can be summed up as follows: (1) acidity of proton, 1,1,2,2> 1,2 and (2) strength of C-X bond, 1,1,2,2 > 1,2 (all protons and C-X bonds of each reagent are equivalent). These factors may contribute to a shift of the mechanism from  $E2_{Ca}$  of 1,2-dibromoethane to concerted E2 of 1,1,2,2-tetrachloroethane on the solid acid, increasing the value of the kinetic isotope effect. The same situation may occur on the alumina catalyst where the low acidity of the proton and a weak C-Br bond may facilitate an E2<sub>Ca</sub> mechanism for 1.2-dibromoethane in spite of binary sites on the catalyst. The value of the isotope effect may, thus, increase for 1,1,2,2-tetrachloroethane because the mechanism is nearer to the typical concerted E2 than that of 1,2-dibromoethane. In the case of solid base, more E1<sub>Cb</sub> nature of 1,1,2,2-tetrachloroethane compared with 1,2-dibromoethane gives a low value for the kinetic isotope effect for the former. Thus, changes in the selectivity and the kinetic isotopic effect in the elimination due to the change of reactants are consistently explained in terms of continuous transitions of the reaction mechanism according to the acid-base nature of reagents as described in Figure 1.

The changes in Table III may correspond to the transitions of the mechanism according to the acid-base nature of the catalyst. As for 1,2-dibromoethane, increasing the basicity of the catalyst should shift the mechanism from  $E2_{Ca}$  to  $E2_{Cb}$  via E2 concerted, as indicated by the isotope effect. Alternatively, elimination from 1,1,2,2-tetrachloroethane proceeds by an E2 concerted mechanism with acidic catalysts but shifts to an  $El_{Cb}$  mechanism via an  $E2_{Cb}$ mechanism with basic catalysts.

Registry No.-1,2-Dichloropropane, 78-87-5; 1,2-dibromopropane, 78-75-1; 1,1,2-trichloroethane, 79-00-3; 1,2-dibromoethane, 106-93-4; 1,1,2,2-tetrachloroethane, 79-34-5; silica, 7631-86-9; alumina, 1344-28-1; KOH, 1310-5S-3.

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# Photolysis of 1-Methoxy-1,2,3-benzotriazole

#### M. Paul Servé

Department of Chemistry, Wright State University, Dayton, Ohio 45431

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Recent experiments in our laboratory regarding the derivatives of 1-methoxy-1,2,3-benzotriazole (1) as potential pesticides prompted us to consider the photolytic decomposition of these molecules to see what harmful products would result upon the absorption of ultraviolet light. The

photolysis of 1,2,3-benzotrizole (2) and several of its 1-substituted derivatives had been reported,<sup>1-5</sup> but the photochemistry of 1 had not been studied. Thus, we decided to photolyze 1 in several solvents in order to (a) obtain information regarding the photolytic reaction pathway and (b) determine whether a solvent effect was operative in the photolysis.

1 was prepared by treating 1-hydroxy-1,2,3-benzotriazole with sodium ethoxide and methyl iodide. Solvents ranging in polarity from cyclohexane and benzene to methanol and acetonitrile were used. All samples were 0.005 M in 1 degassed using a freeze-vacuum-thaw sequence and irradiated under a helium atmosphere at 300 nm for 6 hr, after which the solution had darkened to such an extent that further irradiation proved fruitless. The major products were isolated by chromatography on alumina and silica gel and identified by comparison of their spectral properties with those of known samples. The minor products were identified by comparison of their glpc retention times and tlc  $R_{\rm f}$  values with those of known compounds. The results of the photolyses are listed in Table I.

Table I The Photolysis of 1 at 3000 Å (Per Cent Yields)

Product	In benzene	In methanol	In cyclohexane	In acetonitrile
1-Methoxy-1,2,3- benzotriazole (1)	13	9	15	6
Aniline		4	4	8
Benzotriazole (2)		9	28	
Azobenzene (6)	63	61	11	81
2-Aminobiphenyl	8			
Biphenyl	6			
Bicyclohexyl			8	
N-Čyclohexylaniline			24	

From Table I it is readily apparent that the 1-methoxy group is lost during the photolyses in all the solvent systems studied. The formation of 2 in the methanol and cyclohexane photolyses can most easily be pictured as forming via a homolytic cleavage of the N-OCH3 linkage followed by abstraction of a hydrogen atom from the solvent (Scheme I, path a). Supporting evidence for the occurrence of this pathway came from the isolation of bicyclohexyl from the cyclohexane photolysis. The dimer expected from the methanol photolysis, ethylene glycol, was also detected. Although no 1,2,3-benzotriazole was isolated from the benzene photolysis, its initial formation by the path mentioned above is strongly suggested by the isolation of 2-aminobiphenyl and biphenyl, both of which were found in the reported photolysis of 1,2,3-benzotriazole in benzene.<sup>2</sup>

An interesting feature of the photolyses was the isolation of azobenzene 6 as the major product in all the solvent systems studied with the exception of cyclohexane. The absence of any product containing the N-OCH<sub>3</sub> linkage together with the previously reported isolation of 6 from azidobenzene via phenylnitrene<sup>6</sup> 5 suggested path b (Scheme I) as a possible way of accounting for the formation of 6from the photolysis of 1.1 upon irradiation can lose a molecule of nitrogen to yield the diradical 3, which intramolecularly or intermolecularly abstracts a hydrogen to give the new diradical 4.4 in turn undergoes a homolytic cleavage of the N-O bond to eliminate a molecule of formaldehyde and generate 5. Dimerization of 5 could then yield azobenzene. The isolation of formaldehyde via its 2,4-dinitrophenylhydrazone in acetonitrile lent credence to the proposed path b mechanism.

It was noted above that cyclohexane was the only solvent in which 6 was not found to be the major product. How-



ever, the product N-cyclohexylaniline has been reported to be a principal product resulting from the thermal decomposition of azidobenzene in cyclohexane, where a triplet nitrene was pictured as the intermediate.<sup>7</sup> Thus, if both 6 and N-cyclohexylaniline are assumed to be formed via 5, a summation of the yields of these two products would indicate that the generation of the nitrene intmediate in cyclohexane is the principal reaction pathway in cyclohexane as it is in all the other solvents studied.<sup>8</sup>

To check the veracity of the path b mechanism and to attempt to gain some insight into the intramolecularity or intermolecularity of the proposed H shift, 1 was photolyzed in CD<sub>3</sub>OD. Mass spectral analysis of the azobenzene isolated from the reaction revealed that the product contained no excess deuterium. The failure of the 6 produced to have incorporated any deuterium from the solvent lends support to the proposed mechanism and strongly suggest that the hydrogen abstraction proposed in path b proceeds intramolecularly.

Using 3-methoxyacetophenone  $E_{\rm T} = 72$  kcal/mol,<sup>9</sup> the photolysis of 1 could be sensitized at 350 nm in all solvent systems examined. Solutions of 1 in the solvents of interest showed no reaction when irradiated at 350 nmin the absence of sensitizer. Quenching experiments were attempted using 1,3-cyclohexadiene  $E_{\rm T} = 52.5$  kcal/mol.<sup>10</sup> Solutions of 1 containing 1,3-cyclohexadiene, when irradiated at 300 nm, showed a definite decrease in product formation compared to equimolar solutions of 1 containing no 1,3-cyclohexadiene. The reaction, however, could not be totally quenched.

In conclusion, it appears that the photolysis of 1 in the solvent systems studied proceeds via two pathways. The principal pathway involves the loss of  $N_2$  (path b). A minor mode of reaction involves cleavage of the N-OCH<sub>3</sub> linkage (path a).

## **Experimental Section**

Photolyses were conducted in a Rayonet photochemical reactor at 300 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. 1-Hydroxy-1,2,3-benzotriazole was prepared according to procedure of Macbeth and Price.<sup>11</sup> 1 was prepared by the method of Brady and Reynolds.<sup>12</sup>

Irradiation of 1. In a quartz vessel 80 ml of a solution (0.005 Min 1 in the appropriate solvent) was degassed using a freeze-vacuum-thaw sequence and irradiated at 300 nm for 6 hr. The reaction was then analyzed by glpc (6 ft, 3% SE-30 column) and thinlayer chromatography (tlc). The products were identified by comparing their retention times with those of known samples. Infrared spectra of the products isolated by column chromatography were superimposable with the infrared spectra of known samples. The major products and their per cent yields are listed in Table I. A trace of ethylene glycol was also established by glpc.

Isolation of Formaldehyde-2,4-dinitrophenylhydrazone. In a quartz vessel 80 ml of a solution of 1 (0.005 M in acetonitrile) was degassed and irradiated at 300 nm for 6 hr as described above. The photolysis vessel was then cooled in a chlorobenzene slush bath  $(-45^{\circ})$ . The photolysis vessel was then cracked and its contents was placed in a flask containing 25 ml of a saturated solution of 2,4-dinitrophenylhydrazine in 2  $\overline{N}$  HCl. The solution was then brought to room temperature and refluxed for 30 min. Upon cooling platelets formed which were collected and crystallized from ethanol, mp 165-166° (lit.<sup>13</sup> 166°). A mixture melting point of the platelets with an authentic sample of formaldehyde-2,4-dinitrophenylhydrazone showed no melting point depression.

Irradiation of 1 in  $CD_3OD$ . In a quartz vessel a 0.005 M solution of 1 in CD<sub>3</sub>OD was degassed by a freeze-vacuum-thaw sequence and irradiated at 300 nm for 6 hr. The azobenzene isolated from the reaction by column chromatography was subjected to high-resolution mass spectral analysis. The mass peaks at 182, 183, and 184 corresponding to 6 containing 0, 1, and 2 deuteriums, respectively, showed no added deuterium had been incorporated.

Sensitization of the Photolysis of 1. A solution (10 ml) 0.005 M in 1 in the appropriate solvent was divided into two equal parts. To one portion 0.01 ml of 3-methoxyacetophenone was added. Both samples were then placed in Pyrex vessels, degassed, and irradiated at 350 nm for 76 hr. At the end of that period glpc analysis showed that in the vessel containing the 3-methoxyacetophenone reaction had occurred while in the vessels containing no sensitizer, no product had formed.

Attempted Quenching of the Photolysis of 1. A 10-ml sample of a 0.005 M solution of 1 in the appropriate solvent was divided into two equal parts. To one part 0.01 ml of 1,3-cyclohexadiene was added. Both solutions were placed in quartz vessels, degassed, and irradiated at 300 nm for 3 hr. During that time aliquots were removed from each photolysis vessel and analyzed by glpc. In all the solvents investigated, the photolysis of the solution containing the 1,3-cyclohexadiene was significantly retarded relative to the solution containing no quencher. However, in no case could the reaction be completely quenched.

# Registry No.--1, 22713-34-4.

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