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A 1,4-PHOTOCHEMICAL ARYL SHIFT

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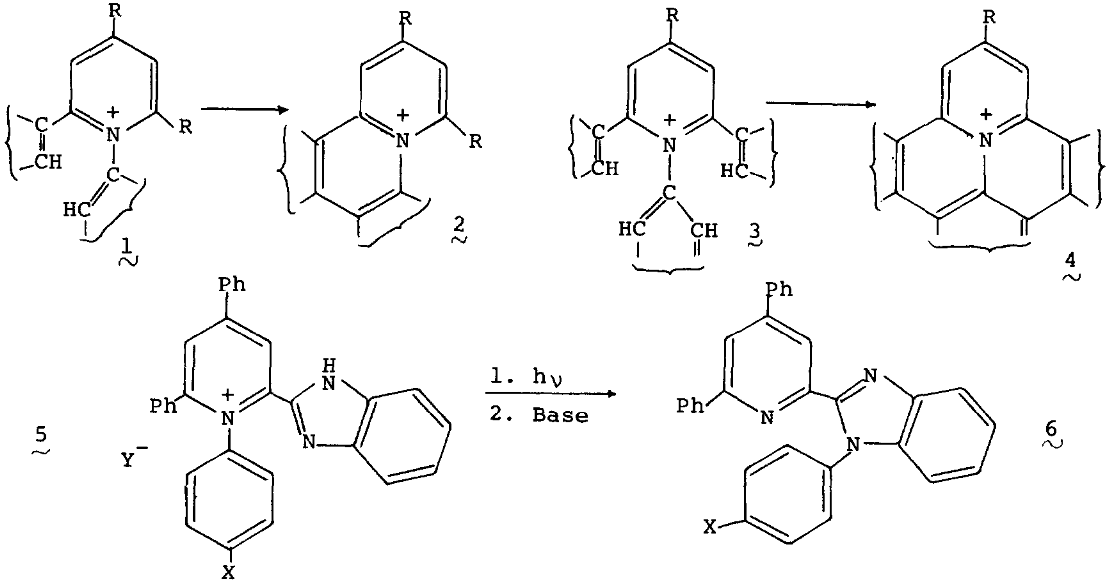
Experimental Station E356/317A, E.I. Du Pont de Nemours, Wilmington, De., 19898, USA.

Abstract: 1-Aryl-2-(2'-benzimidazolyl)-4,6-diphenyl-pyridiniums are converted photochemically into 2-[2'-(1'-arylbenzimidazolyl)]-4,6-diphenylpyridines. X-Ray crystal analysis comfirms the structure for the p-chlorophenyl derivative.

1,2-Di- and 1,2,6-tri-aryl- and -heteroaryl-pyridiniums undergo photochemical cyclisations of type 1 → 2[1,2,3] and 3 → 4.[2,3] We now find that 1-aryl-2-(2'-benzimidazolyl)pyridiniums 5, by contrast, undergo photo-rearrangement of the aryl group onto the benzimidazolyl nitrogen 5 → 6,

[BLOCK 1]

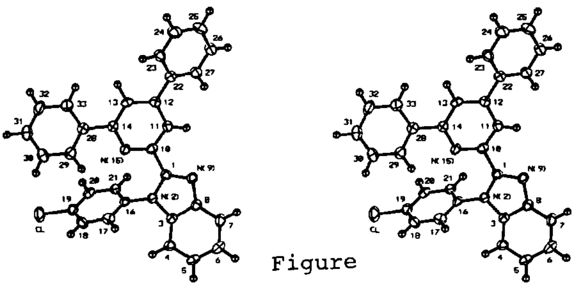


a, $X = H$, $Y = BF_4$; b, $X = Cl$, $Y = ClO_4$; c, $X = Me$, $Y = ClO_4$

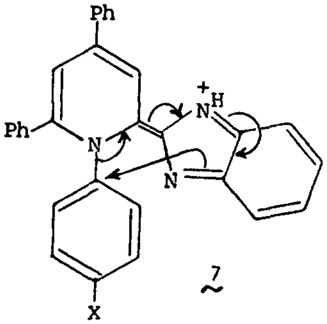
The starting pyridiniums were readily prepared, by the usual procedure,[4] from the corresponding 2-2'-benzimidazolylpyrylium.[5] They crystallised from acetone/HBF$_4$ or H$_2$O/HClO$_4$, and had m.p.'s: 5a, 252-259 °C; 5b, 252-254 °C; 5c, 194-197 °C.[6] The photochemical transformations were carried out in MeOH[7] over 3 - 5 days and were followed by a work up with sodium ethoxide in ethanol. In this way, each of the novel free bases 6a-c were obtained.[7] They had m.p.'s: 6a, 163-169 °C; 6b, 178-182 °C; 6c, 157-159 °C in yields respectively 87, 82 and 85%. UV of a 6a-c showed pyridine like absorptions at 315 nm: no peaks at 350-450 were observed as required for cyclized 4.[2,3] After NaOEt/EtOH work up, BF_4 absorption at 1050 cm^{-1} in IR was lost: pyridine bands at 1600 cm^{-1} were identified. ^{1}H NMR showed bands between 7 and 8 ppm: absence of low field peaks indicated non cyclisation (cf. 4[2,3]). Mass spectra of the free bases 5b,6b agreed with the assigned molecular weight.

X-Ray Crystallographic Data.- This study[8] on 6b conclusively indicated the structure assigned, confirming N to N' aryl migration. See Figure for stereodrawing of 6b.

The N to N' 1,4-aryl migration, with retention of the substitution pattern on the aryl ring, is novel. The closest literature analogy appears to be the rearrangement of 2-aryloxypyridine 1-oxides into 1-aryloxy-2-pyridones.[9] A possible mechanism is shown in 7.



Figure



7

The work described in this paper is significant in attempts to extend the pyrylium mediated transformation of aliphatic amines[4] to their aryl analogues. It shows that the N-aryl bond can be broken under quite mild conditions and will stimulate further work in this area.

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6. Satisfactory microanalytical data were obtained for all new compounds reported: 5b and 5c were isolated as bisperchlorates.
7. The pyridinium salt (1-4g) was dissolved in methanol (100 ml) in a quartz vessel and irradiated in a Rayonet photochemical reactor using 350 nm lamps. Conversion to the product was followed by the decrease in absorption at 310 nm from ε = ca. 30000 to ca. 10000. On completion (ca. 3-5d), the solution was evaporated to a small volume and the product was filtered off and washed with ether (5 ml). This was then warmed with sodium ethoxide in ethanol (5 ml, 70 °C, 15 m), cooled and the free product filtered off and recrystallised from ether (5 ml).
8. Crystal-Structure Information; Orthorhombic, space group Pbca; at -100 °C, a = 11.058(2), b = 34.578(6), c = 11.804(2) Å; omega scans of 1.0°, $4° < 2\Theta < 48°$, 4118 reflections. The structure was refined by full-matrix, least-squares techniques: 2203 reflections with $I > 2\sigma(I)$, 387 variables (Cl, N & O with anisotropic thermal parameters; H with isotropic), R = 0.051, R_w = 0.042. The peaks in the final difference Fourier were all less than 0.28 $e\text{Å}^{-3}$. The mathematical and computational details can be found in Inorganic Chem., 1979, 18, 2030.
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