Total Syntheses of Diosindigo B, Mamegakinone, Biramentaceone, and Rotundiquinone

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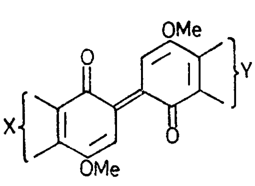
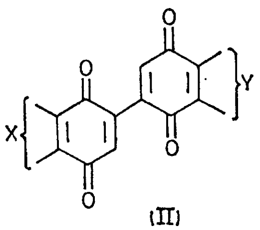
Summary 4-Methoxy-7-methylnaphthalene-1,5-diol, prepared *via* a new selective acetylation procedure, is oxidised by lead(IV) oxide to diosindigo B (Ia) which on further oxidation with nitric acid affords biramentaceone (IIa); related reactions produce mamegakinone (IIb) and rotundiquinone (IIc).

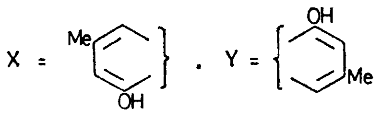
We recently isolated a new bisnaphthaleneindigo, diosindigo B (Ia), from the wood of *Diospyros celebica* Bakh (Macassar ebony) and sought to synthesise it using a modification of the sequence which was successful in the preparation of the isomeric compound diosindigo A (Ib).[1] In that case the selective methylation of the C-1 hydroxy group of 7-methylnaphthalene-1,4,5-triol (III; $R^1 = R^2 = R^3 = H$) gave the 1-methoxy-4,5-diol (III; $R^1 = Me$, $R^2 = R^3 = H$) which when treated with lead(IV) oxide gave (Ib). For the preparation of (Ia) the necessary intermediate was the 4-methoxy-1,5-diol (III; $R^1 = R^3 = H$, $R^2 = Me$) and we therefore developed a method which permits the selective methylation of the C-4 hydroxy group of (III; $R^1 = R^2 = R^3 = H$).



(I)



(II)

a;


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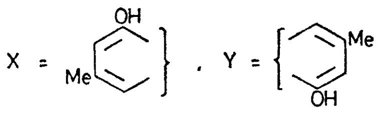

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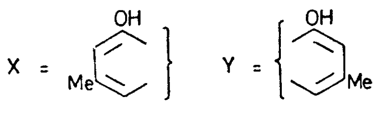
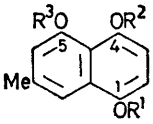
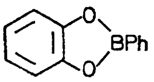
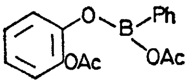




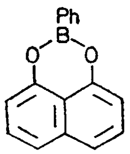
(III)



(IV)



(V)



(VI)

A dihydric phenol with hydroxy groups on adjacent carbon atoms readily forms a cyclic phenylboronate and we have found that acetylation of the latter followed by treatment with water gives the corresponding acetoxyphenol. Thus treatment of (IV)[2] with acetic anhydride and anhydrous sodium acetate at 20 °C for 2 h, followed by warm water, gave 2-acetoxyphenol (52%). The initial product is presumably the mixed anhydride (V) which would undergo hydrolysis readily. A similar reaction with (VI)[2] was significantly slower but, after 27 h, gave 8-acetoxy-1-naphthol (37%). Acetylation of the related phenylboronate prepared from (III; $R^1 = R^2 = R^3 = H$) gave the expected mixture of (III; $R^1 = R^2 = Ac$, $R^3 = H$) and (III; $R^1 = R^3 = Ac$, $R^2 = H$) which we treated with ethereal diazomethane. Fractional crystallisation of the resulting mixture of monomethyl ethers gave, as the major product, (III; $R^1 = R^3 = Ac$, $R^2 = Me$) which on alkaline hydrolysis and subsequent treatment in $CHCl_3$ with lead(IV) oxide gave (Ia). On being treated with 4 M HNO_3 the latter underwent oxidative demethylation in high yield to give (IIa) while a similar oxidation of (Ib) afforded (IIb), so confirming the structures assigned[3,4] to these symmetrical bisnaphthoquinones.

Using related reactions we have also synthesised the unsymmetrical bisnaphthoquinone (IIc) which was recently reported[5] to be present in the wood of *Diospyros rotundifolia*. Alkaline hydrolysis of a 1 : 1 mixture of (III; $R^1 = Me$, $R^2 = R^3 = Ac$)[1] and (III; $R^1 = R^3 = Ac$, $R^2 = Me$) followed by oxidation of the resulting mixture of methoxy-diols with lead(IV) oxide gave a mixture of the symmetrical diosindigos A and B and their unsymmetrical counterpart (Ic) which was separated into its components by t.l.c. Oxidation of the last named compound with 4 M HNO_3 afforded (IIc).

(*Received*, 22*nd January* 1976; *Com.* 065.)

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