Efficient Syntheses of 'Ellipticine Quinone' and the Other Three Isomeric 5*H*-Pyrido[*x*,*y*-*b*]carbazole-5,11(6*H*)-diones[1]

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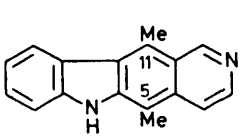
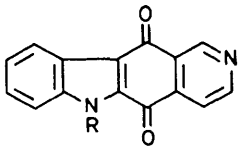
Summary 6*H*-Pyrido[*x'*,*y'*: 5,6]oxepino[3,2-*b*]indol-5-(12*H*)-ones (**3**) are efficiently converted by hot alcoholic base in air into the corresponding 5*H*-pyrido[*x*,*y*-*b*]-carbazole-5,11(6*H*)-diones (**5**).

GREAT interest[2] has been shown in syntheses of the anti-cancer alkaloid ellipticine (**1**) and related systems. 'Ellipticine quinone' (**2a**) and its *N*-methoxymethyl-analogue (**2b**) have been prepared by different routes[3,4] and both transformed into ellipticine[3,4] and (**2a**) into 5,11-differently substituted analogues;[4] the *N*-methyl (**2c**) and *N*-benzyl (**2d**) quinones correspondingly gave[3] *N*-substituted ellipticines. Clearly compounds of the pyrido-carbazole-quinone type have considerable potential for the synthesis of ellipticine analogues and we describe here a simple method for their synthesis.

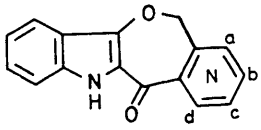
The four pyrido-oxepino-indolones (**3**), available[1] from precursors (**4**) *via* efficient cyclisations involving intramolecular indole-β-nucleophilic substitution reactions, were transformed, with varying speed but eventually in each case, in good yield into the quinones (**5**) by refluxing in



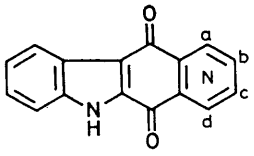
(1)



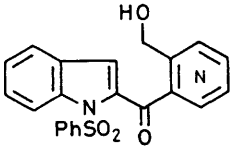
(2) R
a; H
b; $MeOCH_2$
c; Me
d; $PhCH_2$



(3)



(5)



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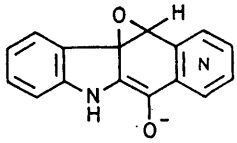
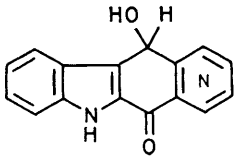


(6)



(7)

MeOH–3M aq. NaOH (2:1) in the presence of air. Thus the quinone (**5**, N at position a) (89% after 12 h reflux) had m.p. 365 °C, decomp., λ_{max} (EtOH–NaOH) 272, 327, and 445 nm (log ϵ 4·23, 4·16, and 3·75); the quinone[4] (**5**, N at position b) (46% after 93 h reflux), was identical to that obtained previously;[4] the quinone (**5**, N at position c) (76% after 1 h reflux) had m.p. 317—320 °C, λ_{max} (EtOH–NaOH) 270, 303, and 450 nm (log ϵ 4·30, 4·37, and 3·72); and the quinone (**5**, N at position d) (71% after 33 h reflux) had m.p. 315—319 °C, λ_{max} (EtOH–NaOH) 260, 330, and 448 nm (log ϵ 4·26, 4·06, and 3·72).

The two quinones which formed most readily, (**5**, N at c and a), were those in which the pyridine nitrogen was γ- (1 h reflux) or α- (12 h reflux) to the methylene of the methylene-oxy-bridge respectively. Because of this we envisage the transformations as involving initial deprotonation at the methylene and then the intermediacy of (**6**) and (**7**) which were aerially oxidised.

We thank the S.R.C. for maintenance grants (W.R.A. and M.G.B.) and Glaxo Group Research Limited, Ware, for their interest and support in that part of this work (M.G.B.) which was undertaken as part of an S.R.C. CASE project.

(*Received*, 24*th June* 1981; *Com.* 741.)

[1] For Part 3 of the series Indole-β-nucleophilic Substitution, see M. G. Beal, W. R. Ashcroft, M. M. Cooper, and J. A. Joule, *J. Chem. Soc., Perkin Trans.* 1, 1981, submitted for publication.

[2] For a review see M. Sainsbury, *Synthesis*, 1977, 437 and for recent contributions see R. B. Millar and T. Moock, *Tetrahedron Lett.*, 1980, 3319; J. Bergman and H. Goonewardena, *Acta. Chem. Scand., Sect. B*, 1980, **34**, 763; references 3 and 4 and references contained therein.

[3] M. Watanabe and V. Snieckus, *J. Am. Chem. Soc.*, 1980, **102**, 1457.

[4] D. A. Taylor, M. M. Baradarani, and J. A. Joule, *J. Chem. Research*, 1979, (*S*), 387; (*M*), 4801.