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PHOTOCHEMICAL REACTIONS OF BENZOTRIAZOLES

Kazuo Tsujimoto, Mamoru Ohashi, and Teijiro Yonezawa

Department of Materials Science, The University of Electro-Communications,
Chofu, Tokyo 182 and Department of Hydrocarbon Chemistry, Faculty of
Engineering, Kyoto University, Kyoto 606

Photochemical transformations of 1H-, 1-alkyl-(CH_3, C_2H_5, C_3H_7, C_4H_9, C_8H_{17}, and $CH_2C_6H_5$), 1-phenyl- and 1-acyl-($COCH_3$, $COC(CH_3)_3$, COC_6H_4X)benzotriazoles are briefly reviewed. Intermediates produced by the loss of nitrogen from 1H- and 1-alkylbenzotriazoles react with hydrogen donating solvents and yield either reduced or substituted products depending on the dipole character of the solvents. Irradiation of 1-methylbenzotriazole in toluene gave a mixture of 2'-methyl and 4'-methyl-2-biphenylamine derivatives in the ratio of 4:1 which consists with the k_o/k_p value obtained by a radical reaction. INDO calculations on the intermediate derived from 1*H*-benzotriazole indicated that a triplet diradical state is the most stable and the next is a singlet zwitterionic state.

On irradiation 1-phenylbenzotriazole gave carbazole quantitatively while 1-phenyl-4,5,6,7-tetrahydrobenzotriazole afforded cyclopentanecarboxanilide. The fact that 4',5-dichloro-1-phenylbenzotriazole gave 3,6-dichlorocarbazole as the sole product indicated that a benzoazacyclopropene derivative can be excluded from possible intermediates.

The photolysis of 1-benzoylbenzotriazoles in acetone gave cyclopentadiene derivatives through the Wolff rearrangement. Para-substituents (CH_3, $C(CH_3)_3$, OCH_3, and Cl) on the benzoyl group did not affect the reaction.

Comparing with the thermolytic and mass spectrometric fragmentations of these benzotriazoles, their photochemical reactions are discussed according to the electronic configuration of the intermediates.