Oxidative Coupling: *ortho/para*-Cyclisation of Hydroxybenzophenones

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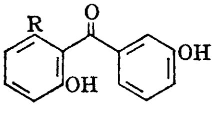
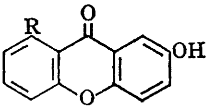
IN continuing our studies on the conversion of benzophenones into xanthones,[1] we have examined several oxidations designed to give a synthesis of naturally occurring xanthones, and find that oxidative coupling occurs in the *ortho*- and in the *para*-position without the necessity for blocking groups to be present to direct the position of ring closure.[2]

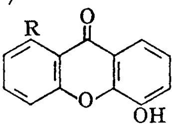
Thus oxidation of 2,3′-dihydroxybenzophenone (I; R = H) at pH 13, with aqueous potassium ferricyanide in excess, gave 2-hydroxyxanthone (II; R = H) (53%) together with 4-hydroxyxanthone (III; R = H) (10%).



(I)



(II)



(III)

Oxidation of 2,3′,6-trihydroxybenzophenone† (I; R = OH) in aqueous acetone with potassium permanganate furnished 1,7-dihydroxyxanthone (II; R = OH) (32%) together with 1,5-dihydroxyxanthone (III; R = OH) (5%). Ferricyanide was ineffective on this phenol.

Under similar conditions 2,3′,4,6-tetrahydroxybenzophenone and 2,3′,4,4′,6-pentahydroxybenzophenone (maclurin) produced only the *para*-cyclised xanthone in 66% and 67% yield respectively, pH and the amount of oxidising agent being critical factors in obtaining satisfactory results.

The utility of these conversions as a biogenetic pathway is further strengthened by the isolation of 2- and 4-hydroxyxanthone together with 1,5- and 1,7-dihydroxyxanthone from *Mammea americana*[3] and of 1,3,6,7- and 1,3,5,6-tetrahydroxyxanthone together with maclurin from *Symphonia globulifera*.[4] Other hydroxylated xanthones suggesting *ortho*- or *para*-cyclisation of a benzophenone intermediate may be seen in a recent publication listing naturally occurring xanthones.[4]

It has also been found that benzophenones are converted into xanthones by enzymic oxidations utilising peroxidase or the laccase from *Polystictus versicolor*. Thus 2,3′-dihydroxybenzophenone (I; R = H) on incubation for 3 days with either peroxidase or the laccase gave a mixture of 2- and 4-hydroxyanthone; 2,3′,4,6-tetrahydroxybenzophenone under similar incubation gave 1,3,7-trihydroxyxanthone only. Yields in these enzymic oxidations were low, *ca.* 5%.

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† Satisfactory analyses and spectra have been obtained from all new compounds.

[1] Previous Paper: J. R. Lewis and B. H. Warrington, *J. Chem. Soc.*, 1964, 5074.

[2] D. F. Bowman and F. R. Hewgill, *Chem. Comm.*, 1967, 471.

[3] R. D. Finnegan, J. K. Patel, and P. L. Bachman, *Tetrahedron Letters*, 1966, 6087.

[4] H. D. Locksley, I. Moore, and F. Scheinmann, *Tetrahedron*, 1967, **23**, 2229.