

PHOTOCHEMISTRY OF HETEROCYCLIC COMPOUNDS. I.

PHOTODEHYDRODIMERIZATION OF BENZIMIDAZOLE

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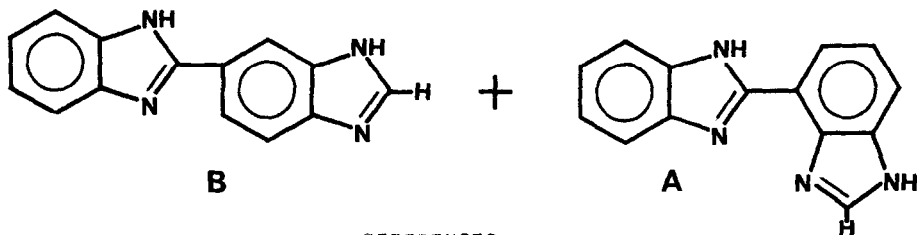
In contrast to other heterocyclic systems the photochemistry of benzimidazole has received only brief attention.¹ It has now been found that exposure of a 1% ethanolic solution of benzimidazole to U.V. light (253.7 nm) for 48 hours resulted in the formation of two major products, A (16% yield) and B (25% yield) which were separated by column chromatography (Alumina). The recovery of unchanged benzimidazole (50%) from the mixture accounted for 91% of starting material.

Compound A (M.P. 255-257⁰) had a molecular formula C₁₄H₁₀N₄ (elemental analysis and mass spectral data) and was identified as a dehydrodimer of benzimidazole, 2,4'-bisbenzimidazole, by interpretation of its n.m.r. spectrum: (d-D.M.S.O) σ 7.1 - 7.4 (symmetrical multiplet, 2H, H₅ and H₆), 7.46 (d, 1H, H₆, J_o = 7.2 Hz), 7.6 - 7.9 (complex multiplet, 3H, H₄, H₇ and H₅), 8.18 (two doublets, 1H, H₇, J_o = 7.2, J_m = 1.2 Hz), 8.46 (s, 1H, H₂), 10.9 (broad, 2H, H₁ and H₁, lost on D₂O exchange).

Compound B (M.P. 350-352⁰) also had a molecular formula C₁₄H₁₀N₄ and was similarly confirmed to be another dehydrodimer of benzimidazole, 2,5'-bisbenzimidazole. Its n.m.r. spectrum (d - D.M.S.O) had peaks at σ 7.44 (symmetrical multiplet, 4H, H₄, H₅, H₆, H₇), 7.79 (d, 1H, H₇, J_o = 9Hz), 8.12 (two doublets, 1H H₆, J_o = 9Hz, J_m = 1.6 Hz), 8.38 (s, 1H, H₂), 8.47 (d, 1H, H₄, J_m = 1.6 Hz), 9.5 (broad, 2H, H₁ and H₁, lost on D₂O exchange). The assignments of the

structures of compounds A and B were further supported by U.V. and I.R. spectra.

The products identified result from the dehydrodimerization of the benzimidazole, and an interesting feature is their unsymmetrical structure. Photochemical dehydrodimerization is a fairly novel reaction and the few examples quoted in the literature result in symmetrical products.^{2,3} The formation of compounds A and B may be explained by assumption of the intermediacy of a 2-benzimidazolyl radical generated either directly by the action of U.V. radiation or produced by rearrangement of a pre-formed 1-benzimidazolyl radical. The existence of a 2-benzimidazolyl radical has already been suggested in both an e.s.r.⁴ and a chemical study.⁵ The preferred substrate for this radical in the present case must be the benzimidazole. Hydrogen abstraction from the solvent, a common photochemical reaction of other heterocyclic systems is ruled out by the absence of reduced products or benzimidazole-solvent adducts. The absence of 2,2'-bisbenzimidazole, a possible product which could be formed by coupling of two 2-benzimidazolyl radicals, is another noteworthy result.



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