

Boron Complexes as Control Synthons in Photocyclisations: an Improved Phenanthridine Synthesis

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Summary Irradiation of boron complexes of various *N*-phenylbenzohydroxamic acids gives excellent yields of the cyclised products, which on reduction afford the corresponding phenanthridines.

THE photochemical methods currently employed for entry into the phenanthridine skeleton involve the use of benzanilides¹ and *N*-benzylideneanilines.^{2a,b} Because of the unfavourable geometry assumed by benzanilides in solution,³ the photocyclisation of *o*-halogenobenzanilides proceeds only in modest yield and requires prolonged irradiation.^{4a,b} In

photocyclisations of *N*-benzylideneanilines in a neutral medium, the competitive $n \rightarrow \pi^*$ excitation and the preferred *E* geometry of the substrates^{2b} result in lowered yields of the phenanthridines and in some cases in complete failure.

We report here that by utilising boron complexes⁵ of *N*-arylbenzohydroxamic acids both these adverse effects (electronic and steric) are largely overcome and a fast, high-yield photocyclisation results. The boron complexes of *N*-phenylbenzohydroxamic acids of the type (1) on photolysis (Philips HPR 125 W) in benzene† (Pyrex filter, 37–40 °C) undergo rapid ring closures to the corresponding phenanthridine derivatives of the type (2) (Table).

† The concentrations were usually within the range 5×10^{-2} to 6×10^{-3} M.

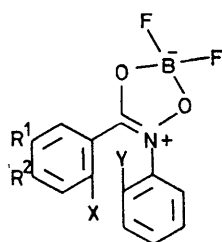
TABLE

Compound	M.p./°C	Product	M.p./°C	% Yield	Irradiation time/h
(1a)	199—200	(2a)	295—297	95 ^a	33
(1b)	146—149	(2a)	"	99	2
(1c)	169—171	(2b)	315—317	99	2
(1d)	171—174	(2a)	295—297	76	7.5
(1e)	163—165	—	—	0	8

^a In the presence of 1 equiv. of iodine.

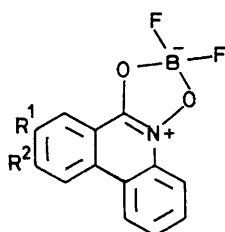
Reduction of the complex (2a) with an excess of lithium aluminium hydride (tetrahydrofuran, 72 h, room temp.) afforded the phenanthridine⁶ (6a), m.p. 164—165 °C, δ (CDCl₃) 9.14 (1H, s, 6-H), 7.86 (1H, s, 10-H), 7.43 (1H, s,

followed by reduction in the usual manner yielded benzo[*c*]phenanthridine (4), m.p. 137 °C (lit.⁸ 136 °C), a system present in many alkaloids possessing anti-leukaemic and cytotoxic properties.⁹



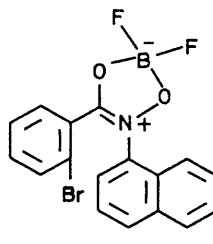
(1)

- a, R¹ = R² = OMe; X = Y = H
 b, R¹ = R² = OMe; X = Br; Y = H
 c, R¹ R² = OCH₂O; X = Br; Y = H
 d, R¹ = R² = OMe; X = H; Y = Cl
 e, R¹ = R² = OMe; X = H; Y = *p*-MeC₆H₄SO₃

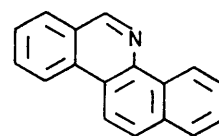


(2)

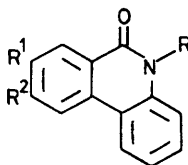
- a, R¹ = R² = OMe
 b, R¹ R² = OCH₂O



(3)

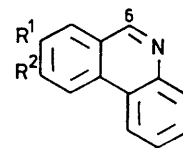


(4)



(5)

- a, R¹ R² = OCH₂O; R = OCH₂Ph
 b, R¹ R² = OCH₂O; R = H



(6)

- a, R¹ = R² = OMe
 b, R¹ R² = OCH₂O

7-H), 8.48—7.62 (4H, m, ArH), 4.07 (3H, s, OMe), and 4.13 (3H, s, OMe), in 66% yield. Similarly the complex (2b) yielded the phenanthridine⁶ (6b) (73%), m.p. 138 °C. Treatment of the complex (2b) in aqueous ethanolic alkali (pH *ca.* 12) with benzyl chloride gave a quantitative yield of the *O*-benzyl ether (5a), m.p. 190 °C, ν_{\max} (KBr) 1658 cm⁻¹, δ (CDCl₃) 7.94 (1H, s, 10-H), 7.64 (1H, s, 7-H), 8.08 (1H, dd, *J*_o 7.7 Hz *J*_m 1.2 Hz, 1-H), 7.78—7.32 (8H, m, ArH), 5.34 (2H, s, OCH₂Ph), and 6.19 (2H, s, OCH₂O), which on pyrolysis⁷ (sealed tube, 1 h, 220 °C), afforded the phenanthridone^{4a} (5b), m.p. 342 °C (decomp.). The boron complex (3), m.p. 146 °C, derived from *N*-1-naphthyl-*o*-bromobenzohydroxamic acid in benzene, on photolysis

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