Studies on Quinones. Part 27.[1] Diels–Alder Reaction of 8,8-Dimethylnaphthalene-1,4,5(8*H*)-trione

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The Diels–Alder reaction of the title quinone **1** with various symmetrical and unsymmetrical dienes in ethanol solution is reported. The cycloaddition takes place, in all cases, across the external quinone double bond affording with cyclopentadiene, buta-1,3-diene and 2,3-dimethylbuta-1,3-diene, the corresponding adducts **3**, **4** and **5**. The cycloaddition of **1** with 2-methylbuta-1,3-diene and penta-1,3-diene provided 90:10 and 65:35 mixtures of regioisomers **6**–**7** and **17**–**18**, respectively. Enolisation of these adduct mixtures afforded the corresponding anthracenones **10**–**11** and **21**–**22**. Compounds **11** and **22**, the minor components of the anthracenone mixtures, were synthesized from acetylnaphthalenes **14** and **23**.

The reaction of **1** with (*E*)-1-trimethylsilyloxybuta-1,3-diene yielded exclusively adduct **19** and with (*E*)-1-methoxybuta-1,3-diene gave a mixture of compounds **28**, **31** and **32**.

The regioselectivity of the Diels–Alder reactions of quinone **1** with 2-methylbuta-1,3-diene and penta-1,3-diene is in agreement with that predicted by frontier molecular orbital (FMO) theory. On the basis of frontier molecular orbital interactions, compound **19** is proposed as the regioisomer generated in the reaction of **1** with the (*E*)-1-trimethylsilyloxybuta-1,3-diene.

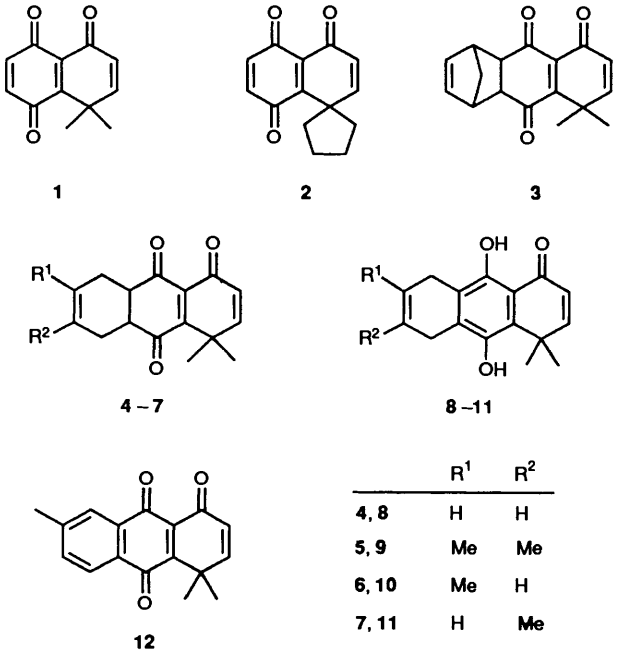
In connection with studies on the synthesis of angular polycyclic quinones related to naturally occurring quinones, we have recently reported [2] a regiospecific method to prepare dihydroxyanthra- and benz-[*a*]anthraquinones starting from naphthalenetriones **1** and **2**. This route involves the aromatization of the cyclohexadienone ring by dienone–phenol rearrangement [3] followed by extension of the ring system by the cycloaddition of (*E*)-1-trimethylsilyloxybuta-1,3-diene.

An alternative route to prepare anthra- and benz-[*a*]-anthraquinones from compounds **1** and **2** could be based on cycloaddition to the external quinone double bond followed by aromatisation and dienone–phenol rearrangement. The hypothesis that the cycloaddition to quinones **1** and **2** takes place across the external quinonic double bond is supported by the fact that the substituents at C-8 would be expected to prevent attack of the dienes on the internal double bond. On the other hand, considering the electron-withdrawing effect of the carbonyl group at C-5, it is reasonable to expect regioselective control of the cycloaddition of polarised dienes.

In this communication we wish to describe the behaviour of quinone **1** in the Diels–Alder reaction with several symmetrical and unsymmetrical dienes, providing a route for the synthesis of anthracene-1,9,10-triones. The FMO (frontier molecular orbital) theoretical prediction of the preferred cycloaddition of **1** and the unsymmetrical dienes is in accord with the observed regioselectivity.

Quinone **1**, prepared as reported,[3] was allowed to react with an excess of cyclopentadiene at room temperature for 2 days in benzene solution to afford adduct **3** in 84% yield. The appearance in the ^{1}H NMR spectrum of two olefinic proton doublets at δ 6.28 and 6.76 with J 10 Hz, and the absence of the quinone protons of substrate **1**, indicates that the addition took place across the external quinone double bond.

Under similar conditions, quinone **1** reacted with buta-1,3-diene and 2,3-dimethylbuta-1,3-diene to afford, after 3 days, the corresponding adducts **4** and **5**. It is noteworthy that adduct **3** was easily purified through a silica gel column. Adducts **4** and **5**, however, underwent enolisation to the corresponding anthracenones **8** and **9** under these conditions. Dihydroxyanthracenones **8** and **9** were prepared in high yields by treatment of the corresponding adducts **4** and **5** with silica gel in benzene solution.

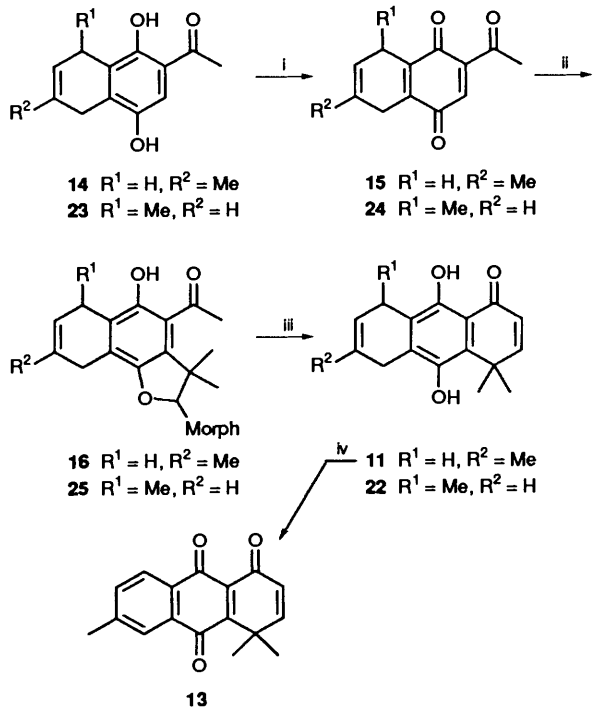


	R^1	R^2
4, 8	H	H
5, 9	Me	Me
6, 10	Me	H
7, 11	H	Me

The behaviour of quinone **1** towards the cycloaddition of unsymmetrical dienes was first explored with 2-methylbuta-1,3-diene in ethanol solution. After 5 days a mixture of adducts **6**–**7** was obtained in 94% yield, and the major regioisomer **6** was purified by crystallisation from a light petroleum–benzene mixture. The presence of the two regioisomers generated in this cycloaddition was indirectly established through their enolisation products **10** and **11** which were generated by treatment of the crude adducts mixture with silica gel in benzene solution. The ^{1}H NMR spectrum of the mixture of dihydroxyanthracenones showed the signals of two chelated protons at δ 13.19 and 13.17 in a 90:10 ratio. The major dihydroxyanthracenone **10** was purified by crystallisation from benzene and was then oxidised with active manganese dioxide [4] to anthracenetrione **12**.

The structures of dihydroxyanthracenone **10** and anthra-

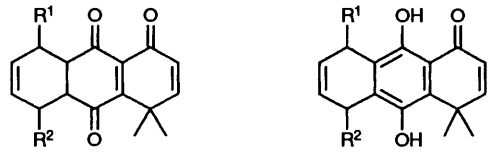
cenetrione **12** were established by comparison of their properties (m.p.s, IR, ^{1}H NMR and ^{13}C NMR) with those of dihydroxyanthracenone **11** and anthracenetrione **13** which were prepared according to the sequence of steps outlined in Scheme 1. Compound **14**, prepared as reported,[5] was oxidised



Scheme 1 *Reagents:* i, MnO_2, CH_2Cl_2; ii, N-(2-methylprop-1-enyl)-morpholine, CH_2Cl_2; iii, H^+, EtOH; iv, MnO_2

with manganese dioxide[6] in dichloromethane solution to give the unstable quinone **15** in 98% yield. The reaction of **15** with the *N*-(2-methylprop-1-enyl)morpholine afforded heterocycle **16** in 74% yield which by acid-induced rearrangement provided anthracenone **11** in 70% yield. Finally, oxidation of **11** with active manganese dioxide gave anthracenetrione **13** in 91% yield.

We also studied the Diels–Alder reaction of quinone **1** with penta-1,3-diene under the usual conditions. The treatment afforded a 65:35 mixture of adducts **17** and **18** which was evaluated by ^{1}H NMR spectroscopy using the signals of the methyl groups at δ 1.23 and 1.28. The mixture of adducts **17**–**18** was converted into the mixture of dihydroxyanthracenones **21**–**22** by treatment with silica gel in benzene solution. The ^{1}H NMR spectrum of the latter mixture showed the signals of the chelated protons at δ 13.20 and 13.45.

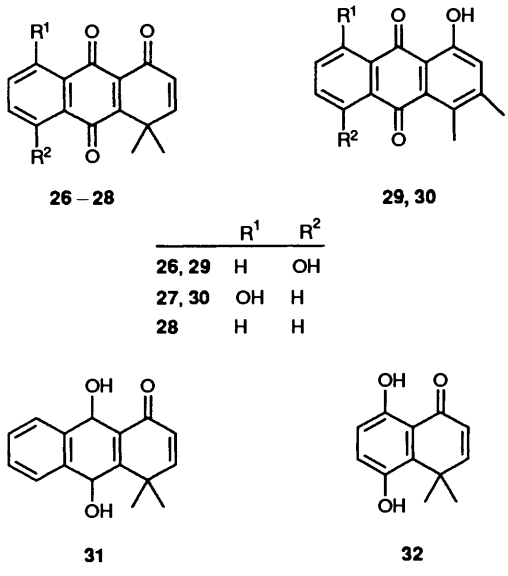


	R^1	R^2
17, 21	H	Me
18, 22	Me	H
19	H	OTMS
20	OTMS	H

The identity of the dihydroxyanthracenones **21** and **22**, which were not separated, was established by comparison of the ^{1}H NMR spectrum of the mixture with the ^{1}H NMR spectrum of pure dihydroxyanthracenone **22**. Compound **22** was synthesised from acetylnaphthalene **23**[5,7] by oxidation with manganese dioxide affording the unstable quinone **24** which was treated with *N*-(2-methylprop-1-enyl)morpholine to provide heterocycle **25**. Subsequent acid-induced rearrangement of **25** gave naphthalenone **22** (Scheme 1).

The ^{1}H NMR spectrum of dihydroxyanthracenone **22** displays the signal of the chelated proton at δ 13.45 in agreement with the signal of the chelated proton of the minor dihydroxynaphthalenone in the mixture. This indicates that cycloaddition of **1** and penta-1,3-diene gave a 65:35 mixture of adducts **17** and **18**, respectively.

We also examined the Diels–Alder reaction of **1** with the electron-rich dienes: (*E*)-1-trimethylsilyloxybuta-1,3-diene and (*E*)-1-methoxybuta-1,3-diene. Cycloaddition with the former afforded exclusively adducts **19** or **20** in 90% yield. We attempted to convert adducts **19** or **20** into hydroxyquinones **26** or **27** which by dienone–phenol rearrangement might provide dihydroxyquinone **29**, or its isomer **30** which we have obtained previously.[2] However, by subjecting the adduct to mild acidic conditions, anthracenone **31** was obtained in 96% yield. Aromatisation of adduct **19** or **20** was also attempted with 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ). However, elimination of the silyloxy group proceeded easily during the oxidation to afford anthracenetrione **28** in 98% yield.



	R^1	R^2
26, 29	H	OH
27, 30	OH	H
28	H	H

The cycloaddition of **1** with (*E*)-1-methoxybuta-1,3-diene gave a mixture of compounds **28**, **31** and **32** which were isolated by column chromatography on silica gel. It is reasonable to deduce that the Diels–Alder adduct generated in the cycloaddition undergoes a facile enolisation–aromatisation to give anthracenone **31**, which through a redox reaction with **1**, affords anthracenetrione **28** and naphthalenone **32**.

The remarkable regioselectivity of the cycloaddition of quinone **1** with unsymmetrical dienes led us to analyse these reactions in terms of frontier molecular orbital (FMO) theory.[8] Fig. 1 shows the LUMO coefficients of quinone **1** and the HOMO coefficients of the dienes, calculated by the semi-empirical AM1 method. These calculations indicate that quinone **1** possesses the highest LUMO coefficients at the internal double bond. Nevertheless, as was experimentally observed in all the cycloadditions, the reactions occur at the external quinone double bond due to the presence of the geminal methyl groups that prevent the approach of the dienes to the internal double bond.

It is interesting to note that the calculations indicate for

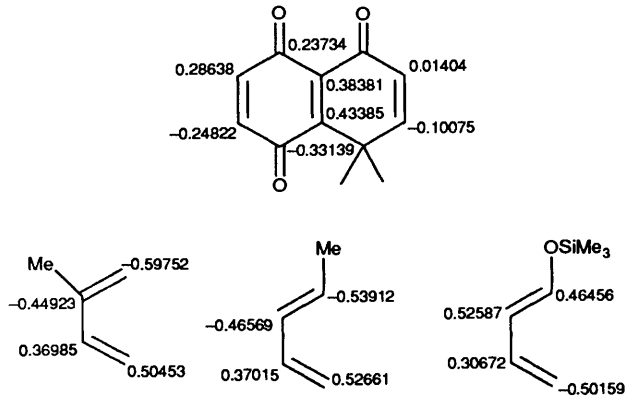


Fig. 1 LUMO coefficients of quinone **1** and HOMO coefficients of 2-methylbuta-1,3-diene, penta-1,3-diene and (*E*)-1-trimethylsilyloxybuta-1,3-diene performed by AM1 method

quinone **1** a small difference between the LUMO coefficients at C-2 and C-3, and a large difference between those at C-1 and C-4.

For the reaction of **1** with 2-methylbuta-1,3-diene the calculations indicate that the primary LUMO/HOMO interactions favour the regioisomer **6**; this prediction agrees with the experimental result of 90:10 preference for adduct **6**.

For penta-1,3-diene the calculations show that the primary HOMO coefficients are nearly of the same magnitude, therefore the secondary LUMO/HOMO orbital[9] interactions favour the regioisomer **17**. This prediction agrees with the experimental results of 65:35 preference for adduct **17**.

For the reaction of **1** with (*E*)-1-trimethylsilyloxybuta-1,3-diene, the calculation shows that the HOMO of the diene, which contains the strong π-donor $OSiMe_3$ group, is heavily concentrated on the 2- and 4-positions. This fact, along with the magnitude of the coefficient at C-1 of the LUMO of **1** which significantly exceeds that at C-4, leads to the prediction that adduct **19** is the favoured regioisomer generated through a transition state allowed by primary and secondary orbital interactions.

In summary, the cycloaddition of quinone **1** with dienes took place through the external quinone double bond and is highly regiocontrolled with polarised unsymmetrical dienes. The regiochemistry of these cycloadditions, which is in accord with that predicted by FMO theory, is potentially applicable to the synthesis of anthra- and benz-[*a*]anthraquinones. The extension of these results to quinone **2** and the cycloaddition of 1-aza dienes to quinones **1** and **2** is under investigation.

Experimental

M.p.s were measured on a Kofler hot-stage apparatus and are uncorrected. Unless otherwise stated IR spectra were recorded on a Perkin-Elmer 1310 spectrophotometer; ^1H NMR spectra were obtained on a Varian XL-100 or Bruker AC-200P spectrometers. ^{13}C NMR spectra were recorded on Bruker AM-200 or Varian XL-300 spectrometers. Samples were dissolved in $CDCl_3$, chemical shifts are expressed in ppm (δ), downfield from $SiMe_4$ and coupling constants (J) are given in Hz. Mass spectra were recorded on a VG-12-250 spectrometer. Silica gel Merck 60 (70–230 mesh) and DC-Alufolien 60 F_{254} were used for preparative column and analytical TLC, respectively.

Reaction of Quinone **1** *with Cyclopentadiene.*—A solution of compound **1**[3] (172 mg, 0.85 mmol) and freshly distilled cyclopentadiene (57 mg, 0.86 mmol) in ethanol (5 cm^3) was left at room temperature for 2 days. Evaporation of the solvent followed by purification of the crude residue by filtration over silica gel ($CHCl_3$) afforded 5,8-methano-4,4-dimethyl-5,8,8a,-10a-tetrahydroanthracene-1,9,10(4*H*)-trione **3** (190 mg, 84%), m.p. 100–102 °C (benzene) (Found: C, 76.1; H, 6.2. $C_{17}H_{16}O_3$ requires C, 76.1; H, 6.0%); ν_{max}/cm^{-1} 1700, 1675 and 1656; δ_H(100 MHz) 1.45 (s, 3 H, 4-Me), 1.48 (s, 3 H, 4-Me'), 1.52–1.72 (m, 2 H, 11-CH_2), 3.36–3.60 (m, 4 H, 5-H, 8-H, 8a-H and 10a-H), 6.00–6.23 (m, 2 H, 6-H and 7-H), 6.28 (d, 1 H, *J* 10, 2-H) and 6.76 (d, 1 H, *J* 10, 3-H).

Reaction of Quinone **1** *with Buta-*1,3*-diene.*—Butadiene was bubbled for 3 min through a solution of the quinone **1** (200 mg, 1 mmol) in ethanol (10 cm^3), and the mixture was left in a sealed flask at room temperature for 3 days. Evaporation of the solvent afforded 4,4-dimethyl-5,8,8a,10a-tetrahydroanthracene-1,9,10-(4*H*)-trione **4** (248 mg, 97%) as a pale yellow solid, m.p. 105–107 °C [benzene–light petroleum (b.p. 40–60 °C)] (Found: C, 75.0; H, 6.2. $C_{16}H_{16}O_3$ requires C, 75.0; H, 6.3%); ν_{max}/cm^{-1} 1705 and 1445; δ_H(100 MHz) 1.50 (s, 6 H, 4-Me_2), 2.00–2.70 (m, 4 H, 5-H and 8-H), 3.10–3.60 (m, 2 H, 8a-H and 10a-H), 5.73 (br s, 2 H, 6-H and 7-H), 6.23 (d, 1 H, *J* 10, 2-H) and 6.84 (d, 1 H, *J* 10, 3-H).

Reaction of Quinone **1** *with* 2,3*-Dimethylbuta-*1,3*-diene.*—A solution of quinone **1** (200 mg, 1 mmol) and the diene (150 mg, 1.8 mmol) in ethanol (10 cm^3) was kept at room temperature for 3 days. The solvent was removed to give 4,4,6,7-tetramethyl-5,8,8a,10a-tetrahydroanthracene-1,9,10(4*H*)-trione **5** (280 mg, 99%) as a pale yellow solid, m.p. 108–111 °C [benzene–light petroleum (b.p. 40–60 °C)] (Found: C, 76.4; H, 7.3. $C_{18}H_{20}O_3$ requires C, 76.0; H, 7.1%); ν_{max}/cm^{-1} 1715, 1670 and 1650; δ_H(100 MHz) 1.51 (s, 6 H, 8-Me_2), 1.64 (br s, 6 H, 6-Me and 7-Me), 1.89–2.61 (m, 4 H, 5-H and 8-H), 3.12–3.54 (m, 2 H, 8a-H and 10a-H), 6.32 (d, 1 H, *J* 10, 2-H) and 6.83 (d, 1 H, *J* 10, 3-H).

9,10*-Dihydroxy-*4,4*-dimethyl-*5,8*-dihydroanthracen-*1(4H)*-one* **8**.—A solution of adduct **4** (250 mg, 0.98 mmol) and silica gel (3 g) in benzene (10 cm^3) was stirred overnight at room temperature. The mixture was filtered and the solid was washed with dichloromethane. Evaporation of the solvent gave anthracenone **8** (230 mg, 92%) as a yellow solid, m.p. 225–228 °C (benzene) (Found: C, 75.1; H, 5.9. $C_{16}H_{16}O_3$ requires C, 75.0; H, 6.2%); ν_{max}/cm^{-1} 3400, 1645, 1615 and 1585; δ_H(100 MHz) 1.62 (s, 6 H, 4-Me_2), 3.20 (br s, 4 H, 5-H and 8-H), 4.48 (br s, 1 H, OH), 5.76–6.12 (m, 2 H, 6-H and 7-H), 6.25 (d, 1 H, *J* 10, 2-H), 6.85 (d, 1 H, *J* 10, 3-H) and 13.08 (s, 1 H, OH); δ_C 23.30, 24.32, 25.21, 37.85, 111.78, 120.45, 122.76, 123.26, 133.29, 133.34, 143.87, 153.57, 161.89 and 190.86.

9,10*-Dihydroxy-*4,4,6,7*-tetramethyl-*5,8*-dihydroanthracen-*1(4H)*-one* **9**.—A mixture of adduct **5** (200 mg, 0.7 mmol) and silica gel (3 g) in benzene solution (15 cm^3) was stirred for 3 h at room temperature. Work-up in the usual way afforded anthracenone **9** (190 mg, 95%), m.p. 211–213 °C (benzene) (Found: C, 76.0 H, 7.2. $C_{18}H_{20}O_3$ requires C, 76.0; H, 7.1%); ν_{max}/cm^{-1} 3415, 1640, 1610 and 1585; δ_H(100 MHz) 1.60 (s, 6 H, 4-Me_2), 1.81 (s, 6 H, 6-Me and 7-Me), 3.04–3.34 (m, 4 H, 5-H and 8-H), 6.25 (d, 1 H, *J* 10, 2-H), 6.82 (d, 1 H, *J* 10, 3-H), 7.28 (s, 1 H, OH) and 13.12 (s, 1 H, OH); δ_C 18.24, 18.40, 24.41, 24.81, 30.08, 31.96, 38.94, 111.60, 121.07, 123.24, 132.94, 133.92, 143.43, 153.19, 161.88 and 190.88.

Reaction of Quinone **1** *with* 2*-Methylbuta-*1,3*-diene.*—A solution of quinone **1** (490 mg, 2.42 mmol) and the diene (240 mg, 3.5 mmol) in ethanol (10 cm^3) was left at room temperature for 5 days. Removal of the solvent afforded a mixture of 4,4,7-trimethyl- and 4,4,6-trimethyl-5,8,8a,10a-tetrahydroanthracene-1,9,10(4*H*)-trione **6** and **7** in a 90:10 ratio (620 mg, 94%).

An analytical sample of the major regioisomer **6** was obtained by crystallisation from a 1:1 benzene–light petroleum mixture, m.p. 88–90 °C (Found: C, 75.2; H, 6.6. $C_{17}H_{18}O_3$ requires C, 75.5; H, 6.7); ν_{max}/cm^{-1} 1705, 1685 and 1655; δ_H(100 MHz) 1.47 (s, 3 H, 4-Me), 1.50 (s, 3 H, 4-Me'), 1.70 (br s, 3 H, 7-Me), 1.88–2.60 (m, 4 H, 5-H and 8-H), 3.06–3.56 (m, 2 H, 8a-H and 10a-H), 5.37 (br s, 1 H, 6-H), 6.30 (d, 1 H, *J* 10, 2-H) and 6.78 (d, 1 H, *J* 10, 3-H).

9,10-*Dihydroxy*-4,4,7-*trimethyl*-5,8-*dihydroanthracen*-1(4H)-*one* **10**.—A suspension of adducts **6**–**7** (600 mg, 2.22 mmol) and silica gel (3 g) in benzene (10 cm^3) was stirred for 2 h at room temperature. The mixture was filtered and the solid was washed with dichloromethane. Evaporation of the solvent gave a 90:10 mixture of anthracenones **10** and **11** (540 mg, 90%) evaluated by ^{1}H NMR spectroscopy at 300 MHz. An analytical sample of anthracenone **10** was obtained by crystallisation from benzene, m.p. 222–223 °C (Found: 75.3; H, 6.4. $C_{17}H_{18}O_3$ requires C, 75.6; H, 6.6%); ν_{max}/cm^{-1} 3320, 1645, 1610 and 1580; δ_H(100 MHz) 1.64 (s, 6 H, 4-Me$_2$), 1.88 (br s, 3 H, 7-Me), 3.14–3.54 (m, 4 H, 5-H and 8-H), 5.64 (br s, 1 H, 6-H), 6.14 (s, 1 H, OH), 6.29 (d, 1 H, *J* 10, 2-H), 6.91 (d, 1 H, *J* 10, 3 H) and 13.20 (s, 1 H, OH); δ_C 22.90, 24.70, 24.80, 26.15, 28.09, 37.86, 111.78, 116.97, 120.75, 123.24, 130.06, 133.17, 133.24, 143.83, 153.43, 162.00 and 190.89.

4,4,7-*Trimethylanthracene*-1,9,10(4H)-*trione* **12**.—A mixture of anthracenone **10** (220 mg, 0.81 mmol) and active manganese dioxide[4] (600 mg) in benzene (30 cm^3) was refluxed in a Dean–Stark apparatus for 3 h. The solution was filtered, the solids were washed with dichloromethane and the filtrate was evaporated under reduced pressure to afford compound **12** (200 mg, 93%), m.p. 138–140 °C (Found: 76.6; H, 5.4. $C_{17}H_{14}O_3$ requires C, 76.1; H, 5.3); ν_{max}/cm^{-1} 1680, 1655 and 1640; δ_H(100 MHz) 1.66 (s, 6 H, 4-Me$_2$), 2.54 (s, 3 H, 7-Me), 6.41 (d, 1 H, *J* 10, 2-H), 6.90 (d, 1 H, *J* 10, 3-H), 7.60 (dd, 1 H, *J* 8 and 2, 6-H), 7.88 (d, 1 H, *J* 2, 8-H) and 8.00 (d, 1 H, *J* 8, 5-H).

2-*Acetyl*-6-*methyl*-5,8-*dihydronaphthalene*-1,4-*dione* **15**.—Compound **14**[5] (600 mg, 2.71 mmol) and manganese dioxide[6] (190 mg) in dichloromethane (30 cm^3) were stirred vigorously for 25 min at room temperature. The resulting mixture was filtered and the filtrate was concentrated to give the unstable quinone **15** (580 mg, 98%) which was used immediately in the next preparation; ν_{max}/cm^{-1} 1698, 1655 and 1645; δ_H(100 MHz) 1.79 (s, 3 H, 6-Me), 2.56 (s, 3 H, COMe), 2.82–3.31 (m, 4 H, 5-H, and 8-H), 5.44–5.64 (m, 1 H, 7-H) and 6.94 (s, 1 H, 3-H).

4-*Acetyl*-5-*hydroxy*-3,3,8-*trimethyl*-2-*morpholino*-6,9-*dihydronaphtho*[1,2-b]*furan* **16**.—A solution of quinone **15** (540 mg, 2.68 mmol) in dichloromethane (30 cm^3) was added dropwise to a cooled solution (0–5 °C) of *N*-(2-methylprop-1-enyl)morpholine (380 mg, 2.7 mmol) in dichloromethane (25 cm^3) and the resulting red solution was left for 1 h at ambient temperature. The solvent was removed and the residue, which solidified upon cooling, was washed with light petroleum to give heterocycle **16** (710 mg, 74%), m.p. 163–165 °C [benzene–light petroleum (1:1)] (Found: C, 70.7; H, 7.3; N, 3.7. $C_{21}H_{27}NO_4$ requires C, 70.6; H, 7.6; N, 3.9%); ν_{max}/cm^{-1} 3240 and 1675; δ_H(100 MHz) 1.40 (s, 3 H, 3-Me), 1.48 (s, 3 H, 3-Me'), 1.85 (s, 3 H, 8-Me), 2.28–2.80 (m, 4 H, 6-H and 9-H), 2.62 (s, 3 H, COMe), 3.20 (m, 4 H, CH_2–N), 3.62 (t, 4 H, CH_2–O), 4.73 (s, 1 H, 2-H) and 5.61 (br s, 1 H, OH).

9,10-*Dihydroxy*-4,4,6-*trimethyl*-5,8-*dihydroanthracen*-1(4H)-*one* **11**.—A solution of compound **16** (340 mg, 1.02 mmol) in ethanol (10 cm^3) containing concentrated hydrochloric acid (0.3 cm^3) was refluxed for 25 min. The mixture was poured into ice–water and the precipitate was filtered off to afford anthracenone **11** (170 mg, 70%), m.p. 216–218 °C (benzene) (Found: C, 75.5; H, 6.6. $C_{17}H_{18}O_3$ requires C, 75.6; H, 6.6%); ν_{max}/cm^{-1} 3410, 1640 and 1580; δ_H(100 MHz) 1.64 (s, 6 H, 4-Me$_2$), 1.88 (br s, 3 H, 6-Me), 3.14–3.54 (m, 4 H, 5-H and 8-H), 5.64 (br s, 1 H, 7-H), 6.14 (s, 1 H, OH), 6.29 (d, 1 H, *J* 10, 2-H), 6.91 (d, 1 H, *J* 10, 3-H) and 13.2 (s, 1 H, OH); δ_C 23.07, 24.22, 24.72, 24.80, 24.99, 37.88, 111.70, 117.60, 120.37, 129.49, 123.26, 133.35, 133.65, 143.69, 153.55, 161.98 and 190.92.

4,4,6-*Trimethylanthracene*-1,9,10(4H)-*trione* **13**.—A mixture of anthracenone **11** (200 mg, 0.74 mmol) and active manganese dioxide[4] (550 mg) in benzene (30 cm^3) was refluxed in a Dean–Stark apparatus for 3 h. The solution was filtered, the solids were washed with dichloromethane and the filtrate was evaporated under reduced pressure to afford compound **13** (180 mg, 91%), m.p. 184–185 °C (Found: 77.0; H, 5.2. $C_{17}H_{14}O_3$ requires C, 76.7; H, 5.3%); ν_{max}/cm^{-1} 1690, 1665 and 1635; δ_H(100 MHz) 1.66 (s, 6 H, 4-Me$_2$), 2.54 (s, 3 H, 7-Me), 6.41 (d, 1 H, *J* 10, 2-H), 6.90 (d, 1 H, *J* 10, 3-H), 7.60 (dd, 1 H, *J* 8 and 2, 6-H), 7.88 (br s, 1 H, 8-H) and 8.00 (d, 1 H, *J* 8, 5-H).

Reaction of Quinone **1** *with Penta*-1,3-*diene*.—A solution of quinone **1** (340 mg, 1.68 mmol) and the diene (0.25 cm^3, 2.5 mmol) in ethanol (10 cm^3) was left at room temperature for 4 days. Removal of the solvent gave a 65:35 mixture of 4,4,5-trimethyl-5,8,8a,10a-tetrahydroanthracene-1,9,10(4*H*)-trione **17** and 4,4,8-trimethyl-5,8,8a,10a-tetrahydroanthracene-1,9,10(4*H*)-trione **18** as an oily liquid; ν_{max}/cm^{-1} 1710, 1676 and 1640; δ_H(100 MHz) 0.92 (d, 1.95 H, *J* 7, 5-Me), 1.12 (d, 1.15 H, *J* 7, 8-Me), 1.50, 1.53 and 1.58 (3 s, 6 H, 4-Me$_2$), 1.92–2.88 (m, 3 H, 5-H and 8-H), 3.23–3.63 (m, 2 H, 8a-H and 10a-H), 5.58–5.76 (m, 2 H, 6-H and 7-H), 6.33 (d, 1 H, *J* 10, 2-H) and 6.65 (d, 1 H, *J* 10, 3-H).

9,10-*Dihydroxy*-4,4,5-*trimethyl*-5,8-*dihydro- and* 9,10-*Dihydroxy*-4,4,8-*trimethyl*-5,8-*dihydro-anthracen*-1(4H)-*one* **21** *and* **22**.—The 65:35 mixture of adducts **17** and **18** (440 mg, 1.63 mmol) and silica gel (2 g) in benzene (10 cm^3) was stirred for 2 h. The solution was filtered and the solids were washed with dichloromethane. Removal of the solvent afforded a 70:30 mixture of anthracenones **21** and **22** as a yellow solid (400 mg, 91%) (Found: C, 75.6; H, 6.6. $C_{17}H_{18}O_3$ requires C, 75.5; H, 6.7%); ν_{max}/cm^{-1} 3440, 1640, 1610 and 1580; δ_H(200 MHz) 1.27 (d, 2.1 H, *J* 7, 8-Me), 1.29 (d, 0.9 H, *J* 7, 5-Me), 1.59 (s, 0.9 H, 4-Me), 1.60 (s, 2.1 H, 4-Me), 1.62 (s, 0.9 H, 4-Me'), 1.63 (s, 2.1 H, 4-Me'), 3.05–3.60 (m, 2 H, 5-H and 8-H), 3.51 (m, 2.1 H, 5-H), 3.70 (m, 0.9 H, 8-H), 4.35 (s, 0.9 H, OH), 4.49 (s, 2.1 H, OH), 5.80–6.05 (m, 2 H, 6-H and 7-H), 6.24 (d, 1 H, *J* 10, 2-H), 6.80 (d, 0.3 H, *J* 10, 2-H), 6.82 (d, 0.7 H, *J* 10, 2-H), 13.12 (s, 0.7 H, OH) and 13.23 (s, 0.3 H, OH).

3-*Acetyl*-5-*methyl*-5,8-*dihydronaphthalene*-1,4-*dione* **24**.—A solution of acetylnaphthalene **23**[5,7] (310 mg, 1.42 mmol) and manganese dioxide[6] (1.25 g) in dichloromethane (25 cm^3) was stirred vigorously for 30 min at room temperature. The mixture was evaporated to afford crude quinone **24** (300 mg, 98%). This unstable compound was used immediately in the next preparation; ν_{max}/cm^{-1} 1690 and 1650; δ_H(100 MHz) 1.20 (d, 3 H, *J* 7, 5-Me), 2.55 (s, 3 H, COMe), 2.93–3.26 (m, 2 H, 8-H), 3.28–3.62 (m, 1 H, 5-H), 5.62–5.09 (m, 2 H, 6-H and 7-H) and 7.39 (s, 1 H, 2-H).

4-*Acetyl*-5-*hydroxy*-3,3,6-*trimethyl*-2-*morpholino*-6,9-*dihydronaphtho*[1,2-b]*furan* **25**.—A solution of compound **24** (308 mg, 1.42 mmol) in dichloromethane (15 cm^3) was added dropwise to a cooled solution (0–5 °C) of *N*-(2-methylprop-1-enyl)morpholine (220 mg, 1.56 mmol) in dichloromethane (10

cm^3) and the mixture was left at room temperature for 2 h. Removal of the solvent afforded a red oily liquid which was poured into diethyl ether–light petroleum (1:1; 30 cm^3) and cooled at 0–5 °C for 24 h. The precipitate was filtered off to afford **25** (270 mg, 53%) as a 1:4 mixture of two epimers (evaluated by ^1H NMR spectroscopy). A pure sample of the mixture was obtained by recrystallisation from diethyl ether–chloroform (1:1) (Found: M^+, 357.1930. $C_{21}H_{27}NO_4$ requires *M*, 357.1940); ν_{max}/cm^{-1} 3300 and 1685; δ_H(200 MHz) 1.23 (d, 0.6 H, *J* 7, 9-Me), 1.28 (d, 2.4 H, *J* 7, 9-Me'), 1.42 (s, 3 H, 3-Me), 1.46 (s, 3 H, 3-Me), 2.28–2.80 (m, 5 H, CH_2–N and 9-H), 2.64 (s, 3 H, COMe), 3.28 (br s, 2 H, 6-H), 3.62 (t, 4 H, *J* 5, CH_2–O), 4.71 (s, 1 H, 2-H) and 5.92 (m, 2 H, 7-H and 8-H).

9,10-*Dihydroxy*-4,4,8-*trimethyl*-5,8-*dihydroanthracen*-1(4H)-*one* **22**.—A solution of heterocycle **25** (250 mg, 0.64 mmol) and hydrochloric acid (25%; 0.25 cm^3) in ethanol (10 cm^3) was refluxed for 2 h. The mixture was poured into water (150 cm^3) and extracted with chloroform (2 × 30 cm^3) and the organic extracts were washed consecutively with water, aq. hydrogen carbonate and water and dried ($MgSO_4$). The chloroform was removed and the residue was chromatographed on silica gel (chloroform) to afford anthracenone **22** (67 mg, 39%), m.p. 194–196 °C (benzene) (Found: M^+, 270.1257. $C_{17}H_{18}O_3$ requires *M*, 270.1247); ν_{max}/cm^{-1} 3360, 1650, 1610 and 1580; δ_H(200 MHz) 1.29 (d, 3 H, *J* 7, 8-Me), 1.59 (s, 3 H, 4-Me), 1.62 (s, 3 H, 4-Me'), 3.05–3.20 (m, 2 H, 5-H), 3.71 (m, 1 H, 8-H), 4.36 (s, 1 H, OH), 5.80–6.05 (m, 2 H, 6-H and 7-H), 6.23 (d, 1 H, *J* 10, 2-H), 6.80 (d, 1 H, *J* 10, 3-H) and 13.23 (s, 1 H, OH).

Reaction of Quinone **1** *with* (E)-1-*Trimethylsilyloxybuta*-1,3-*diene*.—A solution of quinone **1** (280 mg, 1.38 mmol) and the diene (0.3 cm^3) in dichloromethane (10 cm^3) was kept at room tem rature for 90 min. The solvent was removed and the residue was kept under vacuum for 2 h at 60–70 °C. The solid residue was washed with light petroleum to afford 4,4-dimethyl-5-trimethylsilyloxy-5,8,8a,10a-tetrahydroanthracene-1,9,10-(4*H*)-trione **19** (427 mg, 90%). An analytical sample of **19** was obtained by filtration through silica gel (benzene) followed by recrystallisation from hexane, m.p. 175–177 °C (Found: C, 66.3; H, 7.1. $C_{19}H_{24}O_4Si$ requires C, 66.3; H, 7.0%); ν_{max}/cm^{-1} 1720, 1690, 1660, 1060 and 840; δ_H(200 MHz) 0.05 (s, 9 H, $OSiMe_3$), 2.00 (dd, 1 H, *J* 18 and 7.5, 8-H), 2.85–3.50 (m, 3 H, 8'-H and 10a-H), 4.43 (t, 1 H, *J* 4.5, 5-H), 5.87 (m, 2 H, 6-H and 7-H), 6.30 (d, 1 H, *J* 10, 2-H) and 6.72 (d, 1 H, *J* 10, 3-H).

Reaction of **19** *in Acid Medium*.—Compound **19** (200 mg, 0.58 mmol) in water–THF (9:1, 5 cm^3) and 1 mol dm^{-3} hydrochloric acid (0.2 cm^3) was left at room temperature for 20 h. The mixture was diluted with water (50 cm^3) and extracted with chloroform (2 × 25 cm^3). The extracts were washed with water, dried ($MgSO_4$) and the solvent evaporated under reduced pressure to afford 9,10-dihydroxy-4,4-dimethylanthracen-1-(4*H*)-one **31** (142 mg, 96%) as red crystals, m.p. 176–178 °C (Found: C, 75.7; H, 5.6. $C_{16}H_{14}O_3$ requires C, 75.6; H, 5.6%); ν_{max}/cm^{-1} 3200, 1630 and 1590; δ_H(100 MHz) 1.70 (s, 6 H, 4-Me_2), 5.09 (br s, 1 H, OH), 6.28 (d, 1 H, *J* 9, 2-H), 6.80 (d, 1 H, *J* 9, 3-H), 7.30–8.00 (m, 3 H, 6 H, 7-H and 5-H or 8-H), 8.50 (br d, 1 H, *J* 8, 8-H or 5-H) and 14.53 (s, 1 H, OH).

Oxidation of Adduct **20** *with DDQ*.—A solution of **20** (98 mg, 0.28 mmol) and DDQ (158 mg, 0.69 mmol) in benzene (25 cm^3) was refluxed for 8 h. The mixture was poured into chloroform (50 cm^3) and then washed with 10% aq. sodium hydrogen carbonate (2 × 15 cm^3). The organic layer was washed with water, dried ($MgSO_4$) and the solvent evaporated under reduced pressure to afford 4,4-dimethylanthracene-1,9,10(4*H*)-trione **28** (69 mg, 98%); m.p. 156–158 °C (Found: C, 76.2; H, 5.2. $C_{16}H_{12}O_3$ requires C, 76.2; H, 4.9%); ν_{max}/cm^{-1} 1690, 1665, 1645 and 1590; δ_H(100 MHz) 1.66 (s, 6 H, 4-Me_2), 6.43 (d, 1 H, *J* 10, 2-H), 6.82 (d, 1 H, *J* 10, 3-H), 7.65–7.90 (m, 2 H, 6-H and 7-H) and 8.05–8.20 (m, 2 H, 5-H and 8-H).

Reaction of Quinone **1** *with* 1-(E)-*Methoxybuta*-1,3-*diene*.—A solution of quinone **1** (230 mg, 1.13 mmol) and the diene (110 mg, 1.30 mmol) in dichloromethane (10 cm^3) was allowed to react at room temperature for 16 h. After this time, naphthalenone **32**, which precipitated as yellow crystals, was isolated by filtration (36 mg). The filtrate was evaporated under reduced pressure and chromatographed on silica gel [light petroleum–ethyl acetate (8:2)] to afford naphthalenone **32**[10] (15 mg; total 51 mg, 19%), anthracenone **31** (125 mg, 37%) and anthracenetrione **28** (62 mg, 19%).

Acknowledgements

Financial support from 'Consejo de Investigación en Ciencia y Tecnología' (FONDECYT, Grants No. 88-316 and 92-603) and Ministerio de Educación y Ciencia de España are gratefully acknowledged. The authors thank Dr. Gert Eckhardt, Institut für Organische Chemie, Universität Bonn, for the high resolution mass spectrum.

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Paper 3/00689A
Received 3rd *February* 1993
Accepted 18th *February* 1993