Dienone-Phenol Rearrangement of Naphthalenetriones. A Route to 10-Acetoxy-5,6,7,8-tetrahydrophenanthrene-1,4-diones

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Naphthalene-1,4,5(8*H*)-triones (**17**) and (**18**) prepared in a three-step approach from the corresponding acylbenzoquinones (**1**) and (**2**), undergo an unusually rapid dienone-phenol rearrangement in acetic anhydride–sulphuric acid solution to give 5-acetoxy-7,8-dimethyl- and 5-acetoxy-6,7,8-trimethyl-1,4-naphthoquinone (**19**) and (**20**) in good yields.

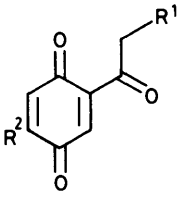
Starting from the acylbenzoquinones (**1**), (**2**), and (**3**) the spironaphthalenetriones, (**30**), (**31**), and (**32**) were synthesized through the following sequence: (a) addition of enamine (**6**) to acylquinones, (b) acid-catalysed rearrangement of the spirobenzofurans (**23**), (**24**), and (**25**), and (c) oxidation, with silver carbonate–Celite reagent, of spironaphthalenones (**27**), (**28**), and (**29**) generated in the latter step. Quinones (**30**), (**31**), and (**32**) were subjected to dienone-phenol rearrangement to produce the corresponding angular tricyclic quinones (**33**), (**34**), and (**35**) in high yields.

The dihydroxyspironaphthalenone (**27**) afforded the substituted phenanthrene (**36**) under dienone-phenol rearrangement conditions. However, the structurally related naphthalenones (**13**) and (**14**) are unreactive to this isomerisation.

Previous work in our laboratory has been concerned with the acid-induced rearrangement of cyclic *O,N*-acetals derived from acylbenzoquinones and enamines.[1–5] This transformation provides entry into the preparation of carbocyclic quinones and quinone precursors by using the appropriate substrates. For example, the *O,N*-ketal (**7**) prepared from 2-acetyl-1,4-benzoquinone (**1**) and enamine (**4**) produces the dione (**9**) by acid-catalysed rearrangement.[4]

Our interest in the synthesis of angular tricyclic quinones which could serve as precursors of tetracyclic quinones related to the rabelomicine antibiotic (**11**)[6] led us to explore the preparation of phenanthrenedione (**10**) from (**8**) employing the above rearrangement. However, the cyclic *O,N*-ketal (**8**) under acidic conditions afforded dibenzofuran (**12**). The behaviour of the ketals (**7**) and (**8**) in acid medium has been explained on the basis of their configurations.[4]

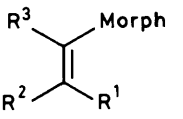
Here we report the synthesis of some 5,6,7,8-tetrahydrophenanthrene-1,4-diones oxygenated at position 10 starting from cyclic *O,N*-acetals containing a spirocyclopentane substituent on the furan ring. The strategy to construct the tricyclic skeleton involves a sequence of two highly efficient acid-induced rearrangement reactions. A preliminary communication of this work has been published.[7]



(**1**) $R^1 = R^2 = H$

(**2**) $R^1 = Me$, $R^2 = H$

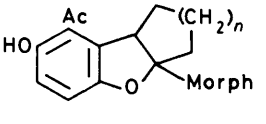
(**3**) $R^1 = H$, $R^2 = Me$



(**4**) $R^1 = H$, $R^2 - R^3 = (CH_2)_3$

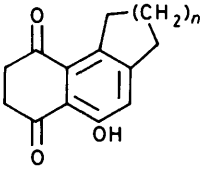
(**5**) $R^1 = R^2 = Me$, $R^3 = H$

(**6**) $R^1 - R^2 = (CH_2)_4$, $R^3 = H$



(**7**) $n = 1$

(**8**) $n = 2$



(**9**) $n = 1$

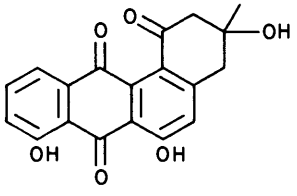
(**10**) $n = 2$

Results and Discussion

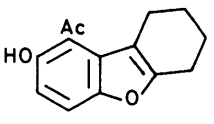
The possibility of constructing angular tricyclic quinones employing cyclic *O,N*-acetal chemistry arose when the Thiele-Winter reaction[8] was attempted on quinone (**17**). In fact, when quinone (**17**), easily obtained by oxidation of the naphthalenone (**13**) with silver carbonate–Celite reagent, was treated under usual Thiele-Winter acetoxylation conditions, a fast reaction occurred and the rearranged quinone (**19**) was isolated in 79% yield.

The structure of compound (**19**) was established by i.r. carbonyl absorptions at 1 760 and 1 650 cm^{-1} and by the resonances for the three methyl groups (δ 2.42, 2.43, and 2.61 p.p.m.), the aromatic proton (δ 7.14 p.p.m.), and the AB pattern of the quinone protons [δ 6.71 (d) and 6.80 (d) p.p.m.] with a coupling constant of 10 Hz in the ^1H n.m.r. spectrum.

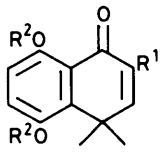
It was evident that naphthoquinone (**19**) was formed *via* a dienone-phenol rearrangement[9] from naphthalenetrione (**17**).



(**11**)



(**12**)

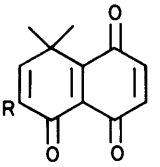


(13) $R^1 = R^2 = H$

(14) $R^1 = Me$, $R^2 = H$

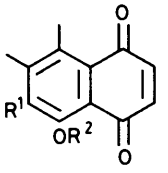
(15) $R^1 = H$, $R^2 = Ac$

(16) $R^1 = Me$, $R^2 = Ac$



(17) R = H

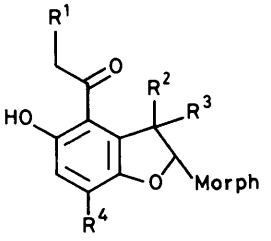
(18) R = Me



(19) $R^1 = H$, $R^2 = Ac$

(20) $R^1 = Me$, $R^2 = Ac$

(21) $R^1 = R^2 = H$

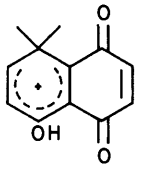


(22) $R^1 = R^2 = R^3 = Me$, $R^4 = H$

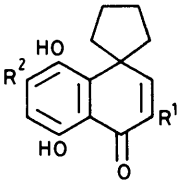
(23) $R^1 = R^4 = H$, $R^2 - R^3 = (CH_2)_4$

(24) $R^1 = Me$, $R^2 - R^3 = (CH_2)_4$, $R^4 = H$

(25) $R^1 = H$, $R^2 - R^3 = (CH_2)_4$, $R^4 = Me$



(26)



(27) $R^1 = R^2 = H$

(28) $R^1 = Me$, $R^2 = H$

(29) $R^1 = H$, $R^2 = Me$

In order to extend this potentially useful transformation, naphthalenetrione (**18**) was synthesized from 2-propionyl-1,4-benzoquinone (**2**) and enamine (**5**).

The reaction of these substrates in dichloromethane solution at room temperature furnished the cyclic *O*,*N*-acetal (**22**), which by acid-catalysed rearrangement in boiling ethanol solution afforded the naphthalenone (**14**). When quinone (**18**) prepared in 93% yield by oxidation of compound (**14**) with silver carbonate–Celite reagent was treated with acetic anhydride–sulphuric acid solution a clean reaction occurred and the expected product (**20**) was isolated in 80% yield.

On the basis of these results, we investigated the possibility of inducing quinone (**17**) to undergo dienone-phenol rearrangement under non-acylating conditions to produce, in one synthetic step, the corresponding substituted juglone (**21**). However, when (**17**) was treated with acetic acid–sulphuric acid and methanol–hydrochloric acid solutions, no reaction was observed (t.l.c.) at room temperature nor under reflux conditions.

The reluctance of quinone (**17**) to undergo dienone-phenol rearrangement was at first rather surprising; however this result may be explained by taking into account the dienone-phenol reaction mechanism. Kinetic evidence of the rearrangement of cyclohexadienones in aqueous sulphuric and perchloric acid had firmly established the existence of a cyclohexadienyl cation produced in a step prior to the isomerisation.[10,11]

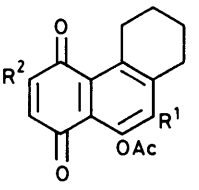
Extension of this mechanism to the acid–catalysed rearrangement of (**17**) in acetic acid or methanol requires the formation of cation (**26**), generated by protonation of the substrate on the carbonyl group at position 5. It is reasonable to assume that formation of intermediate (**26**) is unfavourable because of the presence of two carbonyl deactivating groups, which destabilise the carbonium ion character of the intermediate, preventing the 1,2 migration.

We have no explanation why the dienone-phenol rearrangement of quinones (**17**) and (**18**) is favoured in acetic anhydride solutions, but it is evident that in this medium more stabilised intermediates are involved in the isomerisation. A kinetic study of these reactions is under way in order to shed some light on the course of the dienone-phenol rearrangement in acid anhydride solution.

(30) $R^1 = R^2 = H$

(31) $R^1 = Me$, $R^2 = H$

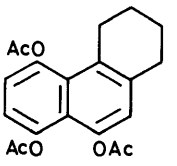
(32) $R^1 = H$, $R^2 = Me$



(33) $R^1 = R^2 = H$

(34) $R^1 = Me$, $R^2 = H$

(35) $R^1 = H$, $R^2 = Me$



(36)

In order to capitalize on the ready dienone-phenol rearrangement observed in quinones (**17**) and (**18**) in acetic anhydride solution, we attempted to apply these results to the synthesis of the angular tricyclic quinone (**33**). A retrosynthetic analysis of quinone (**33**) based on the rearrangement reactions described above requires the use of enamine (**6**). The preparation of compound (**6**) was achieved by the reaction of cyclopentanecarbaldehyde with morpholine using Stork's procedure.[12]

The reaction of this enamine (**6**) with acetylquinone (**1**) in dichloromethane yielded, in 73%, the expected cyclic *O*,*N*-acetal (**23**). Subsequent treatment of heterocycle (**23**) in boiling ethanol containing hydrochloric acid afforded the spironaphthalenone (**27**) in 70% yield. The latter compound was oxidised with silver carbonate–Celite reagent in dichloromethane to give the quinone (**30**) in 70% yield. Finally, quinone (**30**) was subjected to ring expansion in acetic anhydride–sulphuric acid to produce the desired angular tricyclic quinone (**33**) in 87% yield.

The successful construction of angular quinone (**33**) through the aforementioned four-step approach prompted us to extend this synthetic sequence to the preparation of analogues (**34**) and (**35**). The required spirobenzo[*b*]furans (**24**) and (**25**) were prepared in 65 and 60% yields, by reaction of enamine (**6**) with 2-propanoyl- and 2-acetyl-5-methyl-1,4-benzoquinone (**2**) and (**3**). Heterocycles (**24**) and (**25**) were isomerised, under the usual conditions, to the spironaphthalenones (**28**) and (**29**); subsequent oxidation afforded the corresponding quinones (**31**) and (**32**) in good yields. The dienone-phenol rearrangement of substrates (**31**) and (**32**) was carried out under the standard conditions, and the rearranged products (**34**) and (**35**) were obtained in 80 and 82% yields respectively.

An interesting result appeared when a crude sample of quinone (**30**) containing the precursor (**27**) as impurity was subjected to dienone-phenol rearrangement in acetic anhydride–sulphuric acid. The ^{1}H n.m.r. spectrum of the crude product displayed the resonance absorptions of the angular quinone (**33**) accompanied by the signals of a secondary product which were attributed to tetrahydrophenanthrene (**36**). The detected dienone-phenol rearrangement of the naphthalenone (**27**) to produce compound (**36**) was verified in a separate experiment. Thus, naphthalenone (**27**) was treated with acetic anhydride–sulphuric acid solution and the rearranged product (**36**) was obtained in 70% yield.

In order to induce a similar isomerisation, substrates (**13**) and (**14**) were made to react under the usual conditions; however, the respective diacetates (**15**) and (**16**) were generated instead of the dienone-phenol rearrangement products.

The ability of the naphthalenone (**27**) to produce the isomerisation, in contrast with the inertness of structurally related naphthalenones (**13**) and (**14**), may be attributed to the strain imposed by the spiro substituent on the former compound; such strain is alleviated by ring expansion.

In summary, we have developed a novel and efficient route for the preparation of 5,6,7,8-tetrahydrophenanthrene-1,4-diones from acylbenzoquinones through a four-step approach mediated by two well known rearrangement reactions. Diels–Alder reactions of angular tricyclic quinone (**31**) and related quinones with oxygenated dienes, directed towards the construction of angular tetracyclic analogues of rabelamicine (**11**) are in progress.

Experimental

M.p.s were determined with a Kofler hot-stage apparatus and are uncorrected. Unless otherwise stated, i.r. spectra were recorded on a Perkin-Elmer 1310 spectrophotometer for KBr discs and u.v. visible spectra were recorded on a Pye-Unicam SP-1800 spectrophotometer. ^{1}H N.m.r. spectra were measured on a Varian XL-100 spectrometer. Samples were dissolved in $CDCl_3$ and chemical shifts are expressed in p.p.m. downfield from $SiMe_4$. Mass spectra were recorded on a Varian MAT-111 spectrometer. Elemental analyses were performed by the Consejo Superior de Investigaciones Cientificas, Madrid. Unless otherwise stated, all organic extracts were washed with water, dried over $MgSO_4$, and evaporated under reduced pressure.

8,8-*Dimethylnaphthalene*-1,4,5(8H)-*trione* (**17**).—A mixture of compound (**13**)[3] (500 mg, 2.45 mmol), silver carbonate–Celite reagent[13] (2.5 g, 4.38 mmol), and magnesium sulphate (1.0 g) was vigorously stirred at room temperature in dichloromethane solution (30 ml) for 15 min, then filtered and evaporated to dryness. The resultant red-orange quinone (**17**) (470 mg, 95%), essentially pure by t.l.c., was recrystallised from cyclohexane, m.p. 146—147 °C (Found: C, 71.6; H, 5.0. Calc. for $C_{12}H_{10}O_3$: C, 71.3; H, 5.0%); $\nu_{max.}$ 1 680, 1 660, and 1 640 cm^{-1}; δ_H 1.58 (6 H, s, Me_2C), 6.34 (1 H, d, *J* 10 Hz, 6-H), 6.77 (1 H, d, *J* 10 Hz, 7-H), and 6.75 (2 H, s, 2- and 3-H).

5-*Acetoxy*-7,8-*dimethyl*-1,4-*naphthoquinone* (**19**).—Quinone (**17**) (400 mg, 1.98 mmol) was added at room temperature to a stirred solution of acetic anhydride (5 ml) and concentrated sulphuric acid (6 drops). The red solution was stirred for 5 min and then poured into a mixture of ice–water; the product was filtered off, and washed with water to give (**19**) (384 mg, 79%). The title compound was purified by sublimation *in vacuo* to afford yellow crystals, m.p. 102—104 °C (Found: C, 68.9; H, 5.0. Calc. for $C_{14}H_{14}O_4$: C, 68.9; H, 4.95%); $\nu_{max.}$ 1 760 and 1 655 cm^{-1}; δ_H 2.42 (3 H, s, Me), 2.43 (3 H, s, Me), 2.61 (3 H, s, Me), 6.71 (1 H, d, *J* 10 Hz, =CH), 6.80 (1 H, d, *J* 10 Hz, =CH), and 7.14 (1 H, s, 6-H); *m/z* 244 (M^+).

5-*Hydroxy*-3,3-*dimethyl*-2-*morpholino*-4-*propionylbenzo*[b]-*furan* (**22**).—A solution of quinone (**2**)[14] (1.18 g, 11.5 mmol) in dichloromethane (50 ml) was added dropwise to a stirred solution of enamine (**5**) (1.17 g, 12.5 mmol) in dichloromethane (50 ml) at 5 °C, and the mixture stirred for 1 h at room temperature. The resulting solution was evaporated to dryness and the residue was filtered through silica gel. Elution with benzene–diethyl ether (1:1) and evaporation of the solvents gave product (**22**) as a yellow oil which was taken up in hot cyclohexane and cooled to obtain the benzofuran (**22**) (1.75 g, 50%) as colourless crystals, m.p. 133—134 °C (Found: C, 66.8; H, 7.9; N, 4.7. Calc. for $C_{17}H_{23}O_4N$: C, 66.9; H, 7.6; N, 4.6%); $\nu_{max.}$ 3 310 and 1 670 cm^{-1}; δ_H 1.18 (3 H, t, *J* 8 Hz, Et), 1.26 (3 H, s, 3-Me), 1.37 (3 H, s, 3-Me), 2.4—2.8 (4 H, CH_2N), 2.90 (2 H, q, *J* 7 Hz, Et), 3.61 (4 H, t, *J* 5 Hz, CH_2O), 4.67 (1 H, s, 2-H), 5.52 (1 H, br, 5-OH), 6.54 (1 H, d, *J* 9 Hz, 6-H), and 6.64 (1 H, d, *J* 9 Hz, 7-H).

5,8-*Dihydroxy*-2,4,4-*trimethylnaphthalen*-1(4H)-*one* (**14**).—A solution of benzofuran (**22**) (490 mg, 1.60 mmol) in ethanol (40 ml) and hydrochloric acid (5 ml) was refluxed for 3 h. The solution was poured into cold water and extracted with chloroform (100 ml). The extract was washed with aqueous sodium hydrogen carbonate and water, dried, and evaporated to dryness. Crystallisation of the residue from benzene yielded the naphthalenone (**14**) (332 mg, 95%), as orange crystals, m.p. 163—164 °C (Found: C, 71.8; H, 6.8. Calc. for $C_{13}H_{14}O_3$: C, 71.5; H, 6.5%); $\nu_{max.}$ 3 326, 1 660, and 1 620 cm^{-1}; δ_H 1.60 (6 H, s, Me_2C), 2.00 (3 H, s, 2-Me), 5.28 (1 H, br s, D_2O exchangeable, 5-OH), 6.67 (1 H, br s, with fine coupling, 3-H), 6.76 (1 H, d, *J* 8 Hz, 7-H), 6.89 (1 H, d, *J* 8 Hz, 6-H), and 13.00 (1 H, s, 8-OH).

7,8,8-*Trimethylnaphthalene*-1,4,5(8H)-*trione* (**18**).—According to the procedure given for the preparation of quinone (**17**), oxidation of naphthalenone (**14**) (360 mg, 1.65 mmol) with silver carbonate–Celite reagent (1.8 g, 3.15 mmol) gave quinone (**18**) (345 mg, 93%). The product crystallised from cyclohexane as a red solid, m.p. 120—121 °C (Found: C, 72.0; H, 5.8. Calc. for $C_{13}H_{12}O_3$: C, 72.2; H, 5.5%); $\nu_{max.}$ 1 680, 1 650, and 1 630 cm^{-1}; δ_H 1.53 (6 H, s, Me_2C), 1.94 (3 H, s, 6-Me), 6.55 (1 H, s, 7-H), and 6.73 (2 H, s, 2- and 3-H).

5-*Acetoxy*-6,7,8-*trimethyl*-1,4-*naphthoquinone* (**20**).—Treatment similar to that described for the preparation of (**19**), converted (**18**) (270 mg, 1.24 mmol) into rearranged quinone (**20**). The crude product was recrystallised from cyclohexane to afford quinone (**20**) (255 mg, 80%) as orange crystals, m.p. 135—137 °C (Found: C, 69.6; H, 5.7. Calc. for $C_{15}H_{14}O_4$: C, 69.8; H, 5.5%); $\nu_{max.}$ 1 760, 1 650, and 1 620 cm^{-1}; δ_H 2.22 (3 H, s, Me), 2.36 (3 H, s, Me), 2.46 (3 H, s, Me), 2.64 (3 H, s, Me), 6.68 (1 H, d, *J* 7 Hz, =CH), and 6.77 (1 H, d, *J* 7 Hz, =CH).

N-*Cyclopentylidenemethylmorpholine* (**6**).—A solution of cyclopentanecarbaldehyde[15] (9 g, 0.09 mol), and morpholine (9.6 g, 0.1 mol) in benzene (110 ml) was heated to reflux for 2 h with a Dean-Stark water separator. The cooled reaction mixture was evaporated to dryness and the liquid residue was distilled at 105—110 °C (water pump) to afford the enamine (**6**) (12 g, 78%). No correct elemental analysis could be obtained and the structure of this compound was assessed by its spectral data; $\nu_{max.}$ 1 630 cm^{-1}; δ_H 1.63 (4 H, m, $=CHCH_2CH_2$), 2.30 (4 H, m, $=CHCH_2CH_2$), 2.81 (4 H, m, CH_2N), 3.71 (4 H, t, *J* 4 Hz, CH_2O), and 5.54 (1 H, m, $=CHCH_2$); *m/z* 167 (M^+).

General Procedure for the Synthesis of the Spirobenzo[b]*furans.*—A solution of the acylquinone in dichloromethane was added dropwise to a stirred solution of enamine (**6**) in benzene solution at 5 °C and stirring was continued for 15 min at room temperature. After this time the solvent was evaporated off and the residue worked up as indicated below.

4-*Acetyl*-5-*hydroxy*-2-*morpholinospiro*[2,3-*dihydrobenzofuran*-3,1′-*cyclopentane*] (**23**) from acetylquinone (**1**)[16] (1.7 g, 11.3 mmol) and (**6**) (2.08, 12.4 mmol). The solid residue was washed with hot cyclohexane and recrystallised from cyclohexane–benzene (4:1) to afford compound (**23**) (2.6 g, 73%) as yellow crystals, m.p. 169—170 °C (Found: C, 68.2; H, 7.4; N, 4.4. Calc. for $C_{18}H_{23}O_4N$: C, 68.1; H, 7.6; N, 4.4%); $\nu_{max.}$ 3 330 and 1 680 cm^{-1}; δ_H 1.5—2.2 (8 H, m, 4 × CH_2), 2.4—2.8 (4 H, m, CH_2N), 2.6 (3 H, s, COMe), 3.61 (4 H, t, *J* 4 Hz, CH_2O), 4.68 (1 H, s, 2-H), 6.55 (1 H, d, *J* 8 Hz, 6-H), and 6.65 (1 H, d, *J* 8 Hz, 7-H). The proton at position 5 was not observed.

5-*Hydroxy*-2-*morpholino*-4-*propionylspiro*[2,3-*dihydrobenzofuran*-3,1′-*cyclopentane*] (**24**) from 2-propionylbenzoquinone (**2**) (1.75 g, 10.6 mmol) and enamine (**6**) (1.96 g, 11.9 mmol). The solid residue was washed with hot cyclohexane and recrystallised from cyclohexane–benzene (4:1) to give compound (**24**) (2.3 g, 65%) as yellow crystals, m.p. 175—176 °C (Found: C, 69.2; H, 7.3; N, 4.3. Calc. for $C_{19}H_{25}O_4N$: C, 68.86; H, 7.6; N, 4.2%); $\nu_{max.}$ 3 320 and 1 690 cm^{-1}; δ_H 1.17 (3 H, t, *J* 7 Hz, Et), 1.4—2.1 (8 H, m, 4 × CH_2), 2.54 (4 H, m, CH_2N), 2.89 (2 H, q, *J* 7 Hz, Et), 3.60 (4 H, t, *J* 4 Hz, CH_2O), 4.67 (1 H, s, 2-H), 5.59 (1 H, br, 5-OH), 6.53 (1 H, d, *J* 8 Hz, 6-H), and 6.63 (1 H, d, *J* 8 Hz, 7-H).

4-*Acetyl*-5-*hydroxy*-7-*methyl*-2-*morpholinospiro*[2,3-*dihydrobenzofuran*-3,1′-*cyclopentane*] (**25**) from acylbenzoquinone (**3**)[17] (1.6 g, 9.8 mmol) and (**6**) (1.8 g, 10.7 mmol). The solid residue was purified with charcoal in cyclohexane–acetone and the required compound (**25**) filtered off as yellow–white crystals (2.12 g, 66%), m.p. 183—185 °C (Found: C, 68.8; H, 7.9; N, 4.2. Calc. for $C_{19}H_{25}O_4N$: C, 68.85; H, 7.6; N, 4.2%); $\nu_{max.}$ 3 300 and 1 675 cm^{-1}; δ_H 1.6—2.7 (12 H, m, 4 × CH_2 and CH_2N), 2.19 (3 H, s, 7-Me), 2.59 (3 H, s, COMe), 3.61 (4 H, t, *J* 4 Hz, CH_2O), 4.68 (1 H, s, 2-H), 6.44 (1 H, s, 6-H), and 6.72 (1 H, s, D_2O exchangeable, 5-OH).

General Procedure for the Synthesis of Spironaphthalenones.—A solution of the spirobenzofuran in ethanol–hydrochloric acid was refluxed until t.l.c. showed that all the substrate had reacted. The reaction mixture was diluted with water and extracted with ethyl acetate. The solvent was evaporated off and the yellow solid residue crystallised as stated below.

5,8-*Dihydroxyspiro*[*cyclopentane*-1,1′-*naphthalen*]-4′-(1′H)-*one* (**27**) (262 mg, 70%) from substrate (**23**) (516 mg, 1.63 mmol); reflux time 9 h; m.p. (sealed capillary) 237—238 °C (toluene); (Found: C, 72.9; H, 6.4. Calc. for $C_{14}H_{14}O_3$: C, 73.0; H, 6.1%); $\nu_{max.}$ 3 180, 1 650, and 1 620 cm^{-1}; $\delta_H(CD_6SO)$ 1.4—2.3 (8 H, m, 4 × CH_2), 6.18 (1 H, d, *J* 10 Hz, 3′-H), 6.72 (1 H, d, *J* 9 Hz, 6′-H), 7.10 (1 H, d, *J* 10 Hz, 2′-H), 7.19 (1 H, d, *J* 9 Hz, 7′-H), 9.39 (1 H, s, 5′-OH), and 12.56 (1 H, s, 8′-OH).

5′,8′-*Dihydroxy*-3′-*methylspiro*[*cyclopentane*-1,1′-*naphthalen*]-4′-(1′H)-*one* (**28**) (210 mg, 71%), from compound (**24**) (400 mg, 1.21 mmol), reflux time 2 h, m.p. (sealed capillary) 122—123 °C (from benzene–hexane 1:1) (Found: C, 73.5; H, 6.3%. Calc. for $C_{15}H_{16}O_3$: C, 73.75; H, 6.6%); $\nu_{max.}$ 3 420, 3 200, 1 650, and 1 615 cm^{-1}; δ_H 1.6—2.7 (8 H, m, 4 × CH_2), 2.00 (3 H, s, Me), 5.48 (1 H, s, 5′-OH), 6.47 (1 H, d, *J* 9 Hz, 6′-H), 6.86 (1 H, s, 2′-H), 6.89 (1 H, d, *J* 9 Hz, 7′-H), and 13.00 (1 H, s, 8-OH); *m/z* 244 (M^+).

5′,8′-*Dihydroxy*-7′-*methylspiro*[*cyclopentane*-1,1′-*naphthalen*]-4′(1′H)-*one* (**29**) (270 mg, 73%), from substrate (**25**) (500 mg, 1.51 mmol); reflux time 5 h; yellow-brown needles, m.p. 181—182 °C (Found: C, 73.35; H, 6.7. Calc. for $C_{15}H_{16}O_3$: C, 73.8; H, 6.6%); $\nu_{max.}$ 3 350, 1 650, and 1 620 cm^{-1}; δ_H 1.6—2.8 (8 H, m, 4 × CH_2), 2.30 (3 H, s, Me), 4.71 (1 H, s, D_2O exchangeable, 5′-OH), 6.15 (1 H, d, *J* 10 Hz, 3′-H), 6.69 (1 H, s, 6′-H), 6.97 (1 H, d, *J* 10 Hz, 2′-H), and 12.73 (1 H, s, 8′-OH).

General Procedure for the Synthesis of Spironaphthalenetriones.—A solution of the spironaphthalenone and silver carbonate–Celite reagent in the required solvent was vigorously stirred for 2 h at room temperature. After this time the solids were filtered off and the filtrate evaporated to dryness. All quinones were recrystallised from cyclohexane.

Spiro[*cyclopentane*-1,1′-*naphthalene*]-4′(1′H),5′,8′-*trione* (**30**) (430 mg, 90%) from spironaphthalenone (**27**) (480 mg, 2.09 mmol) and silver carbonate–Celite reagent (3.76 g) in benzene–dioxane (9:1) (55 ml); purple crystals m.p. 126—128 °C (Found: C, 73.7; H, 5.3. Calc. for $C_{14}H_{12}O_3$: C, 73.7, H, 5.3%); $\nu_{max.}$ 1 680, 1 660, 1 635, and 1 620 cm^{-1}; $\lambda_{max.}$ 208sh, 230, 251sh, and 410 nm (log ε 4.00, 4.22, 4.03, and 2.98); δ_H 1.6—2.5 (8 H, m, 4 × CH_2), 6.28 (1 H, d, *J* 10 Hz, 3′-H), 6.28 (1 H, d, *J* 10 Hz, 3′-H), 6.76 (2 H, s, 6′- and 7′-H), and 6.95 (1 H, d, *J* 10 Hz, 2′-H).

3′-*Methylspiro*[*cyclopentane*-1,1′-*naphthalene*]-4′(1′H),5′,8′-*trione* (**31**) (382 mg, 87%) from spironaphthalenone (**28**) (350 mg, 1.43 mmol) and silver carbonate–Celite reagent (2.58 g) in benzene–dichloromethane (1:1) (100 ml); purple crystals m.p. 140—142 °C (Found: C, 74.0; H, 6.1%. Calc. for $C_{15}H_{14}O_3$: C, 74.35; H, 5.8%); $\nu_{max.}$ 1 680, 1 660, 1 640, and 1 620 cm^{-1}; δ_H 1.5—2.4 (8 H, m, 4 × CH_2), 1.93 (3 H, s, Me), and 6.74 (3 H, s, 2′-, 6′-, and 7′-H).

7′-*Methylspiro*[*cyclopentane*-1,1′-*naphthalene*]-4′(1′H),5′,8′-trione (**32**) (270 mg, 90%) from spironaphthalene (**29**) (300 mg, 1.23 mmol) and the oxidant reagent (2.25 g) in dichloromethane (50 ml); purple crystals m.p. 140—142 °C (Found: C, 74.1; H, 5.8. Calc. for $C_{15}H_{14}O_3$: C, 74.4; H, 5.8%); $\nu_{max.}$ 1 680, 1 660, 1 640, and 1 620 cm^{-1}; δ_H 1.6—2.5 (8 H, m, 4 × CH_2), 2.06 (3 H, s, Me), 6.22 (1 H, d, *J* 10 Hz, 3′-H), 6.57 (1 H, s, 6′-H), and 6.89 (1 H, d, *J* 10 Hz, 2′-H).

General Procedure for the Synthesis of Tetrahydrophenanthrene-1,4-*diones.*—Quinone was added to a stirred solution of acetic anhydride (5 ml) and concentrated sulphuric acid (6 drops) at room temperature. The red solution was stirred for 10 min then poured into a mixture of ice–water. The yellow product was filtered off and washed thoroughly with water. All quinones were purified by recrystallisation from cyclohexane.

10-*Acetoxy*-5,6,7,8-*tetrahydrophenanthrene*-1,4-*dione*(**33**)(276 mg, 87%) was obtained from compound (**30**) (270 mg, 1.18 mmol); orange crystals, m.p. 120—122 °C (Found: C, 71.1; H, 5.5. Calc. for $C_{16}H_{14}O_4$: C, 71.1; H, 5.2%); $\nu_{max.}$ 1 750, 1 660, 1 650, and 1 615 cm^{-1}; $\lambda_{max.}$ 211, 238, 251, 304, and 372 nm (log ε 4.34, 4.15, 4.15, 3.74, and 3.62); δ_H 1.80 (4 H, m, 6- and 7-CH_2), 2.41 (3 H, s, OCOMe), 2.85 (2 H, m, 8-CH_2), 3.19 (2 H, m, 5-CH_2), 6.68 (1 H, d, *J* 10 Hz, =CH), 6.77 (1 H, d, *J* 10 Hz, =CH), and 7.05 (1 H, s, 9-H).

10-*Acetoxy*-9-*methyl*-5,6,7,8-*tetrahydrophenanthrene*-1,4-*dione* (**34**) (250 mg, 82%) was obtained from quinone (**31**) (260

mg, 1.07 mmol); orange crystals m.p. 137—138 °C (Found: C, 71.9; H, 5.9. Calc. for $C_{17}H_{16}O_4$: C, 71.8; H, 5.7%); $\nu_{max.}$ 1 760, 1 650, and 1 620 cm^{-1}; δ_H 1.80 (4 H, m, 6- and 7-CH_2), 2.48 (3 H, s, Me), 2.73 (2 H, m, 8-CH_2), 3.20 (2 H, m, 5-CH_2), 6.68 (1 H, d, *J* 8 Hz, =CH), and 6.74 (1 H, d, *J* 8 Hz, =CH).

10-*Acetoxy*-3-*methyl*-5,6,7,8-*tetrahydrophenanthrene*-1,4-*dione* (**35**) (235 mg, 80%) was obtained from quinone (**32**) (250 mg, 1.03 mmol); orange crystals m.p. 118—120 °C (Found: C, 72.25; H, 6.1. Calc. for $C_{17}H_{16}O_4$: C, 71.8; H, 5.7%); $\nu_{max.}$ 1 760, 1 650, and 1 620 cm^{-1}; δ_H 1.80 (4 H, m, 6- and 7-CH_2), 2.10 (3 H, s, Me), 2.40 (3 H, s, OCOMe), 2.85 (2 H, m, 8-CH_2), 3.20 (2 H, m, 5-CH_2), 6.85 (1 H, s, 2-H), and 7.02 (1 H, s, 9-H).

1,2,3,4-*Tetrahydrophenanthrene*-5,8,9-*triacetate* (**36**).—Naphthalenone (**27**) (240 mg, 1.04 mmol) was added with stirring to a solution of acetic anhydride (10 ml), containing concentrated sulphuric acid (1 drop), and the mixture was allowed to stand at room temperature for 15 min. The resulting mixture was added to ice–water and the precipitated solid was collected by filtration, washed thoroughly with water, and dried. Crystallisation from cyclohexane afforded compound (**36**) (260 mg, 70%) as yellow needles, m.p. 159—160 °C (Found: C, 67.6; H, 5.7. Calc. for $C_{20}H_{20}O_6$: 67.4; H, 5.6%); $\nu_{max.}$ 1 760 cm^{-1}; δ_H 1.7—1.95 (4 H, m, 6- and 7-CH_2), 2.36 (3 H, s, Me), 2.37 (3 H, s, Me), 2.40 (3 H, s, Me), 2.87 (2 H, m, 8-CH_2), 3.22 (2 H, m, 5-CH_2), 6.84 (1 H, s, 9-H), 6.99 (1 H, d, *J* 8 Hz, ArH), and 7.07 (1 H, d, *J* 8 Hz, ArH).

5,8-*Diacetoxy*-4,4-*dimethylnaphthalen*-1(4H)-*one* (**15**).—Following the procedure used for the transformation (**27**)—(**36**), compound (**13**) (400 mg, 1.96 mmol) was treated for 15 min, after which time work-up gave the diacetate (**15**) (480 mg, 85%) as white needles (from cyclohexane) m.p. 117—118 °C (Found: C, 66.8; H, 5.6. Calc. for $C_{16}H_{16}O_5$: C, 66.7; H, 5.55%); $\nu_{max.}$ 1 770, 1 750, and 1 660 cm^{-1}; δ_H 1.56 (6 H, s, Me_2C), 2.42 (6 H, s, 5- and 8-OAc), 6.19 (1 H, d, *J* 10 Hz, 2-H), 6.69 (1 H, d, *J* 10 Hz, 3-H), 7.05 (1 H, *J* 8 Hz, 7-H), and 7.31 (1 H, d, *J* 8 Hz, 6-H).

5,8-*Diacetoxy*-2,4,4-*trimethylnaphthalen*-1(4H)-*one* (**16**).—As described for the reaction of (**13**) with acetic anhydride, compound (**14**) (276 mg, 1.27 mmol) afforded diacetate (**16**) (280 mg, 73%); white needles, m.p. 151—152 °C (from cyclohexane) (Found: C, 67.1; H, 6.3. Calc. for $C_{17}H_{18}O_5$: C, 67.5; H, 6.3%); $\nu_{max.}$ 1 760 and 1 675 cm^{-1}; δ_H 1.50 (6 H, s, Me_2C), 1.92 (3 H, s, 2-Me), 2.38 (3 H, s, 5-OAc), 2.42 (3 H, s, 8-OAc), 7.01 (1 H, d, *J* 9 Hz, 7-H), and 7.25 (1 H, *J* 9 Hz, 6-H).

Acknowledgements

This work was supported by a grant (35/86) from the Universidad Católica de Chile. We thank the Graduate Program (P.U.C.) for a pre-doctoral fellowship to R. C.

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Received 3rd *February* 1987; *Paper* 7/182