COMMUNICATIONS

Photochemical Synthesis of Benzo[*c*]carbazole and Pyridocarbazoles

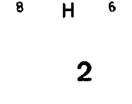
Osmund De Silva and Victor Snieckus

Department of Chemistry, University of Waterloo, Waterloo, Ontario, Canada

Numerous and diverse condensed heteroaromatic compounds are available by photochemical synthesis[1]. We report on the photochemical preparation of 7*H*-benzo[c]carbazole (**2**) and the pyridocarbazoles (**3**, **4**, **5**)[2] which represents a facile entry into these systems and a definite improvement in overall efficiency over the previously reported synthetic methods[3–9].

The readily accessible 1-(2-indolyl)-2-arylethylene derivatives (**1a–d**)[10] were irradiated to give the carbazole derivatives **2–5**. The photoproducts are known compounds and, in most cases, identification was carried out by direct comparison with authentic samples. Table 1 summarizes the reaction conditions and yields for the compounds prepared and Table 2 gives their U.V. and N.M.R. spectral data. In the original preparation of compounds **5** and **3**, the former was not unambiguously assigned[5] and the structure of the latter was not conclusively established[7]. These structural assignments are now confirmed by our photochemical syntheses.

1



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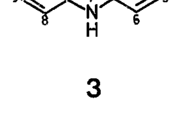

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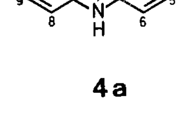
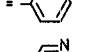


4a

a



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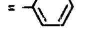

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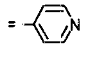

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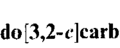

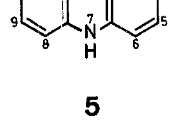

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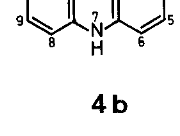

4b

7*H*-Pyrido[3,2-*c*]carbazole (4a) and 7*H*-Pyrido[3,4-*c*]carbazole (4b): A solution of 1-(2-indolyl)-2-(3-pyridyl)-ethylene (**1c**; 0.216 g) and iodine (0.050 g) in ethanol (200 ml) was irradiated (3500 Å) in a Rayonet Photochemical Reactor for 24 hr. The solution was basified with a saturated solution of sodium carbonate and enough sodium thiosulfate was added to destroy the excess iodine. Most of the solvent was removed in vacuo and the solution was diluted with water and extracted with ether. The ether extract was taken to dryness in vacuo and the residue was chromatographed (dichloromethane as eluent); yield: 0.068 g of **4a** and 0.117 g of **4b**.

Table 1. Photochemical Preparation of Compounds **2–5**

Compound	Irradiation time, hr (g reactant)	Yield[a] %	m.p. (Lit. m.p.) (solvent)	Reference
2	20 (0.484)	67	133–134° (132–133°) (C_6H_{12})	8
3	48 (0.050)	56	211–212° (211–212°) (C_6H_{12})	3,7
4a	24 (0.216)	32	172–172° (173–174°) (C_6H_6)	7
4b		54	254–255° (245–246°)[b] (C_6H_6)	6
5	12 (0.129)	85	259–260° (249–250°)[b] (CH_2Cl_2)	5

[a] After chromatography over basic (grade V) alumina in all cases except **2** which was obtained by silica gel chromatography.

[b] Original samples provided by Dr. Manske showed the following m.p. behavior on the Fisher-Johns apparatus: **4b**, m.p. 254–255°; **5**, m.p. 259–260°.

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E. V. Blackburn, C. J. Timmons, Quart. Rev. **23**, 482 (1969).
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Table 2. U.V. and N.M.R. Spectral Data of Compounds **2**–**5**[a]

Compound	U.V. (CH_3OH)	N.M.R., τ values[c]	
	λ_{max} (ε) mμ[b]	NH[e]	other
2	[d]	−1.22	1.16–1.56 (m, 2, H_4, H_{11}), 1.8–2.8 (m, 8).
3	[d]	−1.9	0.82 (q, 1, J = 2, 8, H_3), 1.07 (d, 1, J = 4, H_5), 1.4 (m, 1, H_{11}), 1.74–2.75 (m, 6).
4a	245.5 (48,900) 278 (81,300) 336 (11,000)	−1.65	0.98 (q, 1, J = 2, 5, H_2), 1.02 (m, 1, H_{11}), 1.67 (q, 1, J = 2, 9, H_4), 2.17 (m, 2, H_5, H_6), 2.47 (q, 1, J = 5, 9, H_3), 2.48–2.8 (m, 3).
4b	243 (sh, 43,700) 262 (sh, 89,100) 275 (114,800) 293 (sh, 60,300) 325 (8,500) 337 (sh, 7,600)	−2.01	0.68 (br s, 1, H_4), 1.42 (d, 1, J = 6, H_2), 1.56 (m, 1, H_{11}), 2.05 (d, 1, J = 8, H_5), 2.17 (d, 1, J = 8, H_6), 2.59 (d, 1, J = 6, H_1), 2.27–2.47 (m, 1), 2.63–2.8 (m, 2).
5	232 (sh, 28,800) 242 (34,700) 272 (57,500) 284 (42,700) 342 (10,000) 360 (sh, 8,300) 381 (sh, 600)	−1.8	−0.06 (br s, 1, H_1), 1.42 (d, 1, J = 6, H_3), 1.52 (m, 1, H_{11}), 2.07 (d, 1, J = 8, H_5), 2.2 (d, 1, J = 8, H_6), 2.27–2.7 (m, 4).

[a] All compounds showed mass spectra with correct parent molecular ions (relative intensity = 100%).

[b] sh = shoulder.

[c] Determined in polysol-d using tetramethylsilane as internal standard. Tabulation follows the order: multiplicity, number of protons, coupling constant in Hz, assignment.

[d] cf. Ref. 3.

[e] br s, 1H.

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