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1-Benzyloxy-1,2,3-benzotriazole was photolyzed and found to yield benzaldehyde and azobenzene as the principal products.

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In an earlier paper we reported that the photolysis of 1-methoxy-1,2,3-benzotriazole (**1**) proceeded *via* two different pathways (1). The principal pathway involved the expulsion of a molecule of N_2 , followed by an intramolecular H-abstraction with the concomitant elimination of a molecule of formaldehyde to generate phenyl nitrene (**2**). The second pathway involved the homolytic cleavage of the N-O bond to generate two free radicals. In the original paper, no attempt was made to quantify the amount of formaldehyde formed due to its low boiling point. The existence of **2** was implied based upon the primary photoproducts aniline (**3**) and azobenzene (**4**) which have been reported as being isolated from the **2** generated from the photolysis of phenyl azide (2).

We now report the photolysis of 1-benzyloxy-1,2,3-benzotriazole (**5**) in an attempt to understand more fully the photolysis reaction of 1-alkoxy-1,2,3-benzotriazoles. Compound **5** was selected in order to see the effect that an aromatic ring would have upon the photolysis reaction. In addition if the photolysis of **5** proceeded like the photolysis of **1**, benzaldehyde (**6**) would be eliminated (Scheme I, path a). Benzaldehyde could be easily quantified by glpc.

Solutions of **5**, 0.005 M in benzene, cyclohexane, methanol, and acetonitrile were photolyzed in 300 nm for 8 hours under a nitrogen atmosphere. Identification of the products was accomplished by comparison of glpc and tlc retention times with those of known compounds. In some cases the products were isolated by column chromatography on alumina and the infrared spectrum was compared with that of a known compound. The results of the photolyses are listed in Table I.

In all the solvent systems studied **6** was the major product isolated. This indicated that the photolysis of 1-alkoxy-1,2,3-benzotriazoles could lead to ejection of aromatic aldehydes as well as aliphatic aldehydes (Scheme I, path a). Aniline was found in the photolysis run in cyclohexane and methanol, but not in benzene. Aniline could be envisaged as forming by the abstraction of hydrogen by **2** in the triplet state (2). Sundberg and Smith have shown that no **3** was produced when phenyl azide was photolyzed in benzene (3). Compound **4** was formed in all the solvents studied. Azobenzene has been shown to form by the dimerization of **2** in the triplet state as well as in the excited singlet state (4). Phenyl nitrene has also been shown to insert into cyclohexane (5) and methanol (6) to

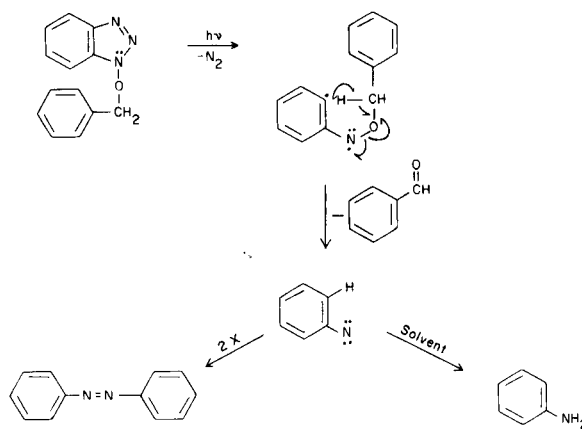
yield *N*-cyclohexylaniline and *p*-anisidine, respectively.

An interesting aspect was the isolation of benzyl alcohol (**7**) in the methanol photolysis. Compound **7** can be viewed as forming from the free radical formed from the homolytic cleavage of the N-O linkage (Scheme I, path b). A comparison of the yield of **7** to the yield of **6** in the methanol photolysis indicated that path a is strongly favored over path b.

Phenyl azide when photolyzed in diethylamine (**8**) has been reported to yield 2-*N,N*-diethylamino-3*H*-azepine (**9**) (7). A solution of **5** in **8** was photolyzed for 6 hours. A 31% yield of **9** was isolated based upon the comparison of its glpc retention time with that of a known sample. This lends support to the involvement of **2** in the photolysis of 1-alkoxy-1,2,3-benzotriazoles.

The triplet mechanism has been proposed for photochemical rearrangements that proceed *via* a phenyl nitrene intermediate (8). Indeed, photolysis of **5** in methanol using 3-methoxyacetophenone (**10**) $E_r = 72$

Scheme I, Path a



Scheme I, Path b

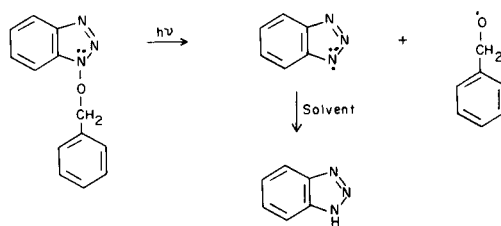


Table I

The Photolysis of **5** at 300 nm (Per Cent Yields) (1,2)

Product	In		
	Benzene	Cyclohexane	Methanol
1-Benzyloxy-1,2,3-benzotriazole (5)	47	39	28
Benzaldehyde (6)	38	53	69
Aniline (3)		23	36
Benzotriazole		14	6
Azobenzene (4)	8	10	8
Bicyclohexyl		4	
<i>N</i> -Cyclohexylaniline		9	
Benzyl Alcohol (7)			9
<i>p</i> -Anisidine			15

(1) With the exception of **5**, the per cent yields are based upon the amount of **5** consumed. (2) The yields are based upon duplicate runs and are $\pm 3\%$.

Kcal./mole (**9**) as the triplet sensitizer did yield a small amount of **6**, while a solution of **5** in methanol, which did not contain **10**, failed to undergo photolysis. Quenching experiments using a variety of quenchers failed to totally quench the reaction. It appears that the photolysis reaction may proceed *via* an excited triplet state, although an excited singlet group state cannot be excluded.

EXPERIMENTAL

Photolyses were conducted in a Rayonet photochemical reactor at 300 or 350 nm as indicated. The infrared spectra were obtained on a Perkin-Elmer 735-B spectrophotometer. Glpc was performed on a Varian Model 1200 HYFI.

Preparation of 1-Benzyloxy-1,2,3-benzotriazole (**5**).

To a solution of potassium 1,2,3-benzotriazole 1-oxide (8.5 g., 0.05 mole) in 125 ml. of water was added a solution of benzyl chloride (12.6 g., 0.10 mole) in 125 ml. of methylene chloride. Tetrabutylammonium bromide (2 g., 0.006 mole) was added and the solution was refluxed vigorously for 24 hours at room temperature. The methylene chloride layer was separated and the solvent was evaporated at room temperature. The resulting oil was distilled to yield 1-benzyloxy-1,2,3-benzotriazole

(5.85 g., 0.026 mole, 52%), b.p. 138-140° (0.05 mm).

Anal. Calcd. for $C_{13}H_{11}N_3O$: C, 69.32; H, 4.92; N, 18.65. Found: C, 69.20; H, 5.04; N, 18.94.

Irradiation of **5**.

In a pyrex vessel, 200 ml. of a solution of **5** in the appropriate solvent was degassed by bubbling nitrogen gas through the solution for 8 hours. After irradiation, the reaction was analyzed by glpc (6 ft., 3% SE-30 column) and thin-layer chromatography. Infrared spectra of the products isolated by column chromatography were superimposable with the spectra of known samples. The major products and their percent yields are listed in Table I.

Irradiation of **5** in Diethylamine.

A 0.005 *M* solution of **5** in diethylamine was photolyzed in a nitrogen atmosphere for 12 hours. The reaction was immediately analyzed by glpc. The retention time of a known sample of 2-*N,N*-diethylamino-3-*H*-azepine (**9**), was identical to the retention time of a peak from the photolysis reaction. Tlc retention times for a known sample of **9** and the photolysis reaction product were also identical. The yield of **9** from the photolysis reaction was 31%.

Sensitization of the Photolysis of **5**.

A solution of (10 ml.) 0.005 *M* in methanol was divided into two parts. To one solution sufficient 3-methoxyacetophenone was added to make the final concentration 1.0 *M* in the sensitizer. An equal quantity of solvent was added to the other solution. Both samples were placed in pyrex vessels and irradiated at 350 nm for 76 hours. The solutions were analyzed by glpc. The vessel containing no 3-methoxyacetophenone showed no evidence of reaction while the solution containing the sensitizer showed the production of **6** in 17% yield.

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