

Synthesis of 1-Methyl-1,2,3-benzotriazole 2-Oxide

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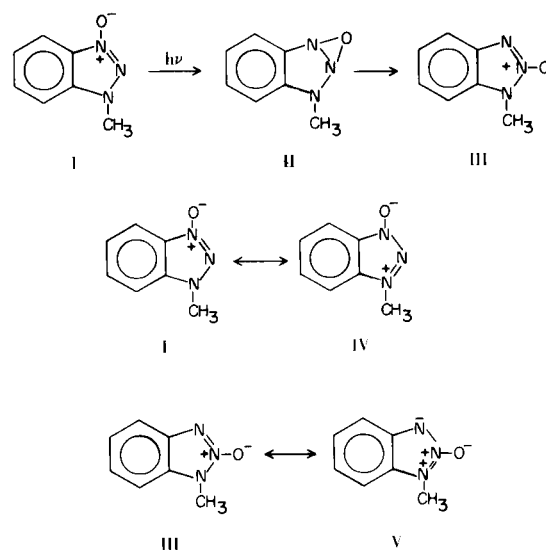
Sir:

Although many aromatic *N*-oxides have been reported (1) the 1,2,3-benzotriazole 2-oxide system appears to have been overlooked. We report here the synthesis of 1-methyl-1,2,3-benzotriazole 2-oxide (III), the first 1-alkyl derivative of the 1,2,3-benzotriazole 2-oxide system. Compound III was prepared by irradiating a degassed 0.005 *M* solution of 1-methyl-1,2,3-benzotriazole 3-oxide (I) in methanol at 300 nm for 4 hours. The isolation of III (38% yield) along with 1-methyl-1,2,3-benzotriazole (VI) (48% yield) and smaller amounts of other products was accomplished by preparative tlc.

The identification of III was based on the following data. Combustion analysis established the formula $C_7H_7N_3O$ (*Anal. Calcd.* C, 56.37; H, 4.73; N, 28.17). Found C, 56.58; H, 4.42; N, 27.92. A high resolution mass spectrum (CEC-21-110 at 70 eV) of III showed a molecular ion at 149.0597 ($C_7H_7N_3O = 149.0588$). There are also prominent fragments at 120.0817 ($C_6H_4N_2O = 120.0813$) and 119.0643 ($C_7H_7N_2 = 119.0609$), which may be ascribed to M-NCH₃ and M-NO respectively. The nmr of III showed at multiplet centered at 7.35 ppm and a singlet at 4.0 ppm in the ratio of 4:3.

The ultraviolet spectrum of III in methanol contained a long wavelength absorbance at 295 nm ($\log \epsilon$ 2.35). This compared with the long wavelength absorbance of I at 321 nm ($\log \epsilon$ 2.76) in methanol. The longer wavelength absorbance of I versus III can be explained by noting the expected contributions of the respective resonance structures IV and V. Structure IV would be expected to contribute to the stability of I more than structure V to the stability of III because of the added generated charges in V. These qualitative ideas are supported by calculations using simple Huckel MO theory (2). For I the bond orders of both the 1-2 and 2-3 bonds are high indicating a strong contribution from both resonance forms I and IV. Results for III show a high bond (strong double bond character) for the 2-3 bond and a low bond order (little double bond character) for the 1-2 bond, thus indicating that contributions of resonance forms like V are quite small for this isomer.

Hydrogenation of III over 5% palladium on carbon



yielded 1-methyl-1,2,3-benzotriazole indicating III contained the same relative arrangements of carbon and nitrogen as its precursor I.

Quenching experiments using 1,3-cyclohexadiene ($E_T = 52.5 \frac{\text{kcal}}{\text{mole}}$) (3) did not reduce the formation of III, but did significantly inhibit the formation of 1-methyl-1,2,3-benzotriazole. This strongly suggests that III forms via an excited singlet state or hot ground state of I.

As a possible mechanistic pathway, we suggest that I upon the absorption of light forms the oxadiaziridine (II) which then opens to yield III.

A 0.001 *M* degassed methanolic solution of III was photolyzed at 300 nm for 4 hours. Glpc analysis indicated the presence of VI suggesting that III as well as I could be photochemically deoxygenated to VI. Thus the yield of III found for the photolysis of I might not truly indicate the total amount of III actually formed.

Now that a method has been found to prepare the 1,2,3-benzotriazole 2-oxide system further examples of this new heterocyclic *N*-oxide system are being investigated.

EXPERIMENTAL

1-Methyl-1,2,3-benzotriazole 3-oxide (I) was prepared by the method of Brady and Reynolds (4).

Irradiation of 1-Methyl-1,2,3-benzotriazole 3-Oxide.

A 0.005 *M* solution of I in methanol was degassed using a freeze-vacuum-thaw sequence. The solution was then irradiated at 300 nm for 4 hours, in a Rayonet photoreactor. Gas liquid partition chromatography (glpc) (6 foot, 3% se-30 column) indicated two major products. The products were isolated using thin layer chromatography (tlc). The product VI was identified by comparing its physical and spectral properties with that of a known sample. The structure of III (m.p. 125-126°) was determined by the evidence listed in the text. The % yields of the major products were determined by glpc.

Irradiation of 1-Methyl-1,2,3-benzotriazole 2-Oxide.

A 0.001 *M* solution of III in methanol was degassed using a freeze-vacuum-thaw sequence and irradiated at 300 nm for 4 hours. Glpc analysis indicated that compound VI had formed in approximately 28% yield.

REFERENCES

(1) A. R. Katritzky and J. M. Lagowski, "Chemistry of the Heterocyclic *N*-Oxides," Academic Press, New York, New York, 1971, and references therein.

(2) The parameter values for the Huckel MO calculations were taken from Streitwieser (A. Streitwieser, Jr., "Molecular Orbital Chemists," John Wiley and Sons, Inc., New York, New York, 1961). The methyl group was treated as a heteroatom contributing two pi electrons; the parameter β (N=N) was chosen as 1.1.

(3) P. G. Wagner and G. S. Hammond in "Advances in Photochemistry," Interscience Publishers, New York, New York, 1968, Vol. 5, p. 80.