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Activation of Molecular Oxygen into Hydrogen Peroxide via α-Azobenzyl Hydroperoxide. A Generation of Hydrogen Peroxide from Organic Hydroperoxide by the Amine-base Catalyzed Reaction

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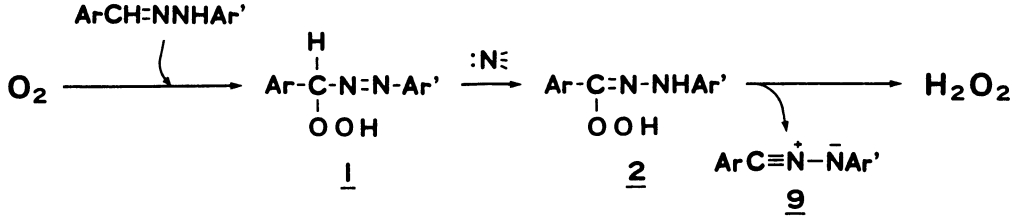
Hydrogen peroxide is generated together with nitrile imine from α-azobenzyl hydroperoxide, which is formed readily by autoxidation of arylaldehyde hydrazone, via peroxycarboximidic acid by the amine-base catalyzed reaction in benzene. This provides a new type of activation reaction of molecular oxygen into hydrogen peroxide by aldehyde hydrazone.

In recent years, activation of molecular oxygen by organic chemical means has been an important subject of intense investigation in connection with the biochemical problems. Attention has been especially focused on activation of molecular oxygen into hydrogen peroxide by the metal catalyzed (enzymatic or non-enzymatic) and/or non-metal catalyzed reactions.[1-3] In this paper, we report a new type of activation reaction of molecular oxygen into hydrogen peroxide; molecular oxygen reacts with arylaldehyde hydrazone to give α-azobenzyl hydroperoxide (1) which then generates hydrogen peroxide via peroxycarboximidic acid (2) by the amine-base catalyzed reaction (Scheme 1).

Arylaldehyde hydrazones were autoxidized to give α-azobenzyl hydroperoxides (1a-c) in high yields.[4] The hydroperoxide 1 was stable in benzene, and no reaction took place when a benzene solution of 1 was kept standing at room temperature for a couple of weeks. However, to our surprise, the addition of an amine base such as triethylamine, N-methylmorpholine, dimethylaniline, and pyridine to the above benzene solution caused the facile reaction of 1 to give hydrogen peroxide (10 - 20%) accompanied with other products[5,6] such as benzoic acids (3) (≈35%) and aroyldiazene (4) (≈45%) or the dehydration product of 1.



Scheme 1.

Hydrogen peroxide in the reaction of 1 was identified as follows. A benzene solution of freshly prepared 1 (10^{-2} M) was stirred in the presence of triethylamine (0.1 mol equiv.), for example, in the dark under nitrogen atmosphere until all of 1 decomposed (ca. 1 h). Soon after completion of the reaction, the reaction mixture was extracted with water, and the water extract was subjected to hydrogen peroxide test by the $TiCl_4$ + sulfuric acid reagent, the KI + starch + $FeSO_4$ reagent,[7] catalase, and manganese dioxide. All these showed positive tests for hydrogen peroxide. The amount of hydrogen peroxide in the water extract was determined by iodometric and/or potassium permanganate titration. This assigned the yield of hydrogen peroxide generated from 1 by the amine catalyzed reaction to be 10 - 20%.[8]

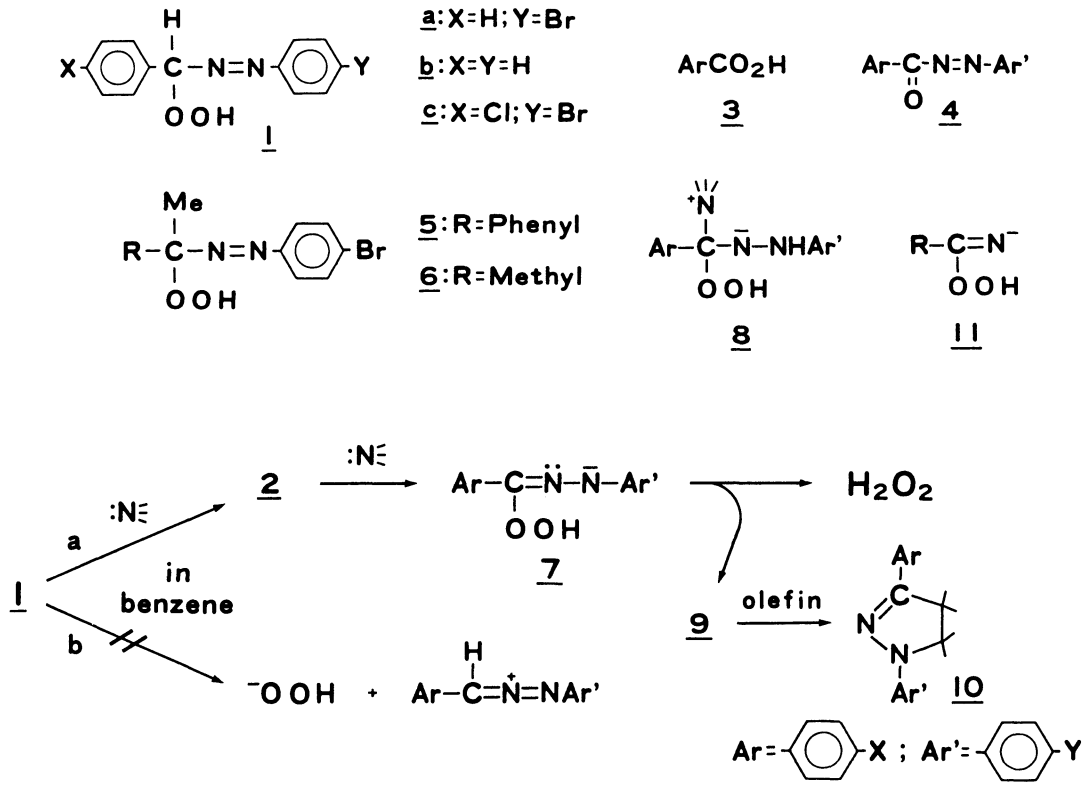
In the similar manner, hydrogen peroxide was generated from 1 accompanied with 3 and 4 when the other weak amines described above were used as the base.[9] However, diazabicycloundecene (DBU) which is a strong amine base acted inefficiently as the catalyst for the generation of hydrogen peroxide, because it caused facile direct dehydration of 1 to give aroyldiazene (4)[5] in a high yield (80%).

In the absence of the amine base, on the other hand, α-azobenzyl hydroperoxide (1) did not generate hydrogen peroxide in benzene. Tertiary α-azohydroperoxide having no α-hydrogen such as 5 and 6 did not generate hydrogen peroxide regardless of the presence or absence of amine in benzene. These facts indicate that the direct extrusion of the -OOH group from the sp^3 carbon of α-azohydroperoxide in the manner indicated in Scheme 2-b[10] does not occur. Only α-azobenzyl hydroperoxide (1) having the α-hydrogen atom generates hydrogen peroxide in the reaction catalyzed by the amine base.

All of these observations suggest the following mechanism for the generation of hydrogen peroxide from 1. The α-proton of α-azobenzyl hydroperoxide (1) is abstracted by the amine base to give rise to the isomeric peroxycarboximidic acid (2)[5,11] which then liberates hydrogen peroxide together with nitrile imine (9) via 7 or via an intermediate (8) formed by the addition of amine to 2[12] (Scheme 2-a). The decomposition of 2 into the -OOH and nitrile imine (9) moieties by the amine catalyzed reaction has some analogy with the generation of the 1,3-dipolar species from halohydrazone by the base catalyzed reaction.[13]

To clarify the mechanism, the trapping test for nitrile imine (9) with olefin was undertaken. A benzene solution of 1 and norbornene, cyclopentene, or dimethyl fumarate (excess) was stirred in the presence of the amine base such as triethylamine (0.1 mol equiv.) or pyridine (1 mol equiv.) until all of 1 decomposed. Then the above mixture was refluxed for a few hours.[12] Purification of the reaction mixture by silica gel column chromatography followed by TLC afforded the 1,3-dipolar adduct (10), identical to the authentic sample prepared by the method reported in the literature,[13] although the yield was low.[14,15] These observations support the proposed mechanism (Scheme 2-a). It is seen from our present and previous data[5] that a portion (20 - 40%) of the peroxycarboximidic acid (2) formed from 1 by the amine catalyzed reaction gives off hydrogen peroxide together with nitrile imine (9), while the other portion (60 - 80%) of 2 yields benzoic acids (3).

Finally, it is worthy to note the following. In recent years the generation



Scheme 2.

of hydrogen peroxide from flavin hydroperoxide has attracted much attention.[2] It is well known that hydrogen peroxide is generated from alkyl hydroperoxide by the direct extrusion of the -OOH group from the sp^3 carbon in the acid catalyzed or non-catalyzed reaction.[16] In contrast, to our knowledge only a few is known about the generation of hydrogen peroxide from alkyl hydroperoxide by base catalyzed reactions, while there have been many intensive studies on the reaction of alkyl hydroperoxide with base.[17] Recently, the liberation of hydrogen peroxide from the peroxycarboximidic acid intermediate (11) formed from nitrile and hydrogen peroxide by the base catalyzed reaction has been suggested, although there has been no experimental proof.[18] Our present results are novel because hydrogen peroxide was generated from the hydroperoxide 1 by the amine-base catalyzed reaction and because the liberation of the -OOH group from hydroperoxide occured via the sp^2 carbon atom of the vinyl type (imino) hydroperoxide 2. Although the yield is not high at the present time, this study will provide an interesting new route for activation of molecular oxygen.

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7) Note that the water extract does not contain the hydroperoxide 1.

8) The control indicated that a small amount of hydrogen peroxide ($\approx$4% based on 1) was consumed by the reaction with 4 to give 3 under the reaction condition used (Detail of this reaction will be reported elsewhere). The oxidation of the amine by H_2O_2 in benzene was found to be inefficient. We corrected the observed value by using these data.

9) The rate of the reaction depended on the kind and amount of amine used. With pyridine, for example, the reaction proceeded slowly.

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14) This is probably due partly to the reaction of 9 with several species in the reaction mixture such as H_2O generated from 1 (see Refs. 5, 6, and 15).

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