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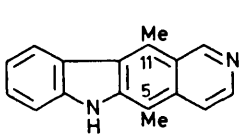
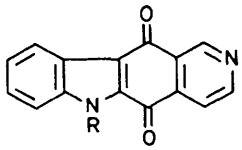
Summary 6*H*-Pyrido[*x'*,*y'*: 5,6]oxepino[3,2-*b*]indol-5-(12*H*)-ones (**3**) are efficiently converted by hot alcoholic base in air into the corresponding 5*H*-pyrido[*x*,*y*-*b*]-carbazole-5,11(6*H*)-diones (**5**).

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.

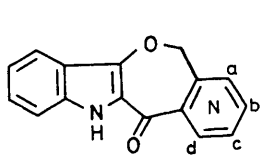
The four pyrido-oxepino-indolones (**3**), available[1] from precursors (**4**) *via* efficient cyclisations involving intramolecular indole-β-nucleophilic substitution reactions, were transformed, with varying speed but eventually in each case, in good yield into the quinones (**5**) by refluxing in



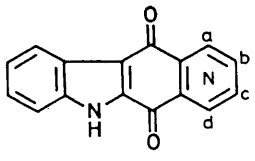
(1)



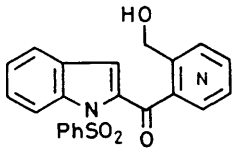
(2) R
a; H
b; $MeOCH_2$
c; Me
d; $PhCH_2$



(3)



(5)



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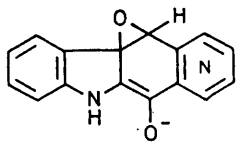
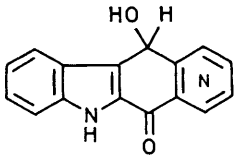


(6)



(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.

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[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.