Oxidative Coupling: Phenoxonium-ion Intermediates in Phenol Oxidation

By J. W. A. FINDLAY, PADMA GUPTA, and J. R. LEWIS*
(*Chemistry Department, The University, Aberdeen,* AB9 2UE)

OXIDATION of 2,3′-dihydroxybenzophenones (I; $R^1 = R^2 = R^3 =$ H or OH) with either aqueous alkaline potassium ferricyanide or aqueous acetone–potassium permanganate solutions affords either one or two xanthones (II and III; $R^1 = R^2 = R^3 =$ H or OH) (arising from *para*- or *ortho*-cyclisation) depending upon the stability of the respective xanthones in the oxidising media.[1] The failure of the corresponding 2-hydroxy-3-methoxybenzophenones (IV; $R^1 = R^2 =$ H or OH) to cyclise under these conditions was considered evidence for the production of radical intermediates in the oxidations.[1]

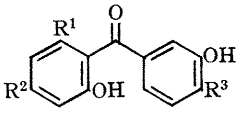
We have now found that dichlorodicyanobenzoquinone (DDQ) will oxidise 2-hydroxy-3′-methoxybenzophenones (IV; $R^1 = R^2 =$ H or OH) to the corresponding methoxyxanthones (V and VI, $R^1 = R^2 =$ H or OH) (see Table). In all cases both *para*- and *ortho*-cyclised products were isolated.

It is evident from the previously reported[2] conversion of 4-methoxy-2,6-di-t-butylphenol to 2,6-di-t-butylbenzoquinone by DDQ, that a phenoxonium ion is involved as an intermediate and this is substantiated by the present oxidations involving a hydroxy- and a methoxy-group. Dichlorodicyanobenzoquinone also oxidises the hydroxybenzophenones to xanthone mixtures, *i.e.* (I) → (II) and (III). Here radical-intermediates are most likely involved owing to their less energetic generation.[3]

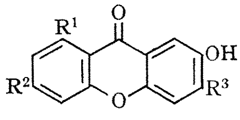
TABLE

Benzophenone	Xanthone (% yield) *ortho*	*para*
2-Hydroxy-3′-methoxy-	11	15
2,3′-Dihydroxy-	5·5	11
2,4,6-Trihydroxy-3′-methoxy-	10	19
2,3′,4,6-Tetrahydroxy-	12	35
2,3,-4,4′,6-Penthaydroxy-	6	28

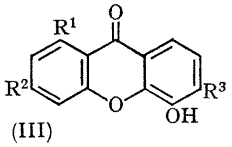
We thank the S.R.C. for an Assistantship (P.G.) and a Studentship (J.W.A.F.).



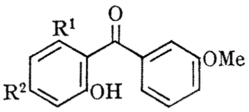
(I)



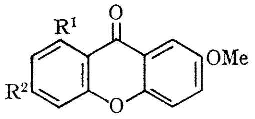
(II)



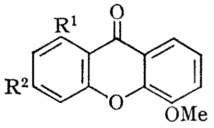
(III)



(IV)



(V)



(VI)

(*Received, December* 30*th*, 1968; *Com.* 1808.)

---

[1] J. E. Atkinson and J. R. Lewis, *J. Chem. Soc.* (*C*), 1969, 281.

[2] H. D. Becker, *J. Org. Chem.*, 1965, **30**, 982.

[3] D. H. R. Barton, *Chem. in Britain*, 1967, 330.