

## The Photolysis of 1-Hydroxy-1,2,3-benzotriazole

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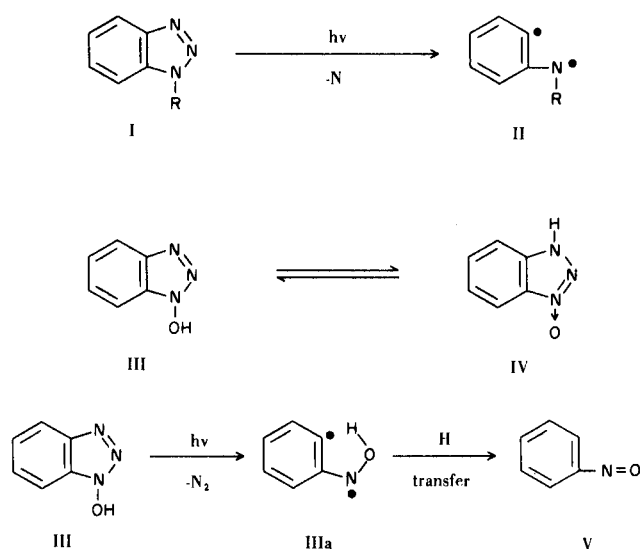
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The 1,2,3-benzotriazole structure (I) has been the subject of recent reports concerning the photolysis of the parent compound and several of its 1-substituted derivatives (1-5). This interest has been stimulated by the facile absorption of ultraviolet irradiation by I followed by the loss of a molecule of nitrogen to yield the diradical II. Compound II can then undergo several modes of reaction which include a carbene mechanism (3), and inter- and intramolecular radical abstraction pathways (2,4). Up to now the substituents in the 1-position of the 1,2,3-benzotriazole molecule which have been photolyzed include the aromatic (1,2), alkyl (3,4) amino (1) and acyl (4,5) groups.

A substituent on the 1-position of the benzotriazole molecule which has not been examined with regard to photolysis is the hydroxy group. 1-Hydroxy-1,2,3-benzotriazole (III) possesses the potential of undergoing a tautomeric shift to form 1,2,3-benzotriazole 3-oxide (IV), although in most solvents III has been shown to exist solely in the form of the hydroxy tautomer (6,7). Nevertheless, a product study of the photolysis of III should provide some insight into the ability of III to undergo a tautomeric shift in the excited state, since the pathways of reaction of III and IV would be expected to greatly differ compound III because of its structural similarities to other 1-substituted-1,2,3-benzotriazoles can easily lose a molecule of nitrogen to yield the diradical IIIa which could then go onto products. Compound IV, on the other hand, would be expected to undergo deoxygenation or rearrangement with the loss of nitrogen analogous to other heterocyclic *N*-oxide systems (8).

We thus, photolyzed 0.01M solutions of III in water and dioxane. These two solvents were selected: (a) because of their ability to dissolve sufficient III, and (b) to determine if a change in solvent could alter the path of the reaction. The solutions were degassed by flushing with helium gas for 6 hours before irradiation at 3000Å was commenced. The photolysis was continued for 6 hours after which the solutions had darkened to such a degree that further irradiation seemed futile. The reactions were analyzed by glpc and tlc. Wherever possible, compounds were isolated by alumina column chromatography



and their ir spectra were compared with those of known samples. The percent yields of the products are listed in Table I.

TABLE I

Photolysis of III at 3000Å

Product	In Water (%) (a)	In Dioxane (%) (b)
Nitrosobenzene (V)	67	45
Azobenzene (VI)	6	11
Diphenylamine (VII)	6	10
2-Hydroxyazobenzene (VIII)	4	13
Azoxybenzene (IX)	8	18

(a) Thirty percent of III was unreacted. (b) Twenty-two percent of III was unreacted.

Table I shows that the principle product in both photolyses was nitrosobenzene (V). The photolysis of V in ethanol has been reported by Tanikaga to yield the products IV-IX listed in Table I (9). Since the conditions Tanikaga used differed from ours, 0.01M solutions of V in water and dioxane were flushed with helium and

TABLE II  
Photolysis of V at 3000 Å

Product	In Water (%) (a)	In Dioxane (%) (b)
Azobenzene (VI)	14	14
Diphenylamine (VII)	19	20
2-Hydroxyazobenzene (VIII)	25	26
Azoxybenzene (IX)	35	33

(a) Sixty percent of V was unreacted. (b) Forty-six percent of V was unreacted.

irradiated at 3000 Å for 4 hours. The results of the photolyses listed in Table II demonstrated quite clearly that products VI-IX may be visualized as being formed from the photolysis of V. It should be noted that the low solubility of V in water forced us to use solutions in the photolysis of V which were only one-tenth as concentrated as the solutions used in the photolysis of III. This reduced solubility of V in water relative to its solubility in dioxane may account for the greater yields of products VI-IX found in dioxane (Table I).

A mechanism accounting for the formation of V from III is presented in Scheme I. Loss of a molecule of nitrogen from III yields the diradical IIIa which can then undergo a hydrogen transfer to yield V (10). To decide whether the hydrogen transfer was inter- or intramolecular, 1-hydroxy-1,2,3-benzotriazole-OD (X) 0.005M was photolyzed in dioxane and the products were analyzed by high resolution mass spectrometry. The ratio of the mass peaks at 108 and 107 showed that the deuterium was > 95% retained thus indicating that the hydrogen transfer which IIIa underwent was intramolecular in nature.

The photolysis of III in dioxane could be sensitized using 3-methoxyacetophenone  $E_T = 72.4 \frac{\text{kcal}}{\text{mole}}$  (11), while quenching reactions with piperylene  $E_T = 59 \frac{\text{kcal}}{\text{mole}}$  (12) proved inconclusive.

In summary, the photolysis of III in water and dioxane yielded V as the primary product. Further photolysis of V resulted in the formation of products VI-IX. The absence of 1,2,3-benzotriazole or any other photoproducts which could be derived from a structure resembling IV strongly mitigates against a tautomeric equilibrium being established in the photolysis of III.

#### EXPERIMENTAL

1-Hydroxy-1,2,3-benzotriazole (III) was prepared by the method of Macbeth and Price (13).

Irradiation of 1-Hydroxy-1,2,3-benzotriazole.

A 0.01M solution of III in water or dioxane was degassed by bubbling helium gas through the solution for 6 hours. The solution was then irradiated in a Rayonet photoreactor at 3000 Å for 6 hours. The reaction was then analyzed by gas liquid partition

chromatography (glpc) (6 foot, 3% SE-30 column) and thin layer chromatography (tlc). The products were identified by comparing their retention times with the retention times of known samples. Infrared spectra of products V-IX isolated by column chromatography on alumina, were superimposable with the infrared spectra of known samples. The products and their % yields are listed in Table I.

Irradiation of Nitrosobenzene (V).

A 0.01M solution of V in water or dioxane was degassed by bubbling helium gas through the solution for 6 hours. The solution was then irradiated at 3000 Å for 6 hours. Analysis by glpc and tlc showed the presence of the products which are listed in Table II along with their % yields.

1-Hydroxy-1,2,3-benzotriazole-OD (X).

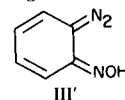
A solution of III (1.0 g.), deuterium oxide (5 ml.) and sodium hydroxide (0.008 g.) was heated for 24 hours. Evaporation of the deuterium oxide resulted in the formation of a precipitate. The solid was extracted with dioxane. Removal of the dioxane resulted in the formation of a white solid when analyzed by nmr showed that the peak representing the hydroxyl hydrogen had disappeared. High resolution mass spectrometry showed a molecular ion peak of 136.

Irradiation of 1-Hydroxy-1,2,3-benzotriazole-OD (X).

A 0.005M solution of X in dioxane was degassed by bubbling helium gas through the solution for 6 hours. After irradiation of the solution for 6 hours at 3000 Å, the nitrosobenzene formed was isolated by silica gel column chromatography and analyzed by high resolution mass spectrometry. The mass peaks at 107 and 108 corresponding to V and V containing one added deuterium respectively showed a >95% retention of the deuterium present in X.

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