitrophenylnitrene or *p*-nitrophenylamino radical with acetic acid remains unexplained.

The thermal decomposition of benzoyl *N*-benzoylcarbamoyl peroxide in crystalline state was examined by measuring its infrared spectrum in Nujol mull, in which the peroxide was hardly soluble. A freshly prepared mull showed a ν_{N-H} band at 3420 cm^{-1} and $\nu_{C=O}$ bands at 1765 and 1685 cm^{-1}. When the same sample was measured after being kept 30 minutes at room temperature, the ν_{N-H} band had almost disappeared and new bands had appeared at 2350 and 2260 cm^{-1}, which are attributable to carbon dioxide and phenyl isocyanate, respectively. The $\nu_{C=O}$ band at 1765 cm^{-1} had considerably decreased in intensity, whereas the $\nu_{C=O}$ band at 1685 cm^{-1} was almost unchanged, although its band width had slightly increased. These facts would suggest that this peroxide decomposes in crystalline state giving carbon dioxide, benzoic acid and transitory benzoylnitrene, which seems to rearrange immediately to phenyl isocyanate.

The results of decompositions of benzoyl *N*-benzoylcarbamoyl peroxide in solutions are summarized in Table 6. The yield of carbon dioxide was higher than 100% in benzene, but lower in ethanol. Benzoic acid was formed nearly quantitatively in ethanol. Biphenyl, which was found in benzene, is a product indicative of the operation of a radical mechanism but in ethanol no such products were detected; for example, benzene, which would have readily resulted from phenyl radicals by abstraction of a hydrogen atom from ethanol, was absent from the reaction mixture. Products containing nitrogen were: in benzene solution, benzamide, phenyl isocyanate, carbanilide and γ-triphenylbiuret, the last two being produced from the reaction of phenyl isocyanate with benzoic acid;[18] and in ethanol solution, ethyl benzhydroxamate.

These findings may be accommodated in the reaction sequences shown in Scheme 2, which are formulated by the analogy with Scheme 1.

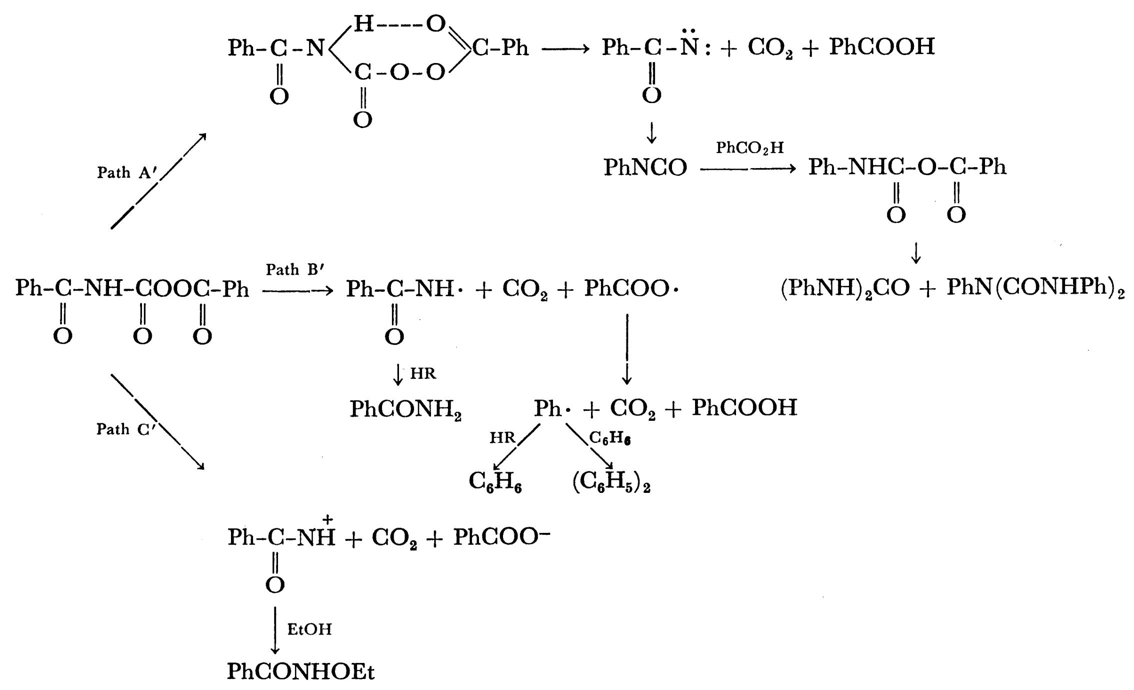
In path A', the intermediate formation of benzoylnitrene is postulated, which immediately rearranges to phenyl isocyanate,[19] and this in turn reacts with benzoic acid to give further products. Path B' represents a homolytic mechanism; the benzoyloxy radical will undergo a series of the usual reactions in benzene and the benzamido radical will abstract a hydrogen atom[20] from intermediate phenylcyclohexadienyl $C_6H_5C_6H_6\cdot$ radicals to give benzamide and biphenyl. Paths A' and B' are both operative in the decomposition in benzene; the former explains the formation of phenyl isocyanate and its subsequent reaction products with benzoic acid (carbanilide and γ-triphenylbiuret) and the latter that of biphenyl, benzamide, and more than 100 mol% of carbon dioxide.

Path C' postulated as a counterpart of path C in

TABLE 6. PRODUCTS OF DECOMPOSITION OF BENZOYL *N*-BENZOYLCARBAMOYL PEROXIDE

Reaction conditions		Products (yield in mol% of peroxide)					
Solvent	Temp. (°C)	Carbon dioxide	Benzoic acid	Biphenyl	Benzamide	Phenyl isocyanate	Ethyl benzhydroxamate
Benzene[a]	80	124	28	34	34	2	
Ethanol	78	72	94				38

a) In addition to the products in this table carbanilide and γ-triphenylbiuret were isolated.



Scheme 2.

Scheme 1 involves protonated benzoylnitrene, which undergoes nucleophilic attack by ethanol, and best explains the formation of ethyl benzhydroxamate as the only isolable nitrogen containing compound in ethanol. It would seem possible that ethyl benzhydroxamate might have been formed by the action of solvent ethanol on benzoylnitrene produced by path A′, thus,

$$C_6H_5CON: + EtOH \rightarrow C_6H_5CONHOEt.$$

Such a reaction is in fact reported by Horner, Bauer and Dorges,[21] but benzoylnitrene does not seem to be a proper intermediate in the present case, since no ethyl *N*-phenylcarbamate was detected, which ought to have been formed from ethanol and phenyl isocyanate, if benzoylnitrene had been involved, and which actually was obtained together with the benzhydroxamate.[21]

Experimental

Isocyanates and peroxy-acids were prepared by reported methods. *t*-Butyl *N*-(*p*-nitrophenyl)peroxycarbamate was prepared according to the directions given by O'Brien and his co-workers.[3]

Preparation of Acyl Carbamoyl Peroxides. A typical procedure is given below for the preparation of benzoyl *N*-(*p*-nitrophenyl)carbamoyl peroxide. Other peroxides were prepared similarly (see Table 1).

Benzoyl N-(p-*Nitrophenyl)carbamoyl Preoxide.* *p*-Nitrophenyl isocyanate (8.9 g, 0.055 mol) and two drops of pyridine were dissolved in 150 ml of absolute ether and to this solution, cooled to −15—−20 °C, was added slowly an ethereal solution (50 ml) of peroxybenzoic acid (purity 95%, 0.055 mol) with stirring while maintaining the temperature below −10 °C. The temperature was gradually raised to 0 °C after completion of the addition of the peroxy-acid. The precipitation of the peroxide set in after about 30 min. The mixture was stirred for a further 3 hr. The peroxide was filtered off and washed with cold ether three times (yield, 55%). The peroxide, at this stage, was almost pure and free from contamination with *p,p′*-dinitrodiphenylurea when pure starting materials were used. Recrystallization of 7.0 g of the peroxide from methylene chloride between 10 and −78 °C gave 4.0 g of almost white crystals, which explosively decomposed at 63 °C when heated at a rate of 4—5 °C per minute.

Benzoyl N-(m-*Chlorophenyl)carbamoyl Peroxide.* Peroxybenzoic acid (3.2 g, 0.022 mol) in 20 ml of ether was added to 20 ml of an ethereal solution of *m*-chlorophenyl isocyanate according to the procedure described above for the *p*-nitroderivative. After being stirred for 4 hr, the reaction mixture was added to 750 ml of petroleum ether (bp 35—40 °C) in order to precipitate the peroxide. Cooling the solution at −78 °C gave 3.3 g (55%) of a white solid material tinged with violet. This solid was certainly the desired peroxide, because it liberated iodine from an acetic acid solution of sodium iodide and violently detonated when allowed to stand for a few minutes at room temperature or heated on a spatula over a flame; it was too unstable to be submitted to elemental analysis and determination of active oxygen.

Benzoyl N-*Methyl*-N-(p-*nitrophenyl)carbamoyl Peroxide.* An aqueous solution (30%) of potassium hydroxide (0.011 mol) was added dropwise with stirring to 170 ml of an ethereal solution of peroxybenzoic acid (1.7 g, 0.011 mole) and *N*-methyl-*N*-(*p*-nitrophenyl)carbamoyl chloride (2.2 g, 0.01 mole). After being stirred for 3 hr at −5 °C, the solution was kept at −78 °C for one day. Precipitated potassium chloride was filtered off and the filtrate was concentrated to 10 ml by evaporating the ether at −10 °C. Addition of cold petroleum ether to the concentrate gave a yellowish orange paste, which liberated iodine from an aqueous acetic acid solution of sodium iodide and decomposed even at 0 °C evolving carbon dioxide. The decomposition products of the peroxide at room temperature were *N*-methyl-*p*-nitroaniline (72%), mp and mixed mp 151 °C (lit,[22] 152 °C), benzoic acid (20%), and a trace of *N,N′*-bis-(p-nitrophenyl)ethylenediamine, mp 218—219°C (lit,[23] 220—221 °C), each of them being isolated by chromatography on alumina.

Thermal Decomposition of Peroxide. The decompositions in solution were all performed under nitrogen or argon. Carbon dioxide evolved was measured by absorption in an Ascarite tube. Gas chromatographic analyses were carried out with a Perkin-Elmer Vapour Fractometer Model 154.

Decomposition of Benzoyl N-(p-*Nitrophenyl)carbamoyl Peroxide in Crystalline State.* The peroxide (1.839 g) was allowed to stand at room temperature (about 20 °C) for a week. The gas (0.261 g) evolved during the decomposition was shown to contain only carbon dioxide by mass spectrometric analysis. The residue was extracted with 400 ml of benzene for 13 hr in a Soxhlet extractor. From the benzene solution, benzoic acid (0.599 g) was recovered by using 5% sodium bicarbonate. The residual benzene solution was dried with anhydrous sodium sulfate, concentrated to 50 ml, and chromatographed on alumina to give *p,p'*-dinitroazobenzene (0.23 g), mp and mixed mp 218—219 °C (lit,[22] 220 °C), and a trace of *p*-nitroaniline, mp and mixed mp 147—148 °C (lit,[22] 148 °C).

Decomposition of Benzoyl N-(p-*Nitrophenyl)carbamoyl Peroxide in Benzene.* Benzene (900 ml) in a two-necked round-bottomed flask fitted with a gas inlet tube and a reflux condenser was flushed with a stream of nitrogen for an hour, and the peroxide (1.522 g, 5.03 mmol) was added quickly and dissolved by stirring. The solution was heated under reflux for 19 hr, nitrogen being slowly bubbled. Carbon dioxide (260 mg, 5.92 mmol) evolved. Removal of benzene by distillation gave 50 ml of a deep-red benzene solution. After the solution was shaken with 5% sodium bicarbonate to remove benzoic acid (297 mg, 2.43 mmol), it was dried with anhydrous sodium sulfate and analyzed; gas chromatography with an Apiezon grease column at 220 °C showed the presence of biphenyl only and chromatography on alumina and elution with benzene gave, in succession, biphenyl (152 mg, 0.99 mmol), *p,p'*-dinitroazobenzene (165 mg, 0.61 mmol), and unidentified brownish orange crystals (34 mg, mp 189—190 °C, from ethanol), and then elution with ether yielded *p*-nitroaniline (103 mg, 0.75 mmol).

Decomposition of Benzoyl N-(p-*Nitrophenyl)carbamoyl Peroxide in Chloroform.* The peroxide (2.673 g, 8.84 mmol) in 700 ml of chloroform was heated under reflux for 6 hr. The procedure was virtually the same as described above for the decomposition in benzene. The amount of carbon dioxide evolved was 494 mg (11.2 mmol). Chloroform was distilled from the reaction mixture through a concentric column of 80 cm in height to give 50 ml of a concentrated solution, a small portion of which was submitted to gas chromatographic analysis using an Apiezon grease column at 80 °C; it contained 227 mg (2.91 mmol) of benzene and no chlorobenzene. Isolation and identification of other products were carried out by chromatography on alumina as described above.

Decomposition of Benzoyl N-(p-*Nitrophenyl)carbamoyl Peroxide in Acetic Acid.* The peroxide (2.696 g, 8.94 mmol) in 665 ml of anhydrous acetic acid was decomposed at 50 °C for 12 hr. Acetic acid was carefully distilled through a 40 cm Vigreux column, an initial fraction (80 ml) boiling at 40—42 °C/35—38 mmHg being collected. This was fractionated through a concentric column of 80 cm in height under atmospheric pressure, an initial fraction (5 ml) being subjected to gas chromatographic analysis using a polyethylene glycol column at 100 °C to determine the quantity of benzene formed. The residual acetic acid solution in the first distillation was further concentrated almost to dryness at the same temperature and pressure as described above to give a brown solid, which was washed with 5% sodium bicarbonate to remove acidic compounds and then dissolved in a large amount of methylene chloride. The acid part extracted consisted of only benzoic acid (5.11 mg, 4.18 mmol), because methylation of the extract with diazomethane followed by gas chromatography showed the presence of methyl benzoate without any trace of other methyl esters such as methyl succinate which would have been formed from acetic acid solvent. Evaporation of the methylene dichloride solution gave only *p*-nitroacetanilide (952 mg, 5.29 mmol), which was identified by mixed melting point determination (213—215 °C, lit,[22] 215—216 °C) and comparison of the infrared spectrum.

Decomposition of Benzoyl N-(p-*Nitrophenyl)carbamoyl Peroxide in Absolute Ethanol.* The peroxide (1.409 g, 4.67 mmol) dissolved in 850 ml of absolute ethanol was heated under reflux for 24 hr. Carbon dioxide evolved weighed 196 mg (4.48 mmol). Removal of the solvent from the reaction mixture, an initial 100 ml of the distillate being retained for later examination, gave 70 ml of a deep-red solution, which was mixed with benzene and subjected to azeotropic distillation for complete removal of ethanol. The remaining benzene solution was filtered from insoluble dark brown precipitate, shaken with 5% sodium bicarbonate to extract benzoic acid (388 mg, 3.17 mmol), dried with anhydrous sodium sulfate and chromatographed on alumina, to give 5-nitro-2-aminophenetole (535 mg, 2.94 mmol) mp 90—91 °C (lit,[22] 91 °C). Found: C, 52.65; H, 5.72; N, 15.62%. Calcd for $C_8H_{10}N_2O_3$: C, 52.74; H, 5.53; N, 15.38%. Subsequent elution with benzene-ether mixture (1 : 9) gave two unidentified compounds in small amounts (20 mg and 30 mg). The dark brown precipitate insoluble in benzene mentioned above was recrystallized from ethanol and identified as 5-nitro-2-benzamidophenol (121 mg, 0.47 mmol), mp 266—267 °C. Found: C, 60.46; H, 4.07; N, 10.99%. Calcd for $C_{13}H_{10}N_2O_4$: C, 60.46; H, 3.90; N, 10.85%. The infrared spectrum in Nujol mull showed characteristic bands at 3340 (ν_{N-H}), 3110 (ν_{O-H}), and 1630 ($\nu_{C=O}$) cm^{-1}.

The initial fraction from the first distillation was submitted to gas chromatographic analysis for benzene using a polypropylene glycol column at 70 °C; but none was detected other than etanol.

Decomposition of Benzoyl N-*benzoylcarbamoyl Peroxide in Benzene.* The peroxide (2.846 g, 10.0 mmoles) was decomposed in 480 ml of benzene by heating under reflux for 49 hr. Carbon dioxide evolved weighed (544 mg 12.4 mmol). On cooling the solution, 0.0215 g of a light brown solid precipitated. It was filtered off and identified as a mixture of carbanilide (*sym*-diphenylurea) and γ-triphenylbiuret by comparing its infrared spectrum with those of authentic samples. The above filtrate, after being concentrated to 23 ml, was shown by gas chromatography (Apiezon grease L, at 150 °C) to contain biphenyl and phenyl isocyanate. The concentrate was shaken with 5% sodium bicarbonate, dried with anhydrous sodium sulphate and chromatographed on alumina to give biphenyl (402 mg), traces of carbanilide and γ-triphenylbiuret. The aqueous extract was dissolved in ether, methylated by diazomethane and submitted to gas chromatography using an Apiezon grease column at 161 °C; methyl benzoate (385 mg, 2.83 mmol) was detected. Evaporation of the ethereal solution and extraction of methyl benzoate from the residue with petroleum ether left benzamide (413 mg, 3.41 mmol), which was identified by the mixed mp (131—133 °C, lit,[22] 132.5—133.5 °C) and the infrared spectrum.

Decomposition of Benzoyl N-*Benzoylcarbamoyl Peroxide in Absolute Ethanol.* The peroxide (2.818 g, 9.89 mmol) was heated in ethanol (500 ml) under reflux for 20 hr, during which period 314 mg (7.13 mmol) of carbon dioxide evolved. The reaction mixture was concentrated to about 5 ml and allowed to stand overnight in a refrigerator. After filtration of precipitated benzoic acid (266 mg), removal of the ethanol and addition of benzene, the solution was shaken with 5% sodium bicarbonate, dried with calcium chloride and evaporated to give 0.580 g of a light brown liquid residue. The acid portion extracted (1.937 g) with bicarbonate was methylated with diazomethane in ether and found to contain 0.861 g of benzoic acid by gas chromatographic determination of the methyl benzoate formed, and the remainder (1.112 g) of the aqueous extract, which was obtained of the extraction of the methyl benzoate with petroleum ether, was shown to be essentially identical with the above light brown liquid by comparison of the infrared spectra. A portion (0.417 g) of this liquid was dissolved in 3 ml of tetrahydrofuran and heated under reflux for 10 hr with 10 ml of 10% aqueous potassium hydroxide giving 0.152 g of benzoic acid and 0.151 g of ethyl benzhydroxamate, mp and mixed mp 63—64 °C (lit,[24] 64—65 °C), which is known to remain intact by treatment with alkali.[24] The light brown liquid was, therefore, considered to consist of ethyl benzhydroxamate (612 mg) and a compound which gave benzoic acid by alkaline hydrolysis.

Decomposition of t-*Butyl* N-*(*p-*Nitrophenyl)peroxycarbamate in Benzene.* Heating this peroxy-ester (1.282 g, 5.04 mmol) in benzene under reflux for 78 hr gave 213 mg (4.84 mmol) of carbon dioxide. The reaction mixture was concentrated to 29 ml and chromatographed on alumina to give biphenyl (29 mg 0.19 mmol), *p,p′*-dinitroazobenzene (103 mg, 0.38 mmol) and *p*-nitroaniline (536 mg, 3.88 mmol).

Decomposition of t-*Butyl* N-*(*p-*Nitrophenyl)peroxycarbamate in Ethanol.* The peroxy-ester (3.995 g, 15.7 mmol) was heated in ethanol (900 ml) under reflux for 22 hr to yield 681 mg (15.5 mmol) of carbon dioxide. Concentration of the reaction mixture to 70 ml and azeotropic distillation after addition of 150 ml of benzene gave 70 ml of a benzene solution and a precipitate (*p*-nitroaniline, 783 mg). The filtered benzene solution was chromatographed on alumina to give *p,p′*-dinitroazobenzene (35 mg, 0.13 mmol) and *p*-nitroaniline (1.145 g).

Decomposition of Benzoyl Peroxide in Benzene. Benzoyl peroxide (1.250 g, 5.17 mmol) was decomposed in boiling benzene for 46 hr to evolve 403 mg (9.18 mmol) of carbon dioxide. After the solution was concentrated to 26 ml, benzoic acid (46 mg, 0.38 mmol) was extracted with 5% sodium bicarbonate and the organic layer was submitted to gas chromatographic analysis for determination of biphenyl (716 mg) and dihydrobiphenyl (284 mg).

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