

Syntheses of Naphtho[2,3-*c*]pyran-5,10-quinones using Ceric Ammonium Nitrate

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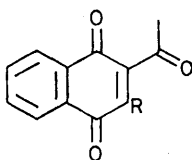
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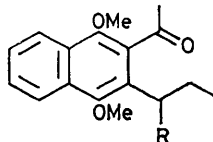
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Summary Two 2-(alk-1-enyl)-3-(1-hydroxyalkyl)-1,4-dimethoxynaphthalenes are oxidised with silver(II) oxide to the corresponding naphthoquinones, while oxidation with cerium(IV) ammonium nitrate affords derivatives of the title compounds.

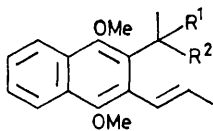
VARIOUS natural quinones containing the naphtho[2,3-*c*]pyran ring system have been identified. These include the eleutherins,^{1,2} ventilagone,³ the nanaomycins^{4,5} and related compounds,⁶ and the aphid pigments.⁷ We report here a convenient synthesis of the ring system.



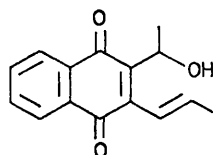
- (1) R = H
(2) R = Prⁿ



- (3) R = H
(4) R = Br



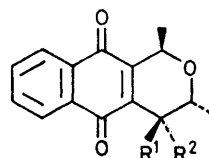
- (5) R¹, R² = O
(6) R¹ = H, R² = OH



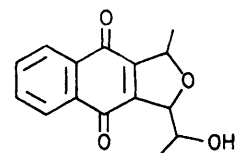
(7)

2-Acetyl-1,4-naphthoquinone (**1**)⁸ was propylated with butanoic acid in the presence of silver nitrate and potassium peroxodisulphonate⁹ to afford the quinone (**2**)† (55%). Reductive methylation gave the naphthalene (**3**)† (100%), which was brominated with *N*-bromosuccinimide to give the benzylic bromide (**4**). This was converted into the *trans*-olefin (**5**)† [61% from (**3**)] with 1,5-diazabicyclo[4.3.0]non-5-ene, and the ketone (**5**) was in turn reduced to the corresponding alcohol (**6**)† (96%) using sodium borohydride.

Oxidative demethylation¹⁰ by silver(II) oxide of the naphthalene dimethyl ether (**6**) provided as the only product the quinonoid alcohol (**7**)† (59%), which did not undergo spontaneous cyclisation to a demethoxy-eleutherin. Alternatively, oxidation of the same dimethyl ether (**6**) with



- (8) R¹ = OH, R² = H
(9) R¹ = H, R² = OH
(10) R¹ = OAc, R² = H
(11) R¹ = H, R² = OAc

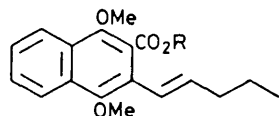


(12)

ceric ammonium nitrate¹¹ afforded a mixture of the two naphthopyranquinones‡ (**8**)† (20%) and (**9**)† (59%), 7,9-dideoxy-analogues of quinones A and A'.¹² None of the quinone (**7**) was observed in the latter oxidation. Assignments (**8**) and (**9**) were distinguished from the alternative (**12**) on the basis of a comparison of the ¹H n.m.r. spectra of

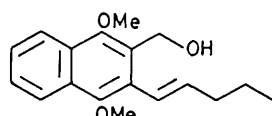
† All new compounds gave satisfactory elemental analyses and their spectroscopic data were in accord with the assigned structures.

‡ Compounds depicted as single enantiomers represent racemates.

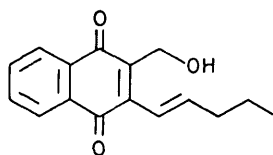


(13) R = H

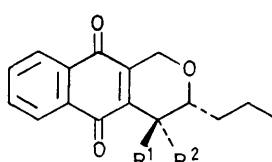
(14) R = Me



(15)



(16)

(17) R¹ = OH, R² = H(18) R¹ = H, R² = OH

the former pair and those of their respective acetates (**10**) and (**11**),[†] while individual assignments for compounds (**8**) and (**9**) were made from the distinctive coupling constants published for quinones A and A'.¹³

A second example supported the generality of the oxidative cyclisation. Thus the methyl ester (**14**)[†] of the *trans*-unsaturated acid (**13**)¹⁴ was reduced to the alcohol (**15**)[†] (89%) with lithium aluminium hydride. Silver(II) oxide oxidation of (**15**) afforded only the quinonoid alcohol (**16**)[†] (62%), whereas ceric ammonium nitrate oxidation of the alcohol (**15**) gave a mixture of the naphthopyranquinones[‡] (**17**)[†] (22%) and (**18**)[†] (32%). In this latter reaction some of the alcohol (**16**) (29%) was also observed.

The acid (**13**) did not yield readily identifiable products with either oxidant.

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