Photocyclization of 2-(Pyridylvinyl)chromen-4-ones

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Summary Irradiation of 2-(pyridylvinyl)-4*H*-chromen-4-ones (**1**) in benzene under air afforded the 12*H*-[1]benzopyrano[1,2-*f* or *h*]-isoquinolin-12-ones and -quinolin-12-ones (**2**).

THE light-induced cyclization of stilbenes and their aza-analogues has been described by many authors.[1] However, photochemical cyclization of 2-styrylchromen-4-ones has not been reported. We have found that irradiation (400 W high-pressure Hg lamp, Pyrex filter, 15 h) of 2-(4-pyridylvinyl)-4*H*-chromen-4-one (**1a**)† in benzene with air bubbled

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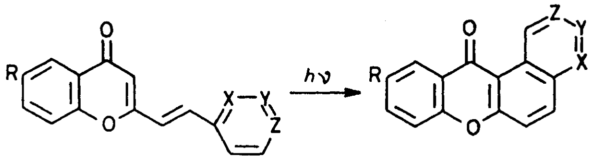
† The 2-(pyridylvinyl)chromen-4-ones were obtained from the reaction of the corresponding pyridine–aldehydes with 2-methyl- and 2,6-dimethyl-chromen-4-one in potassium hydroxide–methanol.

through gave 12*H*-[1]benzopyrano[2,3-*h*]isoquinolin-12-one (**2a**)‡ in 70% yield§ as pale brown crystals, m.p. 200—201 °C (from benzene); ν (KBr) 1640 cm^{-1}; λ_{max}(log ε) 242 (4·36), 264 (4·34), 313 (3·89), 343 (3·49), and 358 nm (3·42); δ(CDCl$_3$) 7·3—7·8 (4 H, m, 4,8,9,10-H), 7·65 (1 H, d, *J* 9 Hz, 6-H), 8·11 (1 H, d, *J* 9 Hz, 5-H), 8·45 (1 H, dd, *J* 1·5 and 8 Hz, 11-H), 8·74 (1 H, d, *J* 5·6 Hz, 3-H), and 11·30 (1 H, s, 1-H).



(1) (2)

a; R = H, X = Y = CH, Z = N
b; R = Me, X = Y = CH, Z = N
c; R = H, X = Z = CH, Y = N
d; R = Me, X = Z = CH, Y = N
e; R = H, X = N, Y = Z = CH
f; R = Me, X = N, Y = Z = CH

Similar photolysis of 6-methyl-2-(4-pyridylvinyl)-4*H*-chromen-4-one (**1b**) in benzene gave 10-methyl-12*H*-[1]-benzopyrano[2,3-*h*]isoquinolin-12-one (**2b**), m.p. 199—201 °C, in 93% yield; ν (KBr) 1640 cm^{-1}; λ_{max} (log ε) 242 (4·49), 269 (4·48), 320 (4·04), 346 (3·68), and 361 nm (3·57); δ (CDCl$_3$) 2·52 (3 H, s, Me), 7·3—7·8 (2 H, m, 8,9-H), 7·71 (1 H, d, *J* 5·6 Hz, 4-H), 7·76 (1 H, d, *J* 9·0 Hz, 6-H), 8·09 (1 H, d, *J* 9·0 Hz, 5-H), 8·23 (1 H, s, 11-H), 8·74 (1 H, d, *J* 5·6 Hz, 3-H), and 11·30 (1 H, s, 1-H).

Irradiation of the 3-pyridyl-chromenones (**1c**) and (**1d**) gave only the isomers formed by cyclization at the γ-position of the pyridine ring, the isoquinolines (**2c**) and (**2d**), the structures of which were assigned from the ^{1}H n.m.r. signals of 1-H. Since the isoquinoline (**2c**) gives a signal at δ 9·80 (1 H, d, *J* 6·1 Hz) and compound (**2d**) one at 9·80 (1 H, d, *J* 6·0 Hz), the nitrogen atom was assigned to the 3-position of these photocyclized products.

Table. Photocyclization of (**1**).

Product	M.p./°C (yield %)	δ (1-H) (*J*/Hz)
(**2a**)	200—201 (70)	11·30, s
(**2b**)	199—201 (93)	11·30, s
(**2c**)	216—218 (41)	9·80, d, (6·1)
(**2d**)	195—196 (29)	9·80, d, (6·0)
(**2e**)	191—193 (4)	10·40, d, (8·9)
(**2f**)	186—189 (6)	10·41, d, (8·8)

Though the yields of the quinolines (**2e**) and (**2f**) were unsatisfactory (Table), this report is the first example of the photocyclization of compounds (**1**) and the reaction described herein provides a convenient synthetic route to the benzopyrano-isoquinolones and -quinolones (**2**).

The detailed mechanism of this photoreaction is under investigation.

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‡ All new compounds gave satisfactory analytical and mass spectroscopic data.

§ 350 mg of compound (**2a**) was obtained from 500 mg of compound (**1a**) in 800 ml of methanol.

[1] F. R. Stermitz in 'Organic Photochemistry,' ed. O. L. Chapman, Marcel Dekker, Inc., New York, 1967; E. V. Blackburn and C. J. Timmons, *Quart. Rev. Chem. Soc.*, 1969, **23**, 482.