LETTERS TO THE EDITOR

PHOTODIMERIZATION OF 2,6-DIPHENYL-4-(5-BROMOFURYL-2)-PYRYLIUM AND PYRIDINIUM PERCHLORATES

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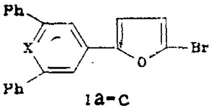
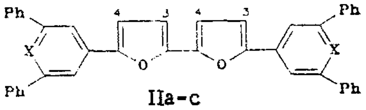
Photodimerization reactions of pyrilium and pyridinium salts involving loss of halogen have not previously been described in the literature. Changes in the absorption and fluorescence spectra of 2,6-diphenyl-4-(5-bromofuryl-2)-pyrylium perchlorate solutions (Ia) [1] upon photoirradiation indicate the formation of a single substance, having the dimeric structure IIa.



Ia-c



IIa-c

I, II a $X=O^+$; b $X=N$; c $X=N^+-H$

The bisperchlorate was isolated preparatively and converted to the bispyridine derivative IIb for structure proof. The PMR spectrum is completely consistent with structure IIb. The mass spectrum contains an intense peak at m/z 592 for the molecular ion. Bispyridine IIb was also prepared by an independent method involving photodimerization of the pyridinium perchlorate Ic and subsequent conversion to the neutral base. Photoirradiation of pyridine Ib did not result in the formation of the dimer IIb, which probably reflects the greater strength of the C—Br bond in the neutral molecule compared to the cation.

The photochemically generated dimers of structure IIa-c are luminophores and are formed in quantum yields approaching unity.

bis[2,6-Diphenyl-4-(2-furyl-5)pyrylium Perchlorate (IIa). A solution of 3 g of perchlorate Ia in 450 ml acetonitrile was irradiated for 16 h in a quartz reactor using a mercury DRT-220 lamp. Compound IIa (0.27 g) was removed by filtration. The solution was evaporated to 100 ml and then cooled, which gave another 0.06 g of compound IIa, which was also filtered. Yield, 11%, mp > 350°C (decomp.). UV spectrum (in acetonitrile): λ_{max} (abs.) 545 nm (log ε 4.82); λ_{max} (fluor.) 610 nm.

bis[2,6-Diphenyl-4-(2-furyl-5)pyridine (IIb). This was prepared from bisperchlorate IIa according to standard methodology [2]. mp 289-291°C (dec. from a 1:1 benzene—hexane mixture). PMR spectrum: 7.11 (4-H); 7.53 ppm (3-H); doublets, J_{34} = 3 Hz. UV spectrum (in acetonitrile): λ_{max} (abs.) 372 nm (log ε 4.61); λ_{max} (fluor.) 430 nm. C, H, and N elemental analyses were all in agreement with calculated values.

LITERATURE CITED

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