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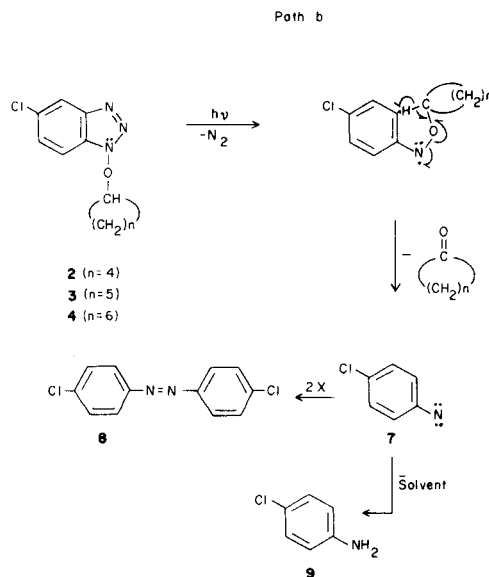
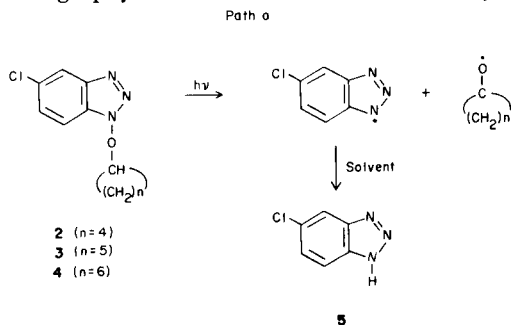
Three 1-cycloalkoxy-5-chloro-1,2,3-benzotriazoles were photolyzed at 254 nm. The major photolytic pathway yielded the corresponding cyclic ketone and 4,4'-dichloroazobenzene.

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It was previously reported that the photolysis of 1-methoxy-1,2,3-benzotriazole (**1**) proceeded *via* two pathways (1). One path involved the homolytic cleavage of the N-OCH₃ bond while a second path proceeded *via* the expulsion of a molecule of nitrogen followed by an intramolecular hydrogen abstraction to yield the phenylnitrene. Dimerization of the phenylnitrene yielded azobenzene. Based on the yields of azobenzene, the second pathway was shown to be the major pathway.

To see whether this photolysis reaction was unique for **1** or if it could be extended to other 1-alkoxy-1,2,3-benzotriazoles, we photolyzed 1-cyclopentoxy- (**2**), 1-cyclohexoxy- (**3**), and 1-cycloheptoxy- (**4**) 5-chloro-1,2,3-benzotriazole. The compounds **2**, **3** and **4** were selected for the following reasons: (a) if **2**, **3**, and **4** reacted *via* the same pathways as **1**, the products would be the cyclic alcohols and the cyclic ketones; these materials would be more easily isolated and characterized than the formaldehyde isolated from the photolysis of **1**; (b) the chlorine would act as a point of reference for any reactions which occurred on the benzene ring; and (c) to aid in determining the mechanistic pathway for the reaction; 4-chlorophenylnitrene has been shown to react with diethylamine to yield 5-chloro-2-dimethylamino-3*H*-azepine (**2**).

Compounds **2**, **3** and **4** were prepared by treating 5-chloro-1-hydroxy-1,2,3-benzotriazole with the appropriate cycloalkyl bromide. The solvents selected for the photolysis study ranged from the polar compounds methanol and acetonitrile to nonpolar cyclohexane. All the samples were 0.005*M* in the 5-chloro-1-alkoxy-1,2,3-benzotriazole and irradiated at 254 nm for 12 hours under an atmosphere of nitrogen. The major products were isolated by chromatography on alumina and characterized by com-



paring their spectral properties with those of known samples. The minor products were identified by a comparison of the glpc retention times and their tlc *R_f* values with those of known compounds. The results of the photolyses are in Table I.

The data in Table I shows that, as in the case of the photolysis of **1**, two pathways are available for the photoexcited **2**, **3** and **4** molecules to rid themselves of the excess energy. The minor pathway (Scheme I, path a) was supported by the isolation of 5-chloro-1,2,3-benzotriazole (**5**). The finding of bicyclohexyl (**6**), which could form *via* the dimerization of two cyclohexyl radicals, in the photolyses performed in cyclohexane as well as the detection by glpc of the cyclic alcohols led credence to this mechanism.

The major pathway for the photolysis reaction of **2**, **3** and **4** involved the loss of a molecule of nitrogen followed by the loss of a molecule of the cyclic ketone as envisaged by Scheme I, path b. The 4-chlorophenylnitrene (**7**) formed could then dimerize to form 4,4'-dichloroazobenzene (**8**) (**3**) or abstract hydrogens from solvent to yield 4-chloroaniline (**9**) (**4**). The photolyses performed in cyclohexane showed a reduced amount of **8**. However, based upon the work of Hall, *et al.* (**5**), the product *N*-cyclohexyl-4-chloroaniline (**10**) can be reconciled as being formed from **7**.

Table I
The Photolysis of **2**, **3** and **4** at 300 nm (Percent Yields) (a,b,c)

Compound/Product	In Acetonitrile	In Methanol	In Cyclohexane
Compound 2			
Cyclopentanone	47	43	43
4-Chloroaniline	3	3	3
4,4'-Dichloroazobenzene	21	18	11
N-Cyclohexyl-4-chloroaniline			9
5-Chloro-1,2,3-benzotriazole	—	5	5
Bicyclohexyl			5
Compound 3			
Cyclohexanone	43	44	40
4-Chloroaniline	4	3	4
4,4'-Dichloroazobenzene	20	17	12
N-Cyclohexyl-4-chloroaniline			8
5-Chloro-1,2,3-benzotriazole		5	5
Bicyclohexyl			5
Compound 4			
Cycloheptanone	45	44	42
4-Chloroaniline	3	3	5
4,4'-Dichloroazobenzene	20	18	13
N-Cyclohexyl-4-chloroaniline			7
5-Chloro-1,2,3-benzotriazole		3	5
Bicyclohexyl			5

(a) The amount of starting material consumed ranged from 65-80%. (b) Percent yields are based upon reacted starting material. (c) Values are duplicate runs and the values reported range from ± 2 to $\pm 5\%$.

Table II
Sensitized Photolyses of **2**, **3** and **4**

Reactant (<i>M</i>)	Solvent	Sensitizer (<i>M</i>)	(a) $h\nu$	% Disappearance of 2 , 3 or 4 (b,c)	% Appearance of 9 (d,e)
2 (0.005)	Acetonitrile	3-Methoxyacetophenone (1.0)	350	36	8
3 (0.005)	Acetonitrile	3-Methoxyacetophenone (1.0)	350	41	10
4 (0.005)	Acetonitrile	3-Methoxyacetophenone (1.0)	350	37	9
2 (0.005)	Methanol	3-Methoxyacetophenone (1.0)	350	44	22
3 (0.005)	Methanol	3-Methoxyacetophenone (1.0)	350	40	23
4 (0.005)	Methanol	3-Methoxyacetophenone (1.0)	350	40	20

(a) Rayonet photoreactor with 350 nm bulbs. (b) Determined by glpc using 1-Dodecane as an internal reference. (c) Duplicate runs with values $\pm 5\%$. (d) 4-Chloroaniline yield based upon the disappearance of **2**, **3** or **4**. (e) Duplicate runs $\pm 3\%$.

Thus, if both **8** and **10** are assumed to form *via* **7**, a summation of the yields of these two products would indicate that the generation of **7** is the principal pathway in cyclohexane as well as the other solvents studied.

Support for path b came from the isolation of 5-chloro-2-diethylamino-3*H*-azepine (**11**) when **2**, **3** and **4** were photolyzed in diethylamine. Odum and Aaronson (2) reported that the photolysis of 4-chlorophenyl azide in diethylamine proceeded *via* **7** and yielded **11**. To examine whether the proposed hydrogen shift in path b was intramolecular, solutions of **2**, **3** and **4** were photolyzed in

methanol-*d*₄ and analyzed by mass spectroscopy. If the hydrogen shift was intramolecular, no added deuterium should be found in **8** isolated from the photolysis. On the other hand if the hydrogen shift proceeded *via* an intermolecular path, there would be a good chance for the **8** isolated to have picked up one or two deuterium atoms. Compound **8** containing 0, 1 and 2 deuteriums would have a *m/e* of 250, 251 and 252, respectively. To compensate for the natural occurring abundances of C¹³, H² and Cl³⁷, which would contribute to *m/e* peaks at 251 and 252 we looked for the increase in peaks 251 and 252 relative to

250. In all cases, the **8** isolated was shown not to contain any excess deuterium.

Saunders and Caress (6) proposed that photochemical rearrangements which involved a phenylimidogen intermediate would most likely proceed *via* a triplet mechanism. To test this hypothesis in the current study, solutions of **2**, **3** and **4** in methanol and acetonitrile were irradiated at 350 nm in the presence and absence of 3-methoxyacetophenone (**12**) $E_t = 72 \frac{\text{kcal}}{\text{mole}}$ (7), a known

triplet sensitizer. Solutions of **2**, **3** and **4** containing no **12** showed no reaction upon photolysis for 78 hours while solutions of **2**, **3** and **4** containing **12** underwent photolysis. Photolysis was measured by a diminution of the starting benzotriazole. The results are listed in Table II. It is noteworthy that the amount of **9** formed increased in the sensitized photolyses relative to the unsensitized photolyses performed at 254 nm. It has been well documented that anilines are readily formed from the triplet nitrenes (8). The formation of azobenzenes from a triplet phenylimidogen has also been reported (9).

EXPERIMENTAL

Photolyses were conducted in a Rayonet photochemical reactor at 254 nm or 350 nm as indicated. The infrared spectra were obtained on a Beckman IR-4 spectrophotometer. High-resolution mass spectra were obtained on a CEC-21-110 instrument. Glpc was performed on a Varian Model 1200 HYFI.

Materials.

5-Chloro-1-hydroxy-1,2,3-benzotriazole was prepared according to the method of Singh and Kapic (10). Compounds **2**, **3** and **4** were prepared using the method of Brady and Reynolds (11).

Irradiation of **2**, **3** and **4**.

In a quartz vessel, 80 ml. of a solution of **2**, **3** or **4** (0.005M in the appropriate solvent) was degassed by bubbling nitrogen gas through the solution and irradiated at 254 nm for 12 hours. Upon removal of the solvent at reduced pressure and room temperature, a dark colored mass was isolated. The colored material was taken up in methylene chloride and analyzed by glpc (6 ft., 3% SE-30 column) and thin layer chromatography (tlc). The products were identified by comparing their retention times with those of known samples of the photolysis products. Column

chromatography on alumina of the photolysis reaction mixture permitted the isolation of the respective cyclic ketones as well as **8**. The infrared spectra of the compounds isolated by column chromatography were superimposable with those of known samples. The major products and their percent yields are listed in Table I.

Irradiation of **2**, **3** and **4** in Methanol- d_4 .

In a quartz vessel a 0.005M solution of **2**, **3** or **4** in methanol- d_4 was irradiated for 6 hours at 254 nm while nitrogen was bubbled through the solution. The 4,4'-dichloroazobenzene isolated from the reaction by column chromatography was subjected to high-resolution mass spectral analysis. The mass peaks at 250, 251 and 252 corresponding to **8** containing 0, 1 and 2 deuteriums, respectively, showed that no added deuterium had been incorporated.

Irradiation of **2**, **3** and **4** in Diethylamine.

A 0.005M solution of **2**, **3** or **4** in diethylamine was irradiated at 254 nm for 8 hours while nitrogen gas was bubbled through the solution. Compound **11** was shown to be present in each photolyzed solution by a comparison of the retention times in glpc and tlc analysis with the R_f of a known sample (2).

Sensitization of the Photolysis of **2**, **3** and **4**.

A solution (10 ml.) 0.005M in **2**, **3** or **4** in the appropriate solvent was divided into two parts. To one solution sufficient 3-methoxyacetophenone was added to make the final concentration 1.0M in the sensitizer. An equal quantity of solvent was added to the other solution. Both samples were placed in Pyrex vessels, degassed and irradiated at 350 nm for 96 hours. The solutions were analyzed by glpc. The results (Table II) are the average of two runs. The yield of 4-chloroaniline was 10%, 12%, 15% in acetonitrile, cyclohexane and methanol, respectively.

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