Photochemical Dimerization of Benzofuran Derivatives

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Summary The photochemical reaction of benzofuran with 2-(1-pyridyl)benzofuran (**1**) results in the formation of cross-dimers (**3**) and (**4**); an excited singlet of benzofuran is implicated as the reactive excited state.

The connection between orientation and multiplicity of excited states in photoinduced dimerizations has attracted a great deal of attention.[1] In studying the photochemical reactions of 3-iodopyridine[2] in the presence of benzofuran, we found that benzofuran reacts with 2-(3-pyridyl)benzofuran (**1**) to give cross-dimers (**3**) and (**4**) on u.v. irradiation.

Irradiation of an acetonitrile solution containing 3-iodopyridine and a four-fold excess of benzofuran with a 350 W high-pressure mercury lamp through a Pyrex filter gave compounds (**1**) (5%; m.p. 78°), (**2**) (5%; HCl salt, m.p. 104°), (**3**) (32%; m.p. 150°), and (**4**) (21%; m.p. 113°). These products were isolated by chromatography over silica gel, and their structures follow from analytical and spectroscopic data.† The stereochemistry of (**3**) and (**4**) was assigned on the basis of their n.m.r. spectra (CCl_4; 100 MHz); compound (**5**) shows three methine protons at δ 4·40 (q, J 1·7 and $<1{\cdot}0$ Hz), 4·57 (q, J 6·5 and $<1{\cdot}0$ Hz), and 5·06 (q, J 6·5 and 1·7 Hz). In addition, the aromatic protons of the pyridine ring and one phenyl ring were shifted upfield from their normal positions, because of the long-range shielding effects of the aromatic rings. The n.m.r. spectrum of

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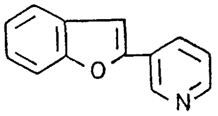
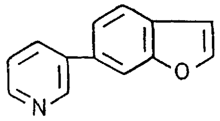
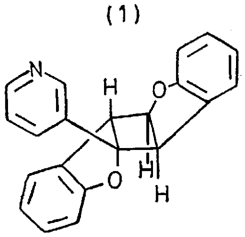
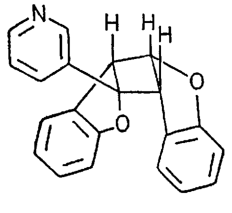
† Satisfactory elemental analyses were obtained for all compounds reported herein.

compound (**4**) shows three methine resonances at δ 4·48 (q, *J* 6·0 and 3·0 Hz), 4·59 (q, *J* 6·5 and 3·0 Hz), and 5·54 (q, *J* 6·5 and 6·0 Hz), and two phenyl resonances at higher field than normal. These n.m.r. spectra indicate that (**3**) is probably the head-to-tail *anti*-dimer and that (**4**) is the head-to-tail *syn*-dimer. Pyrolysis of (**3**) at 210—220° and of (**4**) at 230—240° in a degassed Pyrex tube led to benzofuran and compound (**1**), respectively.


(1)


(2)


(3)


(4)

Irradiation of an acetonitrile solution of benzofuran (0·2M) and (**1**) (0·05M) through a Pyrex filter gave a 3:2 mixture of compounds (**3**) and (**4**). When a similar solution was irradiated at 313 nm so that only compound (**1**) absorbed the incident light, neither (**3**) nor (**4**) was detected.‡ The formation of (**3**) and (**4**) was neither photosensitized by acetophenone (E_T 73·6 kcal/mol) nor quenched by naphthalene (E_T 60·9 kcal/mol). These results suggest that this cross photodimerization proceeds by way of the excited singlet state of benzofuran.

Krauch and his co-workers have shown that photodimerization of benzofuran can be effected only in the presence of triplet sensitizers and head-to-head dimers are formed.[1b] Our present results on this cross-photodimerization are in contrast to this. Furthermore, there are few reported photochemical additions involving the excited singlet of benzofuran, although many addition reactions of benzofuran derivatives have been reported.[1b,3]

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‡ The n.m.r. spectrum of an irradiated mixture showed two aliphatic peaks at δ (CCl_4) 4·87 (s) and 4·73 (s) (ratio 2:1). Similar signals appeared when (**1**) was irradiated alone, and they are presumably due to the formation of dimers of (**1**).

[1] (a) G. O. Schenck, W. Hartmann, S.-P. Mannsfield, W. Metzner, and C. H. Krauch, *Chem. Ber.*, 1962, **95**, 1642; (b) C. H. Krauch, W. Metzner, and G. O. Schenck, *ibid.*, 1966, **99**, 1723; (c) J. Bowyer and Q. N. Porter, *Austral. J. Chem.*, 1965, **19**, 1455; (d) J. J. McGullough, *Canad. J. Chem.*, 1968, **46**, 43; (e) J. W. Hanifin and E. Cohen, *Tetrahedron Letters*, 1966, **1419**; (f) H. Bouas-Laurent, A. Castellan, J. P. Desvergne, G. Dumartin, C. Courseille, J. Gaultier, and C. Hauw, *J.C.S. Chem. Comm.*, 1972, **1267**; (g) R. Kleopfer and H. Morrison, *J. Amer. Chem. Soc.*, 1972, **94**, 255; (h) D. N. Harpp and C. Heitner, *ibid.*, p. 8179.

[2] We have already reported the photolysis of 3-iodopyridine in the presence of five-membered heterocycles; see, H.-S. Ryang and H. Sakurai, *J.C.S. Chem. Comm.*, 1972, 594.

[3] C. H. Krauch, S. Farid, and G. O. Schenck, *Chem. Ber.*, 1965, **98**, 3102; S. Farid and S. E. Shealer, *J.C.S. Chem. Comm.*, 1973, 296.