

The Photolysis of 1-Benzyl-1,2,3-benzotriazole (I)

M. Paul Serve'

Contribution from the Department of Chemistry, Wright State University, Dayton, Ohio 45431

and

Herbert M. Rosenberg

Air Force Materials Laboratory, Wright-Patterson, AFB, Ohio 45433

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The photolysis of 1-substituted-1,2,3-benzotriazoles leads to the expulsion of nitrogen and the generation of diradicals. Stabilization of the diradicals occurs through intramolecular chemical reactions or reaction with solvent, depending on the substituent or solvent.

Thus, Marky and coworkers recently reported the exclusive formation of *N*-benzyl-2-aminobiphenyl in the photolysis of 1-benzyl-1,2,3-benzotriazole (I) in benzene (2). In contrast, the photolysis of 1-phenyl-1,2,3-benzotriazole in benzene affords a nearly quantitative yield of carbazole (3). Finally, Meier and Menzel recently described solvent effects for the photolysis of 1-acyl-1,2,3-benzotriazoles (4).

We thus decided to reexamine the photolysis of I whose photolysis had previously been reported only in benzene to determine whether a solvent effect is present for this system. Compound I was also interesting because of the several reaction pathways available once a photon of light had been absorbed Scheme 1. For example, the *N*-benzyl linkage could cleave to generate a benzotriazole radical and a benzyl radical (path a) which could then undergo further reaction (5). On the other hand, a molecule of nitrogen could be expelled to yield the diradical (II) (path b). Compound II in turn could react with solvent (path c), undergo an intramolecular or intermolecular hydrogen abstraction to yield benzylideneaniline (III) (path d) or finally it could cyclize intramolecularly to yield dihydrophenanthridine or phenanthridine (IV) (path e) analogous to the cyclization of 1-benzoyl-1,2,3-benzotriazole (4). The solvents methanol, benzene, and acetonitrile were selected because of their difference in polarity and reactivity with free radicals.

We thus irradiated 0.01 *M* solutions of I in benzene, methanol, and acetonitrile at 3000 Å in a Rayonet photoreactor under a helium atmosphere for 24 hours. 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 % yields of products obtained in the photolysis are listed in Table I.

The preferred pathway of reaction for the photolysis of I in benzene was the formation of II followed by reaction with solvent. The cleavage of the *N*-benzyl linkage, as evidenced by the appearance of benzotriazole and bibenzyl, appeared to proceed in low yield. However, it is noted that the cleavage of alkyl substituents in the photolysis of 1-alkyl-1,2,3-benzotriazoles has not previously been reported.

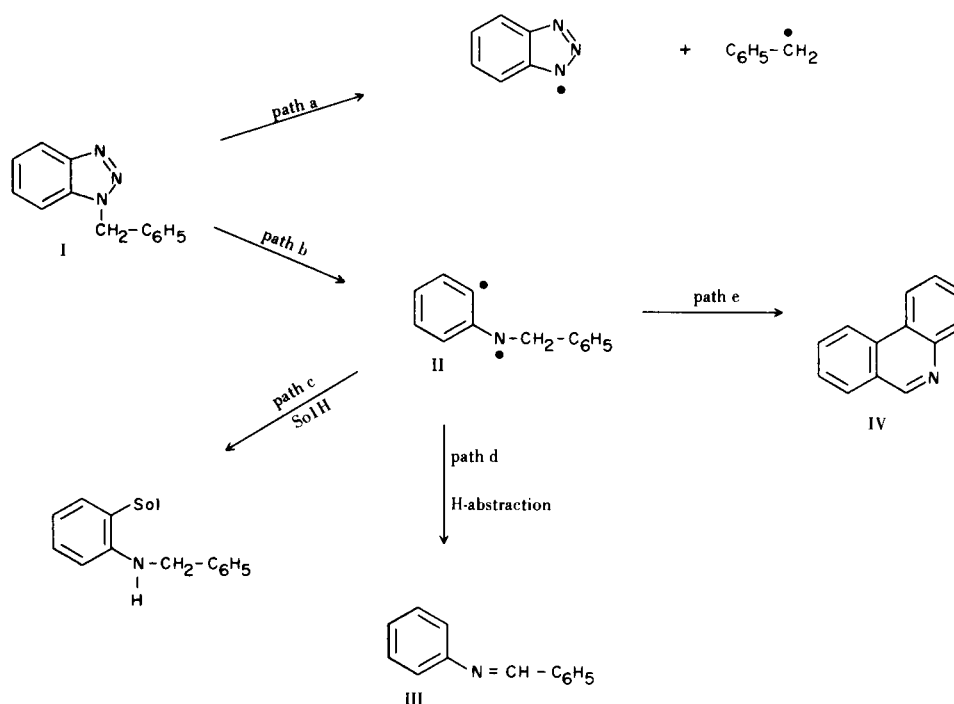
The photolysis in methanol yielded as its major product *N*-benzylideneaniline (III). As stated above, this could form from II *via* an intramolecular or intermolecular hydrogen transfer. To determine whether the hydrogen transfer occurred inter or intramolecularly, I was photolyzed in methanol-D₄. Analysis by mass spectrometry of the *N*-benzylidene aniline formed showed that no deuterium had been incorporated into the product, indicating that the hydrogen shift occurred intramolecularly. To demonstrate conclusively that the hydrogen shift was intramolecular in origin 1-benzyl-1,2,3-benzotriazole-D₂ (V) was synthesized and irradiated in methanol at 3000 Å. The *N*-benzylideneaniline isolated from the photolysis reaction was analyzed by mass spectrometry. The molecule ion peak was found to be 183, corresponding to *N*-benzylideneaniline-D₂. The retention of the deuterium atoms confirms the intramolecularity of the hydrogen shift.

The formation of *N*-benzylaniline and *N*-benzyl-*o*-anisidine are analogous to the results reported by Bayer and Selvajaran (6). They reported that the irradiation of 1,2,3-benzotriazole in methanol yielded aniline and *o*-anisidine. Since 1,2,3-benzotriazole was also formed in the photolysis of I in methanol, the appearance of the aniline and *o*-anisidine can be accounted for as secondary photolysis products.

TABLE I
Photolysis of I at 3000 Å

Product	In Benzene (%)	In Methanol (%)	Acetonitrile (%)
Phenanthridine (IV)	2	1	1
Benzylideneaniline (III)	1	42	69
Bibenzyl	4	3	10
Benzotriazole	2	3	2
<i>N</i> -Benzyl-2-aminophenyl	80		
Aniline		15	8
Benzylamine		5	
<i>o</i> -Anisidine		13	
<i>N</i> -Benzylaniline		5	2
<i>o</i> -Methoxy- <i>N</i> -benzylaniline		2	

Scheme 1



Several products from the photolysis of I in methanol appeared to result from the loss of the benzyl group in addition to the loss of nitrogen. The photolysis of the major product III in methanol has been reported by Furey and Kan to yield none of the products found in the irradiation of I in methanol (7). The photolysis of *N*-benzylaniline in methanol at 3000 Å yielded aniline and benzylamine as the major products. Thus aniline may be formed by two different pathways, and like benzylamine may be looked upon as the product of a secondary

photochemical reaction.

The photolysis of I in acetonitrile gave as the predominant product III. In the polar aprotic solvent there was also some cleavage of the *N*-benzyl linkage as evidenced by the appearance of bibenzyl and benzotriazole. It should be noted that the amount of III formed was the greatest in acetonitrile. There appeared to be little reaction of the diradical, formed from the initial expulsion of nitrogen, with the solvent. To determine whether the diradical or the carbene formed from the

expulsion of nitrogen would react with the solvent analogous to the reaction of I and 1,2,3-benzotriazole in methanol, a solution of 1,2,3-benzotriazole in acetonitrile was degassed and irradiated at 3000 Å. The only product identified by glpc was aniline. No other peaks in the higher temperature ranges of glpc chromatogram were observed.

In all the solvents utilized, phenanthridine, the product of the six-membered cyclic transition state, was formed in small amounts thus indicating that path e is not a favored pathway. This is in contrast to the results reported for the 1-benzoyl-1,2,3-benzotriazole in which substantial amounts of phenanthridone were found for all the solvents tested (4).

In summary, stabilization of the diradical II occurs predominantly through reaction with solvent in benzene and through intramolecular hydrogen transfer in methanol and acetonitrile. This and the difference in the *N*-benzyl bond cleavage in benzene methanol and acetonitrile demonstrate that a solvent effect is involved in the photolysis I and may be operative in the photolyses of other 1-alkyl-1,2,3-benzotriazoles.

EXPERIMENTAL

1-Benzyl-1,2,3-benzotriazole (I) was prepared by the method of Gibson (8).

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

A 0.01 *M* solution of I in benzene or methanol was degassed using a freeze-thaw sequence. The solution was then irradiated in a Rayonet photoreactor at 3000 Å for 18 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. The products and their % yields are listed in Table I.

Irradiation of *N*-Benzylaniline.

A 0.01 *M* solution of *N*-benzylaniline was degassed and irradiated at 3000 Å for 18 hours. Analysis by glpc and tlc indicated the presence of aniline and benzylamine in the ratio of 3:1 as the only identifiable products.

1-Benzyl-1,2,3-benzotriazole-D₂ (IV).

A solution of I (1.0 g.) dioxane (5 ml.), deuterium oxide (5 ml.) and sodium hydroxide (0.006 g.) was refluxed for 48 hours. At the end of that period the dioxane was removed, leaving a two phase system, which was then dissolved in an ether-water mixture. Extraction and separation of the ether layer gave a clear colorless solution. The ether was dried over anhydrous sodium sulfate and evaporated off at room temperature. The white solid remaining was analyzed by nmr, which showed that the peak representing the benzyl protons had completely disappeared.

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