

A NOVEL BASE-CATALYZED TRANSFORMATION OF α -AZOBENZYL HYDROPEROXIDE INTO
BENZOIC ACID. A POSTULATED OXENOID INTERMEDIATE OF THE REACTION

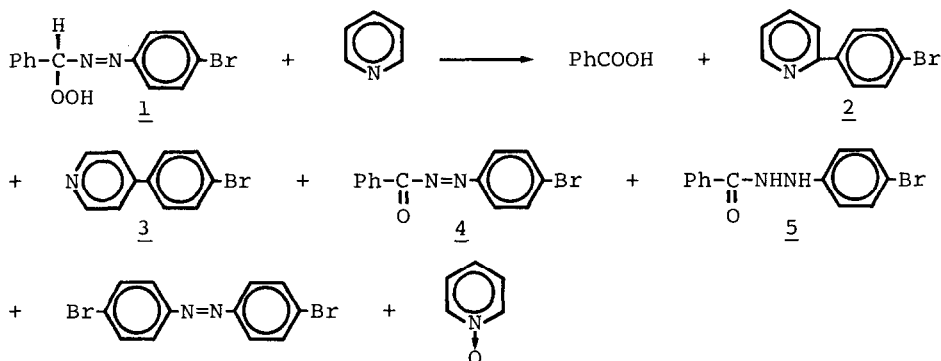
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Abstract: α -Azobenzyl hydroperoxide (1) gives benzoic acid, 4-bromophenylpyridines (2 and 3) in addition to benzyldiazene (4) and benzohydrazide (5) in the reaction catalyzed by pyridine; dioxirane (9) or carbonyl oxide (10) is proposed as an intermediate.

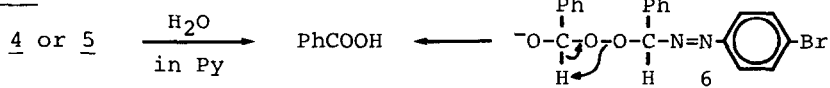
α -Azohydroperoxides such as α -azobenzyl hydroperoxide (1) have recently been reported to generate hydroxyl radical by photolysis in anhydrous organic media.¹ However, only a few is known about the chemical reactivities of α -azohydroperoxides in basic media.² We report a novel transformation of 1 into benzoic acid and several other products in the reaction catalyzed by pyridine, postulating a dioxirane (9) or carbonyl oxide (10) as an intermediate of the reaction.

When an anhydrous pyridine solution of α -azobenzyl hydroperoxide (1) (0.1 M) was stirred at room temperature for 6 hours under a nitrogen atmosphere, benzoic acid, 2-(4-bromophenyl)pyridine (2),³ 4-(4-bromophenyl)pyridine (3),³ N-(4-bromophenyl)-N'-benzyldiazene (4) (mp 68°C),⁴ N-(4-bromophenyl)benzohydrazide (5),⁵ 4,4'-dibromoazobenzene, and pyridine-N-oxide were formed in 27, 25, 5, 17, 18, 3, and 2% yield respectively. It is to be noted that benzaldehyde was not detected under this condition and that the formation of benzoic acid was not the artifact during the workup.



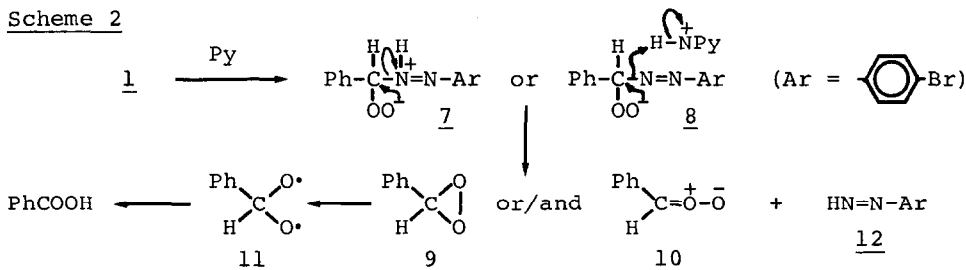
The mechanism of the formation of benzoic acid from 1 in the presence of pyridine is of particular interest. Several mechanistic paths are considered for explaining this; they are as follows. First is the hydrolysis of the benzoyldiazene 4⁴ or benzohydrazide 5 to benzoic acid (see Scheme 1). Second is the oxidation of benzaldehyde which is presumably formed from 1 by the homolytic decomposition, with 1 via a peroxy ether intermediate (6)⁶ (Scheme 1). Third is the mechanism involving an oxenoid⁷ such as a dioxirane

Scheme 1



(9) or carbonyl oxide (10) (Scheme 2). Such oxenoids (9 and 10) are derived by the intramolecular substitution of a zwitterion (7) or peroxy anion (8) which is formed from 1 by the action of pyridine.⁸ Benzoic acid arises from 9 via a diradical 11.

Scheme 2



Of these mechanisms, the third one involving the dioxirane 9 or carbonyl oxide 10 is consistent with our observations. They are the following:

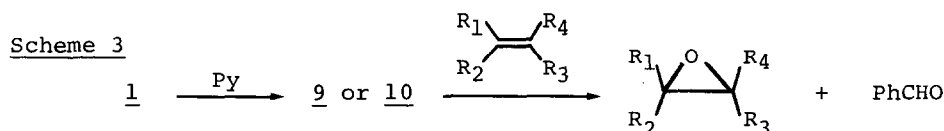
(i) When a pyridine solution of 1 and H_2^{18}O (50% contents) was kept standing at room temperature for 6 hours, benzoic acid was formed in which only 5% of the isotope (^{18}O) was incorporated. The reaction of the benzoyldiazene 4 with H_2^{18}O in pyridine gave benzoic acid containing 28% of the isotope (^{18}O). The control indicated that more than 60% of the oxygen of benzoic acid came from 1, not from the added water. This eliminates the first mechanism involving the benzoyldiazene 4. In addition, the benzohydrazide 5 was found to be stable for hydrolysis under this condition.

(ii) The monitoring of the reaction of 1 in pyridine at -15°C by means of HPLC indicated that benzoic acid was not a secondary product of 4 and 5.

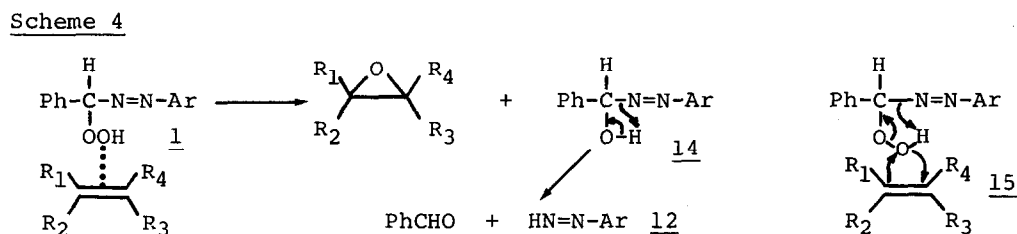
(iii) When the reaction was carried out in the presence of benzaldehyde, the amount of benzoic acid was not increased. This eliminates the second mechanism.

(iv) When a mixture of 1, cyclohexene, and pyridine was kept standing at room temperature for 6 hours, cyclohexene oxide was formed in 15% yield accompanied by benzaldehyde (24%) in addition to benzoic acid (10%), the benzoyldiazene 4 (5%), and benzohydrazide 5 (15%). Tetramethylethylene oxide (24%)

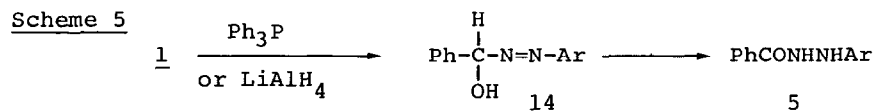
was formed together with benzaldehyde (13%), when a mixture of 1, tetramethylethylene, and pyridine was stirred at room temperature. It is important to note that the amounts of benzoic acid were reduced, while benzaldehyde (13 - 24%) was formed together with the epoxide in the reaction of 1 with the olefin. In the absence of pyridine, neither the epoxide nor benzaldehyde was formed. All these observations are best accounted for by the mechanism involving a dioxirane or carbonyl oxide (9 or 10) shown by Scheme 3.



As to the olefin epoxidation, however, an alternate possibility must be considered. It is assumed that the epoxide is formed by the direct oxygen transfer from 1, together with the azoalcohol 14 which in turn decomposes to benzaldehyde and the aryldiazene 12 (Scheme 4).^{9,10} However, this possibility can be eliminated for the following reasons. First, the epoxidation occurred only in the presence of a base.¹¹ This differs from the epoxidation of olefins by the direct oxygen transfer reaction from a cyclic azohydroperoxide in a neutral medium as reported by Baumstark et al.⁹



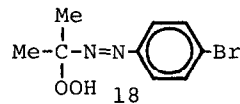
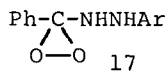
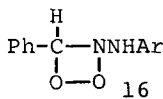
Second, *sec*-azoalcohols such as 14 are known to isomerize to hydrazides such as 5 rather than decomposing to aldehydes.^{5,12,13,14} In fact, we found that the reaction of 1 with triphenylphosphine in benzene at room temperature gave the benzohydrazide 5 in 92% yield accompanied by a small amount of benzaldehyde (2%). Reduction of 1 with lithium aluminium hydride gave similar results (Scheme 5). The azoalcohol 14 is an intermediate of the reaction.



This suggests that a major part of benzaldehyde in the epoxidation arises from an intermediate species such as 9 or 10, not from 14. The direct oxygen transfer in a concerted manner shown by 15 also might account for the formation of epoxide, benzaldehyde, and the aryldiazene 12 in one step.^{8,15}

Alternate oxenoid intermediates such as azadioxetane (16) and dioxirane derivative (17) can be eliminated as possible reactants. This is because

they can not explain the formation of benzoic acid. α -Azohydroperoxide (18) gave methyl acetate in the reaction with pyridine. Cyclohexene oxide was also formed by the reaction of 18 with cyclohexene in the presence of pyridine. This again supports the dioxirane or carbonyl oxide intermediate (9 or 10). The homolytic decomposition of 12⁴ gives 4-bromophenyl radical, which reacts with pyridine to give the arylpyridines 2 and 3. All our observations consist of the mechanism involving a dioxirane or carbonyl oxide (9 or 10) as an intermediate of the reaction. Details of this work will appear in our full paper.¹⁶



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References and Notes

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