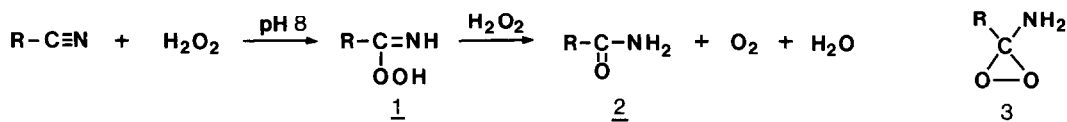


FORMATION AND REACTION OF N-SUBSTITUTED PEROXYCARBOXIMIDIC ACIDS FROM
 α-AZOBENZYL HYDROPEROXIDES BY PYRIDINE-CATALYZED REACTION

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Abstract: α-Azobenzyl hydroperoxides (4) isomerize to N-(4-bromoanilino)-peroxycarboximidic acids (5), which are transformed into benzoic acids (6), by the pyridine-catalyzed reaction.

Peroxy-carboximidic acid (1) is formed in situ by the reaction of nitrile with alkaline hydrogen peroxide and gives amide (2) by further reaction with hydrogen peroxide.¹ The reaction is used for the preparation of aromatic amides.² Recently, peroxy-carboximidic acids (1) having electron withdrawing groups in R were shown to be a potent oxidant for epoxidation of olefins.³⁻⁵ Mechanism of the amide formation from 1 was studied by Wiberg.⁶ The dioxirane



structure (3) for 1 has been suggested recently.⁷ However, to our knowledge, only a few is known about the chemistry of peroxy-carboximidic acids. We wish to report our first observations that α-azobenzyl hydroperoxides (4a-e) generate, by pyridine-catalyzed reaction, N-substituted peroxy-carboximidic acids (5), which are immediately transformed into benzoic acids. The reactivity of 5 differs from that of the parent acid (1).

An anhydrous benzene solution of α-azobenzyl hydroperoxide (4a-e) (10^{-2} - 10^{-4} M) was stirred in the presence of pyridine (10^{-2} M) under a nitrogen atmosphere at room temperature, and the reaction was monitored by HPLC. In all reactions, benzoic acids (6a-e) were formed in 29 - 44% as a main product together with diazene (7) (~50%), and 4-bromodiphenyl (~40%).^{8,9} In addition to these, phenol, benzaldehydes, and pyridine N-oxide were formed in low yields (Table 1).

The formation of benzoic acids is important for our present discussions.

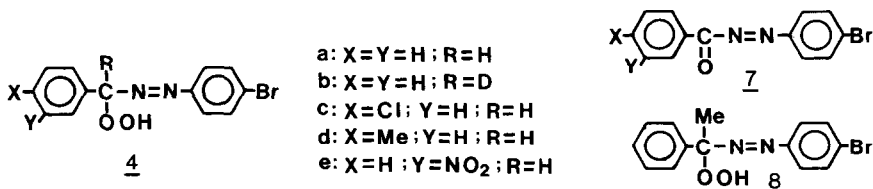


Table 1. Product yields in the reaction of 4 in benzene in the presence of pyridine.

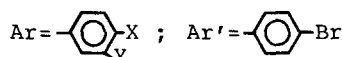
<u>4</u>	Conc. (M)	Addenda	Decomp. ^a (day)	Products (%) ^b					
				ArCO ₂ H (<u>6</u>)	ArCON=NAr' (<u>7</u>)	Ph-Ar'	PhOH	Py→O	ArCHO
<u>4a</u>	10 ⁻²	nil	2	29	30	37	5	6	6
<u>4a</u>	10 ⁻³	nil	4	36	48	28	4	3	2
<u>4a</u>	10 ⁻⁴	nil	7	38	43	26	7	9	3
<u>4b</u>	10 ⁻²	nil	12	37	28	43	— ^d	10	22
<u>4c</u>	10 ⁻²	nil	1	35	50	39	3	8	4
<u>4c</u>	10 ⁻²	DMSO	3	30	— ^c	39	— ^d	— ^d	20
<u>4c</u>	10 ⁻²	MeOH	3	31	— ^c	48	6	1	16
<u>4d</u>	10 ⁻²	nil	4	30	47	21	8	4	10
<u>4e</u>	10 ⁻²	nil	1	44	— ^c	34	3	5	3

a) Period for the total decomposition of 4.

b) Yields are based on 4.

c) Not determined.

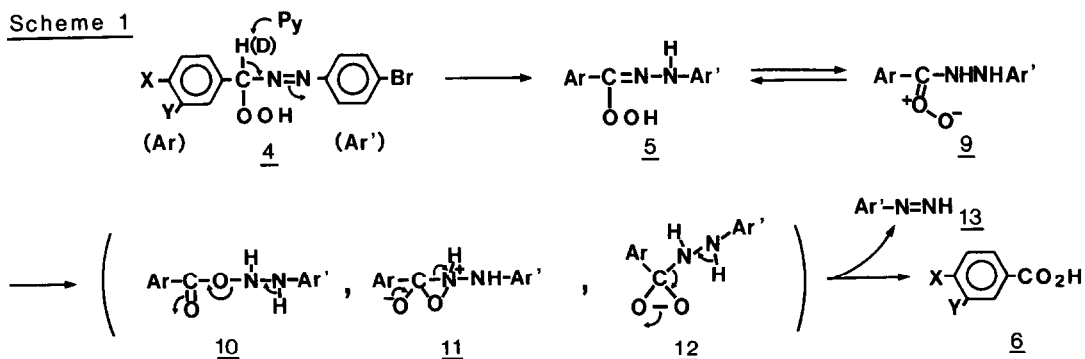
d) Trace.



Benzoic acids (6a-e) arise via the following mechanism involving N-(4-bromoanilino)-peroxycarboximidic acids (5). First, benzoic acids were confirmed not to be the hydrolysis products of 7,^{9,10} but we found remarkable substituent and isotope effects of the reaction. The chloro-substituent (4c) accelerated the rate of the reaction approximately twice of 4a, while the methoxy-substituent (4d) retarded it (Table 1). The primary kinetic isotope effect was observed (Fig. 1). k_H/k_D determined for the disappearance of 4a and 4b, and appearance of benzoic acid from 4a and 4b in the presence of one mole equivalent of pyridine in benzene, was found to be 3.9 at 25°C. This indicates that the rate determining step of the reaction is the abstraction of the α -hydrogen (proton) of 4 by pyridine, and the subsequent reactions leading to benzoic acids are very fast. Therefore, the α -hydrogen of 4 provides the key for the pyridine-catalyzed reaction. In fact, the methyl derivative (8) did not give phenyl acetate and/or methyl benzoate, which correspond to benzoic acids in the reaction of 4, in the reaction in the presence of pyridine. The products of this reaction were acetophenone (84%) and 4-bromodiphenyl (57%). The abstraction of the α -proton by pyridine is also supported by the fact that diazene (7), a dehydration product, was always formed together with benzoic acids in the reactions of 4a-e.

All these observations give us the following mechanistic implication for the benzoic acids and oxenoid formation. Pyridine abstracts the α -proton of 4 to give an N-(4-bromoanilino)-peroxycarboximidic acid (5), a new hydroperoxide, which tautomerizes to carbonyl oxide (9). These intermediates are transformed into benzoic acids via ester (10), oxaziridine (11), or dioxirane (12) (Scheme 1). 10 and 11 are the oxygen insertion products of 9 and 5; 12 is the intramolecular cyclization product of 9 or 5. Benzoic acids arise from

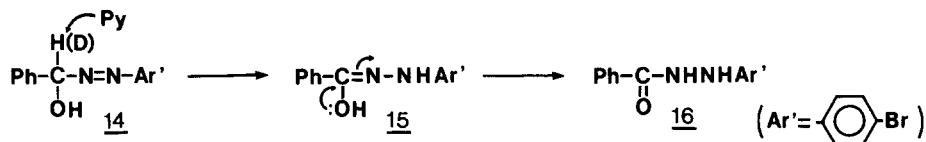
Scheme 1



these species by the elimination of aryldiazene (**13**) which gives diphenyls (Ph-Ar') by the reaction with benzene.¹¹ The abstraction of the α -hydrogen of hydroperoxide by base,¹² and the isomerization of azo to hydrazone derivative are known.¹³

In order to get further support for the mechanism, we compared the pyridine-catalyzed isomerization of azo alcohol (**14**) to hydrazone (**16**) with that of **4**. **14** isomerizes first to an imino alcohol (**15**) and then this gives **16** (Scheme 2). Isomerisation of **14** to **15** has the close similarity to that of α -azobenzyl hydroperoxide (**4**) to **5**. In fact, the isomerization of **14** to **16** was catalyzed by pyridine in benzene; in the absence of pyridine the isomerization of **14** in 10^{-2} M benzene solution at 25°C was extremely retarded.¹⁴⁻¹⁶ The

Scheme 2



kinetic isotope effect (k_H/k_D) of the isomerization determined for the appearance of **16** from deuterated and undeuterated **14** in the presence of one mole equivalent of pyridine, was found to be 3.3 at 25°C. This indicates that the rate determining step of both reactions of **14** and α -azobenzyl hydroperoxide (**4**) is the abstraction of the α -proton by pyridine to give imino alcohol (**15**) and peroxy-carboximidic acid (**5**) respectively.

The analogy of the reaction of **14** to **16** suggests that **5** isomerizes to carbonyl oxide (**9**). The intramolecular hydrogen bonding of the hydroperoxy hydrogen with the β -nitrogen in **5** (see **17**), for example, gives an isomer (**18**) containing the quarternary nitrogen atom. The inductive effect of this quarternary nitrogen moiety ($^+NH_2Ar'$) shifts the π -electron toward the nitrogen side of the C=N bond, resulting in the formation of **9**. This is in contrast to **1**, in which the intramolecular hydrogen bonding is stereochemically rather unfavorable as compared with **17**.¹⁷

The dilution (10^{-2} to 10^{-4} M) in the reaction of **4a** slightly increased the yields of benzoic acid (**6a**) (Table 1), ruling out the bimolecular intermediate such as **19** formed by the reaction of **5** and **4**. Water, methanol, and

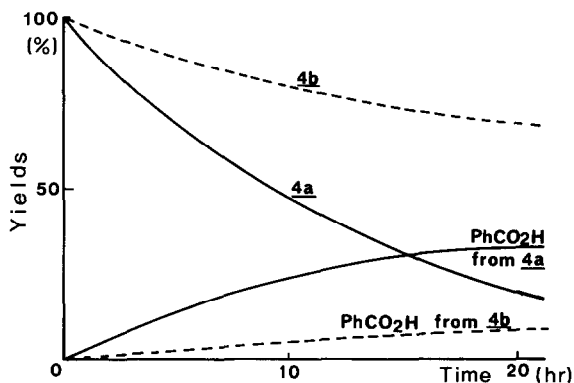
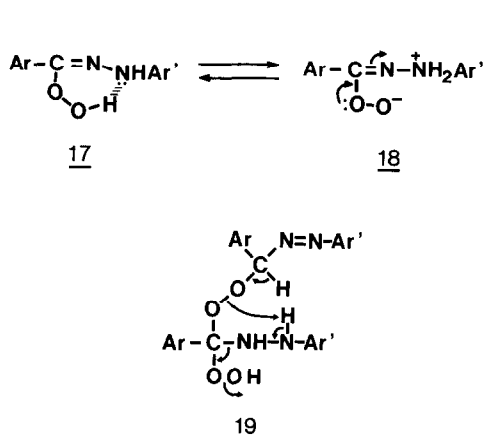


Fig. 1. Time dependent plot for the reaction of 4a and 4b.

t-butyl hydroperoxide added did not affect the yields of benzoic acids. The intramolecular reaction is probably very fast and facile. Radical scavengers such as DMSO and triphenylmethane either did not quench the reaction. Although mechanistic details are to be studied further, the present study revealed for the first time that α -azobenzyl hydroperoxide (4) opens still unknown and fascinating area of the chemistry of peroxy-carboximidic acids and related oxenoids.

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References and Notes

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