

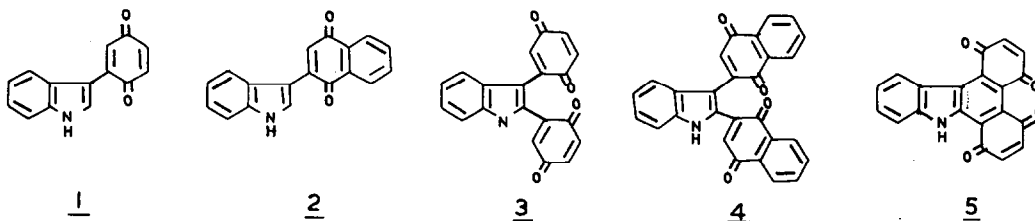
A REINVESTIGATION OF THE REACTION OF INDOLE WITH 1,4-QUINONES

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(Received in UK 12 February 1974; accepted for publication 4 March 1974)

In 1951, Bu'Lock and Harley-Mason¹ reported the formation of two types of adducts from the reaction of indole with 1,4-quinones and proposed indol-3-yl quinone structures 1 and 2 for 1:1 adducts and indol-2,3-ylene bisquinone structures 3 and 4 for 1:2 adducts. Bruce, in 1959², proved the structure of the 1:1 adduct obtained from indole and 1,4-benzoquinone to be 1 by an unambiguous synthesis; thus the structure 2 for the 1:1 adduct obtained from 1,4-naphthoquinone also seems secure.



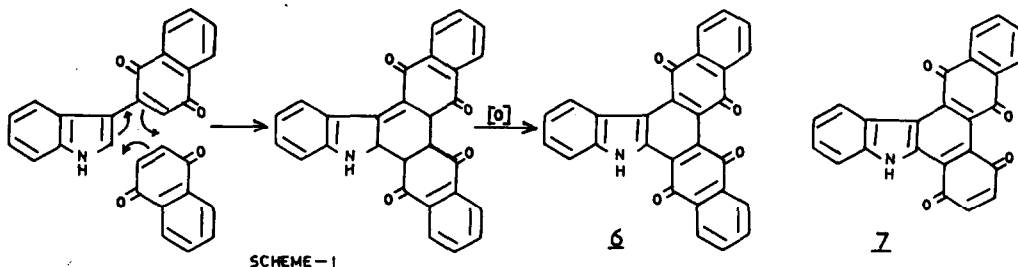
Regarding the structure of 1:2 adducts the assignment of structures 3 and 4 is having no firm evidence and this formulation seems rather insecure, as its formation requires two consecutive nucleophilic additions of indole through positions-2 and 3 on the two quinone moieties. In indole, position-3 is considered to possess the highest reactivity in nucleophilic additions and in indol-3-yl quinones 1 and 2 this reactivity should be transmitted to the quinone part as the vinylic double bond and one of the carbonyl groups are in conjugation with the lone pair of electrons on nitrogen.

Hence an alternative path, worth considering, is the one involving Diels-Alder type cycloaddition, as in scheme-1, between indol-3-yl quinone and the quinone molecule when the final product may be in the fullest aromatic oxidation state. The importance of this path becomes more obvious because of the known reactivity of 3-vinyl indoles with different dienophiles like 1,4-naphthoquinone³, diethylazodicarboxylate⁴ etc., yielding Diels-Alder type adducts.

In order to get better insight into the mode of formation, the structures of these compounds were reinvestigated and it was found that the structures 3 and 4 have to be revised to 5 and 6 respectively, on the basis of the spectral properties.

1:1 adduct¹ 2: m.p. 176°, $\lambda_{\max}^{\text{THF}}(\log \epsilon)$ 224(4.49), 273(4.34), 283(4.35) and 490(3.84); ν_{\max}^{KBr} 3220(NH), 1670(unconjugated CO) and 1630 cm^{-1} (conjugated CO), m/e 273(M⁺).

1:2 adduct¹ 6: m.p. 359-60°; $\lambda_{\max}^{\text{THF}}(\log \epsilon)$ 224(4.64), 260(4.70), 307(4.43) and 385(4.16); ν_{\max}^{KBr} 3400(NH), 1665(CO) and 1645 cm^{-1} (bonded CO). The PMR spectrum of this compound could not be recorded as it was very sparingly soluble in common organic solvents. The mass spectrum showed the molecular ion at m/e 427 which agrees with the molecular weight of structure 6 and not with the formulation 4 which requires the molecular ion at m/e 429.



Similarly the adduct 7: m.p. 325°, $\lambda_{\max}^{\text{THF}}(\log \epsilon)$ 224(4.68), 255(4.62) 299(4.41) and 394(4.12); ν_{\max}^{KBr} 3360(NH), 1680(CO), 1660(CO), 1650 cm^{-1} (bonded CO); prepared from 2-(indol-3-yl)-1,4-naphthoquinone 2 and 1,4-benzoquinone gave the molecular ion at m/e 377 agreeing with structure 7.

The 1:2 adduct¹ 5: m.p. above 360°, $\lambda_{\max}^{\text{THF}}(\log \epsilon)$ 224(4.54)^S, 238(4.59), 256(4.43)^S, 298(4.14) and 400(3.97); ν_{\max}^{KBr} 3310(NH), 1680(CO) and 1660 cm^{-1} (bonded CO); gave the molecular ion at m/e 327 suggesting structure 5.

The IR spectra of these carbazole derivatives 5, 6 and 7 were comparable with certain analogous compounds reported in the literature⁵. All the above compounds gave satisfactory elemental analysis.

The author thanks Dr.G.S.Sidhu for helpful discussions and Dr.V.M. Girijavallabhan, Imperial College, London, for the mass spectra.

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