

PHOTOCHEMISTRY OF HETEROCYCLIC COMPOUNDS I.

PHOTODEHYDRODIMERIZATION OF BENZIMIDAZOLE

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(Received in UK 23 May 1973; accepted for publication 7 June 1973)

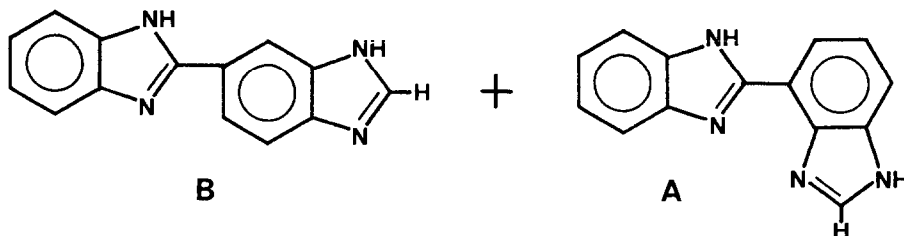
In contrast to other heterocyclic systems the photochemistry of benzimidazole has received only brief attention.<sup>1</sup> It has now been found that exposure of a 1% ethanolic solution of benzimidazole to U.V. light (253.7 nm) for 48 hours resulted in the formation of two major products, A (16% yield) 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. 255-257°) had a molecular formula  $C_{14}H_{10}N_4$  (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)  $\sigma$  7.1 - 7.4 (symmetrical multiplet, 2H,  $H_5$  and  $H_6$ ), 7.46 (d, 1H,  $H_6$ ,  $J_o = 7.2$  Hz), 7.6 - 7.9 (complex multiplet, 3H,  $H_4$ ,  $H_7$  and  $H_5$ ), 8.18 (two doublets, 1H,  $H_7$ ,  $J_o = 7.2$ ,  $J_m = 1.2$  Hz), 8.46 (s, 1H,  $H_2$ ), 10.9 (broad, 2H,  $H_1$  and  $H_{1'}$ , lost on  $D_2O$  exchange).

Compound B (M.P. 350-352°) also had a molecular formula  $C_{14}H_{10}N_4$  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 of  $\sigma$  7.44 (symmetrical multiplet, 4H,  $H_4$ ,  $H_5$ ,  $H_6$ ,  $H_7$ ), 7.79 (d, 1H,  $H_7$ ,  $J_o = 9$ Hz), 8.12 (two doublets, 1H,  $H_6$ ,  $J_o = 9$ Hz,  $J_m = 1.6$  Hz), 8.38 (s, 1H,  $H_2$ ), 8.47 (d, 1H,  $H_4$ ,  $J_m = 1.6$  Hz), 9.5 (broad, 2H,  $H_1$  and  $H_{1'}$ , lost on  $D_2O$  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.<sup>2,3</sup> The formation of compounds A and B may be explained by assumption of the interdemiacy 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 e.s.r.<sup>4</sup> and a chemical study.<sup>5</sup> 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.



## REFERENCES

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