1,4-Di-*o*-tolyl-2,3-naphthoquinone[†]

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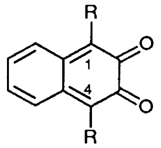
1,4-Di-*o*-tolyl-2,3-naphthoquinone **1**, produced by lead tetraacetate oxidation of 2,3-dihydroxy-1,4-di-*o*-tolylnaphthalene **2** at -30 °C, is sufficiently stable to allow purification involving aqueous work-up and low temperature chromatography. It has been characterised by UV and IR spectroscopy as the adduct **11** formed with norbornadiene and by a comparison of its properties with those of the stable quinone **12**. The spectroscopic properties of **1** and **12** are in good agreement but indicate greater conjugation in the true naphthoquinone **1**. Whilst **1** gives mainly the cyclopentadiene adduct **20** by addition to C-1 and C-4, the quinone **12** resembles other *o*-benzoquinones in undergoing addition at both the diene and heterodiene systems. The hydroquinones required as quinone precursors were prepared *via* the cyclopentadienones **7** and **13**. With dichlorovinylene carbonate, **7** gave the adduct **9** which with Zn–HOAc gave the carbonate **10** of the required hydroquinone **2**.

2,3-Naphthoquinone (**1**; R = H) and its derivatives are of interest as high potential quinones which might have use as dehydrogenation reagents.[1] Unfortunately the parent system is too unstable to be observed although it can be generated by potassium iodate oxidation of naphthalene-2,3-diol (**2**; R = H) and trapped with cyclopentadiene.[2] The diphenyl derivative (**1**; R = Ph) could be generated and trapped at low temperature by lead tetraacetate oxidation of the diol (**2**; R = Ph).[3] The green colour associated with (**1**; R = Ph) survived for *ca.* 45 min at -20 °C. In an effort to prepare a sterically stabilised 2,3-naphthoquinone, stable enough for spectroscopic characterisation, we attempted preparation of the di-*o*-tolyl-2,3-naphthoquinone **1**. It was anticipated that *o*-tolyl groups would show a greater tendency to lie orthogonal to the *o*-quinonoid system and so present a greater steric blockade than phenyl groups. Indeed we had shown that the pyrone **3** underwent Diels–Alder reactions more slowly than (**3**; R = Ph).[4]



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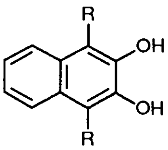

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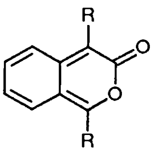

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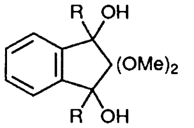
R = *o*-Tolyl unless stated otherwise in the text

Results and Discussion

o-Tolyllithium and ninhydrin dimethyl acetal gave the diol **4** which upon reduction (HI–HOAc) afforded the unstable ketone **5**. Fairly clean bromination of **5** was achieved using phenyltrimethylammonium perbromide. Addition of the monobromide **6** to sodium methoxide in methanol at -50 °C produced a transient green colour which may signal formation of the inden-2-one **7**. Isolation gave the dimer **8** of compound **7** (17%). As in a related case[5] the formal (6 + 6) π-dimer arises when C-1 and C-3 of the inden-2-one are sterically hindered. The properties of **8** were similar to those of the previously described dimer,[5] including IR absorption at 1650 cm^{-1} (enol ether) and a broad peak in the ^{13}C NMR spectrum (δ 88.4–89.6) for the sp^3 carbons attached to oxygen.[‡] Dissociation of dimer **8** in the presence of dichlorovinylene carbonate at 140 °C gave the adduct **9** of **7** in 54% yield. This underwent smooth dechlorination-decarbonylation (Zn–HOAc–Et_2O; 20 °C) to the carbonate **10** from which **2** (m.p. 223–227 °C) was obtained by acid hydrolysis (HCl–H_2O–HOAc).



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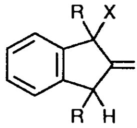
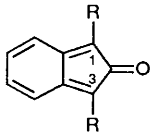


5 X = H
6 X = Br



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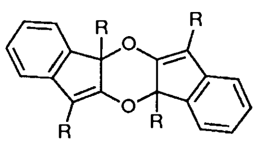

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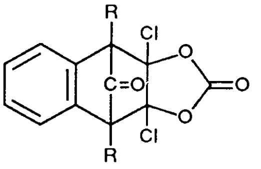

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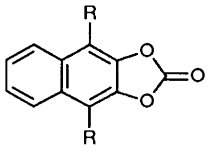

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Portionwise addition of **2** to an excess of lead tetraacetate in CH_2Cl_2 at -40 °C gave a deep green colour that persisted apparently unchanged over 2 h at -20 °C. In contrast the similar green colour due to (**1**; R = Ph) persisted for only 45 min at -20 °C. After addition of ethylene glycol to destroy excess lead tetraacetate the green solution of **1** was washed (× 3) with saturated aqueous sodium hydrogen carbonate and chromatographed rapidly on a short silica column in CH_2Cl_2–Et_2O (9:1) at -30 °C. The green eluate was concentrated, and the IR spectrum obtained at 20 °C, $\nu_{max}(CH_2Cl_2)/cm^{-1}$ 1603m, 1629s, 1655m, 1650sh. Addition of norbornadiene to the solution in the IR cell led to gradual (over 1 h) replacement of these bands by absorptions at ν_{max}/cm^{-1} 1729s, 1740sh and 1600w, shown by the *endo*-norbornadiene adduct **11** independently prepared by oxidation of **2** in the presence of

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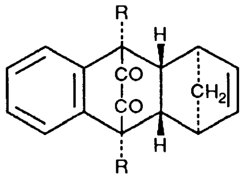
[†] Part of this work was published in preliminary form; D. W. Jones and A. Pomfret, *J. Chem. Soc., Chem. Commun.*, 1983, 703.

[‡] The reason for the line broadening is not known. Slow rotation of the tolyl rings or reversible cleavage of the weak C–O bonds are possible explanations.

norbornadiene.* The green solution (CH_2Cl_2–Et_2O) of **1** obtained after chromatography could be evaporated to a small volume at 20 °C (water pump vacuum) where upon addition of hexane and cooling and scratching at −70 °C led to partially crystalline **1**. This material appeared unchanged on storage at −40 °C over one week and exhibited a marked solvatochromism [$\lambda_{max}(C_6H_{14})$/nm = 636; $\lambda_{max}(CH_2Cl_2)$/nm 720] and IR absorption [ν_{max}(Nujol)/cm^{-1} 1630s, 1656m and 1650sh] very similar to that of the compound in CH_2Cl_2–Et_2O solution. Some additional absorption bands in the carbonyl region suggest that the quinone obtained in this way is probably not of analytical purity (see Experimental section). Accordingly, further evidence in support of the structure of **1** was sought by synthesis of the quinone **12**; incorporation of the B-ring diene system in aromatic rings was expected to reduce the 2,3-naphthoquinonoid character in **12** compared to **1** (R = Ph) and so provide a more stable compound. The compound **12** was prepared from phencyclone **13** in the same way as **1** was prepared from **7**; the terminal step involving lead tetraacetate oxidation of **14** at −40 °C (93% yield). Full details of the preparation are described in the Experimental section. In agreement with reduced 2,3-naphthoquinonoid character, **12** is stable and isolable in pure form. Like **1**, **12** showed marked solvatochromism [λ_{max}/nm 550 (C_6H_{14}) and 600 (CH_2Cl_2)] and low frequency carbonyl absorption [ν_{max}(Nujol)/cm^{-1} 1668m and 1648]. The carbonyl bands of **1** appear *ca.* 15 cm^{-1} to lower frequency than those of **12**. This agrees with the UV spectra in showing greater conjugation in the true naphthoquinone **1**. Similiar effects are seen for the related α-pyrones: **3** (R = Ph) shows ν_{max}(Nujol) = 1693 cm^{-1} wheareas the lactone derived by replacing one CO of **12** by an oxygen atom has ν_{max}(Nujol) = 1707 cm^{-1}, and tetraphenyl-α-pyrone has ν_{max}(Nujol) = 1715 cm^{-1}. In common with other quinones both **1** and **12** show intense (M + 2) peaks in their mass spectra. Such peaks are particularly important for *ortho*-quinones and high potential quinones and are believed to involve reaction with water in the source of the mass spectrometer.[6] The triphenylene quinone **12** differs from **1** and **1** (R = Ph) in the preferred site of addition with cyclopentadiene. Whereas **12** gives mainly the product **15** of addition to the heterodiene system and only a trace of **16**, the 2,3-naphthoquinones give mainly products of the latter type by addition to the 1,3-diene system. The quinone **12** resembles more closely the *o*-benzoquinones in which both modes of addition are important. This again suggests that **12** lacks full 2,3-naphthoquinone character. Although steric effects should be less for addition to the heterodiene system in 1,4-diphenyl-2,3-naphthoquinone, addition still strongly favours the C-1 and C-4 positions; a similar preference is seen for **1**[3] and 2,3-naphthoquinone itself.[2]



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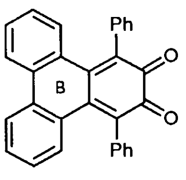

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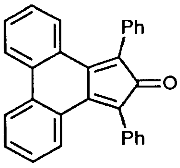

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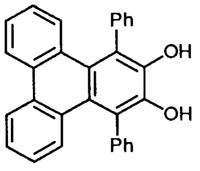

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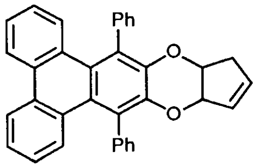

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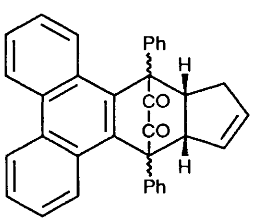

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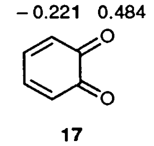
Treatment of these additions as Diels–Alder reactions of inverse electron demand suggests that LUMO quinone ↔ HOMO cyclopentadiene interaction should be dominant. However the LUMO's of *o*-benzoquinone and 2,3-naphthoquinone both have the (much) larger LUMO coefficients at the termini of the heterodiene system as shown in **17** and **18**.



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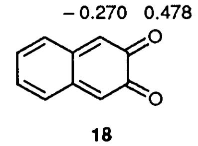

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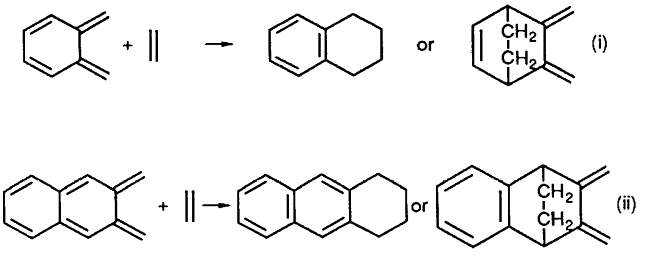
This suggests that dioxene formation should predominate for both types of quinone. Reference to the changes in Hückel π-electron energy (Δ*E*π) for the following model reactions is useful. For both (*i*) and (*ii*) in Scheme 1, the change in π energy should favour addition at the exocyclic diene but the preference [(Δ(Δ*E*π)] is 1.5 β for the additions to *o*- quinodimethane as in (i) and is reduced to 1.2 β for 2,3-naphthoquinodimethane. Relief of buttressing effects as in the addition to C-9 and C-10 of anthracene[7] may also accelerate addition to C-1 and C-4 of 2,3-naphthoquinones. We earlier reported that cyclopentene reacts with the diphenylquinone **1** (R = Ph) to give **2** and no isolatable adduct.[3] However the observation that the di-*o*-tolylquinone **1** gave the adduct **19** together with a trace of the cyclopentadiene adduct **20** prompted us to repeat our earlier work. We now find that use of freshly distilled cyclopentene allows the isolation of the adduct **19** (R = Ph) as well as a little of the cyclopentadiene adduct **20** (R = Ph). The possible role of impurities and the origin of the cyclopentadiene adducts **20** and **20** (R = Ph) remains to be clarified. These observations could be of significance in indicating the dehydrogenation of cyclopentene to cyclopentadiene under the influence of the high potential 2,3-naphthoquinones.



Scheme 1

Finally, we draw attention to the photorearrangement of the quinone **12**. Irradiation of a benzene solution of **12** through Pyrex with a medium pressure Hg arc was attempted as a possible route to the cyclobutadiene **21**. The product was the indenone **22**, a known compound[8] which may arise *via* the biradical **23** as a key intermediate; decarbonylation (**23**; see arrows on structure) then

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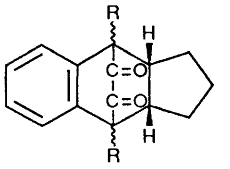
* The high field positions of the methylene protons (δ 0.58 and −1.00) indicate the *endo*-configuration of **11**, c.f. ref. 3.



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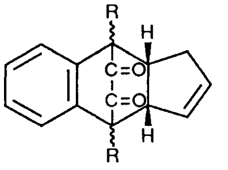

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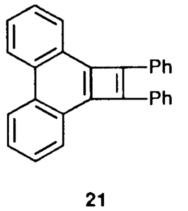

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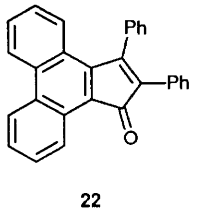

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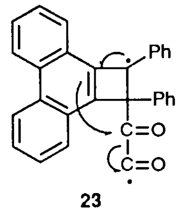

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gives the valence tautomer of **22** and hence **22** itself. Similar irradiation of phencyclone failed to produce **22**.

The evidence presented in this paper supports the independent existence of 2,3-naphthoquinones and argues against the involvement of lead salts, radicals, radical cations or semiquinones in the earlier experiments.[3]

Experimental

For general details see ref. 9. Values of coupling constants *J* are given in Hz. Light petroleum refers to the fraction boiling at 60–80 °C. Ether refers to diethyl ether.

Preparation of 1,3-*Dihydroxy*-2,2-*dimethoxy*-1,3-*di*-o-*tolylindane*.—Ninhydrin dimethyl acetal (5 g, 0.024 mol) in dry ether (75 cm^3) was added dropwise to a solution of *o*-tolyllithium [from *o*-tolylbromide (52 g, 0.31 mol) and lithium shot (4.25 g, 0.61 g atom)] in dry ether (50 cm^3). The solution was stirred at 25 °C for 30 min then quenched with water and the ether layer separated and dried ($MgSO_4$). Evaporation of the solvent and addition of a small volume of methanol to the residue gave the white crystalline *title compound* (6.95 g, 74%) m.p. 174–176 °C from benzene–light petroleum. (Found: C, 77.05; H, 6.55. $C_{25}H_{26}O_4$ requires C, 76.9; H, 6.67%); ν_{max}/cm^{-1} 3550 and 3520; δ 7.90–6.80 (12 H, m, aromatic protons), 3.70 (2 H, br s, 2 × OH, exchange D_2O), 3.10 (6 H, s, 2 × OMe), 2.25 (6 H, br s); *m*/*z* 373, 372, 299, 298 and 119 (22.6, 76.2, 17.61 and 70.2%) (Found: M, 390.183. $C_{25}H_{26}O_4$ requires M, 390.183).

Reduction of 1,3-*Dihydroxy*-2,2-*dimethoxy*-1,3-*di*-o-*tolylindane with Hydriodic Acid*.—A mixture of 1,3-dihydroxy-2,2-dimethoxy-1,3-di-*o*-tolylindane (6.37 g, 16.33 mmol), hydriodic acid (26.6 cm^3; freshly distilled from red phosphorus), glacial acetic acid (54 cm^3) and red phosphorus (300 mg) were stirred under nitrogen at 100 °C for 3 h. The cooled mixture was diluted with methylene chloride, washed with aqueous sodium metabisulphite and water and dried ($MgSO_4$). Evaporation of the solvent left a deep orange oil which was dissolved in ether and washed several times with aqueous sodium hydrogen carbonate. The hydrogen carbonate washings were acidified with conc. hydrochloric acid, extracted with ether, and the ether layer dried ($MgSO_4$). Evaporation of the ether and crystallisation of the residue from benzene–light petroleum gave the acid (2.19 g, 40%) m.p. 176–177 °C (from benzene–light petroleum) (Found: C, 79.95; H, 6.05. $C_{23}H_{20}O_3$ requires C, 80.2; H, 6.05%), ν_{max}/cm^{-1} 2730, 2600 and 1710. The original ether layer was dried ($MgSO_4$) and evaporated, and the residue chromatographed on silica using benzene–light petroleum (4:1) to give an isomeric mixture of 1,3-*di*-o-*tolylindan*-2-*ones* (2 g, 40%) as an unstable pale yellow oil. (Found: M, 312.15. $C_{23}H_{20}O$ requires M, 312.151); ν_{max}(neat)/cm^{-1} 1755; δ_H 7.45–6.30 (12 H, m, aromatic protons), 5.12 (1 H, s), 5.08 (1 H, s), 2.36 (3 H, s) and 2.31 (3 H, s).

Preparation of the Monobromide **6** *and reaction with Sodium Methoxide–Methanol*.—A mixture of 1,3-di-*o*-tolylindan-2-one (4.64 g, 0.0149 mol), phenyltrimethylammonium perbromide (5.6 g, 0.0149 mol) and dry tetrahydrofuran (75 cm^3) was stirred at 25 °C for 1 h. The reaction mixture was poured into a 1:1 mixture of 0.1 mol dm^{-3} sodium thiosulphate solution (100 cm^3) and aqueous sodium hydrogen carbonate solution (100 cm^3) and extracted with ether. The ether layer was washed with water and brine and dried ($MgSO_4$). Evaporation of the solvent gave a pale orange oil which was dissolved in dry ether (15 cm^3) and added to a freshly prepared solution of sodium methoxide in methanol [from sodium (1.4 g, 0.06 g atom) and methanol (60 cm^3)] at −50 °C under nitrogen. The mixture was allowed to warm to −40 °C and after 5 min at this temperature was quenched with water. The mixture was extracted with ether and the ether layer dried ($MgSO_4$). Evaporation of the solvent gave a deep red residue which was extracted with petroleum, filtered and the filtrate evaporated to dryness. Chromatography of the residue on silica using petroleum–light benzene (7:3) gave the *dimer* **8** (780 mg, 17%) m.p. 190–194 °C (d), from methylene chloride–methanol. (Found: C, 88.8; H, 5.9%; M(osmometer), 628. $C_{46}H_{36}O$ requires C, 89.0; H, 5.8%; M, 620); ν_{max}/cm^{-1} 1650 and 1600; δ_H 7.80–6.50 (24 H, m) and 2.50–1.00 (12 H, m); δ_C 19.3, 19.9, 20.3, 20.4, 20.5, 20.7, 21.6, 21.9, 22.9, 88.4–89.6 (br peak for C-1) 119.3, 120.0, 123.6, 125.4, 125.5, 126.1, 127.2, 127.8, 128.5, 129.3, 130.0, 130.5, 130.6, 131.1, 131.2, 132.7, 133.1, 133.2, 135.8, 137.6, 158.4 and 158.8.

Reaction of the Dimer **8** *with Various Reducing Agents*.—(*a*) *Zinc and acetic acid*. Zinc dust (200 mg, 0.0031 g atom) was added portionwise to a solution of the dimer (10 mg, 0.016 mmol) in glacial acetic acid (2 cm^3) under nitrogen with occasional warming and stirring. After the final addition the mixture was boiled under reflux for 1 min and allowed to cool. The mixture was diluted with ether, filtered, washed with aqueous sodium hydrogen carbonate and water and dried ($MgSO_4$). Evaporation of the ether gave an oil (10.7 mg), the ^1H NMR of which was identical with that of 1,3-di-*o*-tolylindan-2-one.

(*b*) *Lithium aluminium hydride*. The dimer (25 mg, 0.0403 mmol), lithium aluminium hydride (25 mg, 0.658 mmol) and dry ether (4 cm^3) were stirred at 25 °C under nitrogen for 2.5 h. Lithium aluminium hydride (100 mg, 2.63 mmol) was added and the mixture stirred for a further 22 h. The mixture was diluted with ether, washed with dilute sulphuric acid and water and dried ($MgSO_4$). Evaporation of the solvent and chromatography of the residue on silica in benzene gave 1,3-di-*o*-tolylindan-2-one (7.8 mg, 31%).

Reaction of the Monobromide **6** *with Diazabicyclononene in the Presence of Bicyclo*[2.2.1]*heptadiene*.—Diazobicyclononene (200 mg, 1.613 mmol) was added to the monobromide **6** (150 mg, 0.384 mmol), bicyclo[2.2.1]heptadiene (2 cm^3) and dry benzene (7 cm^3) under nitrogen. The mixture was boiled under reflux for 45 min, cooled, poured into ether, washed with dilute hydrochloric acid and water and dried ($MgSO_4$). Evaporation of the solvent and chromatography of the residue on silica using benzene–light petroleum (4:1) gave the endo-*bicyclo*[2.2.1]*heptadiene adduct* of **7** (55.3 mg, 35.8%) m.p. 235–244 °C from methylene chloride–methanol. (Found: C, 89.45; H, 6.75. $C_{30}H_{26}O$ requires C, 89.55; H, 6.5%); ν_{max}/cm^{-1} 1770; δ_H 7.80–7.50 (2 H, m, aromatic), 7.50–7.15 (8 H, m, aromatic protons), 6.95–6.70 (2 H, m, aromatic protons), 6.37 (2 H, br s, olefinic), 3.00 (2 H, br s), 2.70 (2 H, s), 1.95 (6 H, s), 0.58 (1 H, d, *J* 10) and −0.86 (1 H, d, *J* 10).

Hydrogenation of Adduct.—The *endo*-adduct (30 mg, 0.0746 mmol), ethyl acetate (4 cm^3) and 10% palladium–carbon (10 mg) were shaken in a hydrogen atmosphere for 30 min. The solution was filtered through Celite and evaporation of the solvent gave the endo-*bicyclo*[2.2.1]*heptene adduct* (30 mg, 99.5%) m.p. 233–243 °C(d), from methylene chloride–ethanol. (Found: C, 89.15; H, 7.0. $C_{30}H_{28}O$ requires C, 89.1, H, 6.9%); ν_{max}/cm^{-1} 1778; δ_H 7.75–7.45 (2 H, m, aromatic protons), 7.45–7.15 (8 H, m, aromatic protons), 6.95–6.70 (2 H, m, aromatic protons), 2.84 (2 H, s), 2.38 (2 H, br s), 1.88 (6 H, s), 1.50 (4 H, br s), 0.45 (1 H, d, *J* 11) and −0.80 (1 H, d, *J* 11) (Found: M, 404.214. $C_{30}H_{28}O$ requires M, 404.214).

Reaction of the Monobromide **6** *with Sodium Methoxide–Methanol and Bicylo*[2.2.1]*heptadiene.*—The monobromide (85.6 mg, 0.2189 mmol) in dry ether (2 cm^3) was added to a freshly prepared solution of sodium methoxide [from sodium (30 mg, 0.0013 g atom) and dry methanol (5 cm^3)] and bicyclo[2.2.1]heptadiene (1 cm^3) at 25 °C under nitrogen. The mixture was stirred for 20 min then quenched with water, extracted with ether, and the ether layer dried ($MgSO_4$). Evaporation of the solvent and chromatography of the residue on silica in benzene–light petroleum (4:1) gave the *endo*-adduct (19.6 mg, 22.3%) identified by its m.p., IR and mixed m.p. with authentic material.

Thermal Dissociation of the 1,3-*Di*-o-*tolylinden*-2-*one Dimer in the Presence of Dichlorovinylene Carbonate.*—The 1,3-di-*o*-tolylinden-2-one dimer **8** (400 mg, 0.645 mmol), dichlorovinylene carbonate (2.8 g, 0.018 mol) and dry, deoxygenated xylene (15 cm^3) were heated under reflux under argon for 6.5 h. Evaporation of the solvent in high vacuum at 100 °C and rapid chromatography of the residue on silica in benzene gave the *dichlorovinylene carbonate adduct* **9** (325.4 mg, 54.2%) m.p. 197–201 °C, from benzene–light petroleum. (Found: C, 67.45; H, 4.1; Cl, 15.2. $C_{26}H_{18}Cl_2O_4$ required C, 67.1; H, 3.9; Cl, 15.2%); ν_{max}/cm^{-1} 1855 and 1800; *m*/*z* 440, 438 and 436 (M − CO), 403 and 401 (M − COCl), 366 (M − $COCl_2$), 332, 291, 277 and 202 (5.4, 23.8, 37.2, 14.8, 27.4, 61.1, 46.2, 100, 88.2 and 50.1%).

Reaction of Adduct **9** *with Zinc and Glacial Acetic Acid.*—The adduct **9** (300 mg, 0.645 mmol), zinc dust (200 mg, 0.0031 g atom), glacial acetic acid (3 cm^3) and dry ether (15 cm^3) were stirred at room temperature for 45 min. The ether layer was decanted and the residue washed with several portions of ether. The combined ether layers were washed with dilute aqueous sodium hydrogen carbonate and water and dried ($MgSO_4$). Evaporation of the ether and crystallisation of the residue from benzene–light petroleum gave 1,4-*di*-o-*tolylnaphthalene*-2,3-*diol carbonate* **10** (129 mg. 54.6%). Evaporation of the filtrate and chromatography of the residue on silica in benzene–ether (1:1) gave **10** (35 mg, 14.8%) m.p. 177–179 °C; (Found: C, 81.7; H, 4.65. $C_{25}H_{18}O_3$ requires C, 82.0; H, 4.9%); ν_{max}/cm^{-1} 1880, 1843 and 1798; λ_{max}(EtOH)/nm 237, 275(sh), 284, 294, 320(sh) and 322, ($\varepsilon/dm^3\ mol^{-1}\ cm^{-1}$ 28 326, 7419, 9667, 10 117, 2698 and 2248), δ_H 7.90–7.00 (12 H, br m, aromatic protons) and 2.50–2.00 (6 H, br s); *m*/*z* 366 (M), 307, 293, 279 and 202 (100, 8.3, 17.4, 17.3 and 25.5%) (Found: M, 366.125. $C_{25}H_{18}O_3$ requires M, 366.125).

Preparation of 1,4-*Di*-o-*tolylnaphthalene*-2,3-*diol* **2**.—A mixture of 1,4-di-*o*-tolylnaphthalene carbonate **10** (120 mg, 0.328 mmol), glacial acetic acid (9.6 cm^3) and concentrated hydrochloric acid (2.4 cm^3) were boiled under reflux for 1 h and then allowed to cool to 25 °C. The white crystalline material deposited was filtered to give 1,4-*di*-o-*tolylnaphthalene*-2,3-*diol* (85.3 mg, 76.5%). The acidic filtrate was neutralised with aqueous sodium hydrogen carbonate and extracted with ether. The ether layer was washed with water and dried ($MgSO_4$). Evaporation of the solvent and crystallisation of the residue from glacial acetic acid gave compound **2** (18.4 mg, 16.5%) m.p. 223–227 °C; (Found: C, 84.45; H, 5.8, $C_{24}H_{20}O_2$ requires C, 84.7; H, 5.9%); ν_{max}/cm^{-1} 3430; λ_{max}(EtOH)/nm 241, 295 and 336 ($\varepsilon/dm^3\ mol^{-1}\ cm^{-1}$ 40 561, 10 498 and 2266); δ_H 7.50–7.28 (8 H, m, aromatic protons), 7.20 (4 H, s, aromatic protons), 5.24 (2 H, br s, 2 × OH, exchange D_2O) and 2.10 (6 H, s); *m*/*z* 340 (M), 293, 279 and 202 (100, 4.2, 5.6 and 7.0%) (Found: M, 340, 1465. $C_{24}H_{20}O_2$ requires M, 340, 1463).

Generation and Trapping of 1,4-*Di*-o-*tolyl*-2,3-*naphthoquinone by Lead Tetraacetate Oxidation of* 1,4-*Di*-o-*tolylnaphthalene*-2,3-*diol.*—(i) *With cyclopentene at* −40 °C. 1,4-Di-*o*-tolylnaphthalene -2,3-*diol* (50 mg, 0.147 mmol) was added in small portions with stirring to lead tetraacetate (70 mg, 0.158 mmol) in methylene chloride (4 cm^3) and cyclopentene (1.5 cm^3) at −40 °C under argon. The mixture was allowed to warm to 25 °C over 1 h, filtered through Celite and evaporated. The residue was chromatographed on silica in benzene–light petroleum (4:1) to give the *cyclopentene adduct* **19** (17 mg, 28.5%), m.p. 282–286 °C, from methylene chloride–methanol; (Found: C, 85.35; H, 6.4. $C_{29}H_{26}O_2$ requires C, 85.7; H, 6.4%); ν_{max}/cm^{-1} 1725; δ_H 7.60–7.20 (8 H, br s, aromatic protons), 7.20–7.00 (2 H, m, aromatic protons), 6.65–6.40 (2 H, m, aromatic protons), 3.60–3.30 (2 H, m), 2.50–2.10 (2 H, m), 1.95 (6 H, s) and 1.90–1.10 (4 H, m); *m*/*z* 406 (M), 350 (M −2 CO), 322, 307, 258 and 215 (1.5, 100, 5.7, 7.3, 10.4 and 17%) (Found: M, 406.193. $C_{29}H_{26}O_2$ requires M, 406.193). Further elution of the column gave the cyclopentadiene adduct **20** (1 mg, 1.7%) from methylene chloride–methanol; δ_H 7.70–7.30 (8 H, m, aromatic protons), 7.30–7.00 (2 H, m, aromatic protons), 7.00–6.70 (2 H, m, aromatic protons), 5.76–5.56 (1 H, m, olefinic protons), 5.50–5.30 (1 H, olefinic proton), 4.24 (1 H, br d, *J* 9), 3.64 (1 H, dt, *J* 4 and 9), 3.20–2.76 (1 H, m), 2.40–2.06 (1 H, m), 1.99 (3 H, s) and 1.95 (3 H, s).

(ii) *With bicyclo*[2.2.1]*heptadiene at* −40 °C. 1,4-Di-*o*-tolylnaphthalene -2,3-diol (30 mg, 0.088 mmol) was added in small portions with stirring to lead tetraacetate (45 mg, 0.1 mmol) in methylene chloride (2 cm^3) and bicyclo[2.2.1]-heptadiene (2 cm^3) at −40 °C under argon. The mixture was allowed to warm to 25 °C, stirred for 1 h, filtered through Celite and evaporated. Chromatography of the residue on silica in benzene gave the endo-*bicyclo*[2.2.1]*heptadiene adduct* **11** (12 mg); m.p. 289–293 °C, from chloroform–methanol. (Found: C, 86.6; H, 6.0. $C_{31}H_{26}O_2$ requires C, 86.5; H, 6.0%); ν_{max}/cm^{-1} 1741 and 1726; δ_H 7.70–7.14 (10 H, m, aromatic protons), 7.14–6.80 (2 H, m, aromatic protons), 6.50 (2 H, brs, olefinic protons), 3.30 (2 H, m), 2.75 (2 H, s), 1.99 (6 H, s), 0.58 (1 H, d, *J* 10) and −1.00 (1 H, d, *J* 10); *m*/*z* 430 (M), 308 and 215 (0.6, 100 and 11.6%) (Found: M, 430.194. $C_{31}H_{26}O_2$ requires M, 430.193).

Generation of 1,4-*Diphenyl*-2,3-*naphthoquinone by Lead Tetraacetate Oxidation of* 1,4-*diphenylnaphthalene*-2,3-*diol and* in situ *Trapping with Cyclopentene at* −40 °C.—Compound **2** (200 mg, 0.64 mmol) was added in small portions with stirring to lead tetraacetate (284 mg, 0.64 mmol) in methylene chloride (4 cm^3) and cyclopentene (4 cm^3) at −40 °C under argon. The mixture was allowed to warm to 25 °C, stirred for 1 h, diluted with methylene chloride, washed with water, and dried ($MgSO_4$). Evaporation of the solvent and chromatography of the residue on silica using benzene–light petroleum (19:1) gave the known trimer (40 mg, 20%) m.p. and IR spectrum identical with an authentic sample. Further elution of the column gave the *cyclopentene adduct* (80 mg, 33%) m.p. 253–255 °C, from methylene chloride–methanol. (Found: C, 85.7; H, 6.1. $C_{27}H_{22}O_2$ requires C, 85.7; H, 5.8%); ν_{max}/cm^{-1} 1735 and 1680; δ_H 8.05–7.35 (10 H, br, aromatic protons), 7.35–6.95 (2 H, m, aromatic protons), 6.65–6.35 (2 H, m, aromatic protons), 3.65–3.38 (2 H, m), 2.55–1.97 (2 H, m), 1.97–1.50 (2 H, m) and 1.50–1.10 (2 H, m); *m/z* 378 (M), 322, 320, 293 and 205 (0.3, 100, 21.9, 12.1 and 21.0%) (Found: M, 378.161. $C_{27}H_{22}O_2$ requires M, 378.162). Further elution of the column gave the *cyclopentadiene adduct* (1.8 mg, 0.75%) m.p. and IR spectrum identical with an authentic sample.

Preparation of a Solution of 1,4-*Di-*o-*tolyl-*2,3-*naphthoquinone in order to obtain its IR Spectrum.*—Compound **2** (10 mg) was added portionwise over *ca.* 10 min to a stirred solution of lead tetraacetate (15 mg), in methylene chloride (2 cm^3) at −40 °C. The deep blue green solution produced was treated with 4 drops of ethylene glycol and stirring continued at −40 °C (5 min). The product was poured into water, extracted into dichloromethane and the organic layer washed with saturated aqueous sodium hydrogen carbonate (× 3). The dichloromethane solution was applied to a 12 g column of silica gel 60 (Camlab 230–400 mesh) constructed in CH_2Cl_2–Et_2O (95:5), and held at −30 °C. The green band was rapidly eluted and collected in a flask held at −40°C. Rejection of the first *ca.* one third of the green band provided a dichloromethane solution which upon concentration under reduced pressure at 20 °C gave strong IR bands at 1628, 1603 and 1655 cm^{-1} and only weak peaks at 1730–1740 and 1950 cm^{-1} associated with impurities. Addition of norbornadiene to the solution in the IR cell led to gradual (over 1 h) replacement of these bands by absorptions at ν_{max}/cm^{-1} 1729s, 1740sh and 1600w shown by the *endo*-norbornadiene adduct described previously. The green (CH_2Cl_2-Et_2O) solution of the quinone obtained after chromatography could be evaporated to a small volume at 20 °C when addition of hexane and cooling and scratching at −70 °C gave partially crystalline **1**. This material appeared stable at −40 °C for 7 days and apart from a weak broad band at ν/cm^{-1} 1740 in the IR spectrum(Nujol), appeared reasonably pure. Other ν_{max} values included 1601w, 1630s, 1655m cm^{-1}; λ_{max}/nm 636 (C_6H_{14}) and 720 (CH_2Cl_2); *m/z* 366 (impurity), 340 (M + 2), 298, 279, 202, 178, 141, 119, 91, 69, 57 and 43 (5.8, 100.0, 5.5, 5.4, 5.3, 7.4, 4.7, 16.8, 16.2, 11.8, 10.7 and 17.8%).

Diels–Alder Addition of Phencyclone and Dichlorovinylene Carbonate.—Phencyclone (1.1 g, 2.96 mmol) was added to a deoxygenated solution of dry toluene (20 cm^3) and dichlorovinylene carbonate (6 g, 0.039 mol) and the mixture boiled under reflux in an argon atmosphere (42 h). Evaporation of the solvent at 100 °C under high vacuum gave a pale yellow oil of the *adduct* (1.15 g, 74%) m.p. 214–220 °C(d). (Found: M, 536.0588. $C_{32}H_{18}{}^{35}Cl_2O_4$ requires M, 536.0582); ν_{max}/cm^{-1} 1842 and 1797; δ_H 8.55–6.80 (18 H, m, aromatic protons); *m/z* 540, 538 and 536 (M), 466 (M − Cl_2), 438 (M − CO − Cl_2), 394, 366, 364 and 363 (0.8, 8, 14.3, 10, 66.7, 32.8, 45.6, 100, 52.9 and 72%).

Reaction of the Foregoing Adduct with Zinc and Glacial Acetic Acid.—The adduct (1.0 g, 1.87 mmol), zinc dust (1.25 g), glacial acetic acid (20 cm^3) and dry ether (100 cm^3) were stirred at 25 °C for 2 h. The mixture was poured into chloroform (500 cm^3) and the solution warmed until all the organic material had dissolved. The warm solution was filtered and the solvent removed under vacuum. Trituration of the product with methylene chloride–methanol gave the 1,4-*diphenyltriphenylene*-2,3-*diolcarbonate* (532 mg, 65%), m.p. > 320 °C; ν_{max}/cm^{-1} 1870 and 1835; (Found: M, 438.125. $C_{31}H_{18}O_3$ requires M, 438.126).

Preparation of 1,4-*Diphenyltriphenylene*-2,3-*diol* **14**.—The 1,4-diphenyltriphenylene-2,3-diol carbonate (500 mg, 1.14 mmol), glacial acetic acid (75 cm^3), conc. hydrochloric acid (19 cm^3) and dioxane (80 cm^3) were boiled under reflux for 4.5 h. Evaporation of the solvent at 100 °C under vacuum and rapid chromatography of the residue on silica using benzene–ether (19:1) gave the *title compound* **14** (290 mg, 62%) m.p. 260–265 °C. (Found: C, 87.3; H, 4.75. $C_{30}H_{20}O_2$ requires C, 87.4; H, 4.85%); ν_{max}/cm^{-1} 3450; δ_H 8.40 (2 H, d, aromatic protons), 7.62–6.87 (16 H, m, aromatic protons), 5.71 (2 H, s, OH, exchange D_2O); *m/z* 412, 393 and 364 (100, 11.3 and 29.6%) (Found: M, 412.146. $C_{30}H_{20}O_2$ requires M, 412.146).

Preparation of 1,4-*Diphenyltriphenylene*-2,3-*dione* **12** *by Lead Tetraacetate Oxidation of* 1,4-*Diphenyltriphenylene*-2,3-*diol* **14**.—The diol **14** (200 mg, 0.485 mmol) was added in small portions over a 20 min period to a stirred solution of lead tetraacetate (280 mg, 0.632 mmol) in methylene chloride (10 cm^3) at −40 °C under argon. The deep green solution was allowed to warm to 25 °C, diluted with methylene chloride, washed with ethylene glycol and aqueous sodium hydrogen carbonate and water and dried (K_2CO_3). Evaporation of the solvent and crystallisation of the residue from benzene–light petroleum gave *compound* **12** (185 mg, 93%), m.p. 240–244 °C; (Found: C, 87.6; H, 4.4. $C_{30}H_{18}O_2$ requires C, 87.8; H, 4.4%); ν_{max}/cm^{-1} 1668 and 1648; δ_H 7.72 (2 H, d, aromatic protons), 7.60–6.70 (16 H, m, aromatic protons), δ_C 123.5, 126.9, 127.8, 128.3, 129.1, 129.6, 130.8, 131.2, 132.1, 133.9, 134.4, 148.3 and 182.6; (Found: M, 410.1305. $C_{30}H_{18}O_2$ requires M, 410.1307).

Reaction of 1,4-*Diphenyltriphenylene*-2,3-*dione with Cyclopentadiene.*—The 2,3-quinone (50 mg, 0.161 mmol) was added to a deoxygenated solution of benzene (3 cm^3) and cyclopentadiene (3 cm^3) and boiled under reflux for 2 h. Evaporation of the solvent and chromatography of the residue on silica using benzene–light petroleum (4:1) gave the *cyclopentadiene adduct* **15** (34.4 mg, 45%), m.p. 230–235 °C, from chloroform–methanol; (Found: C, 88.05; H, 5.0. $C_{32}H_{24}O_2$ requires C, 88.2; H, 5.0%); δ_H 8.34 (2 H, d, aromatic protons), 7.60–6.80 (16 H, m, aromatic protons), 6.00 (1 H, m, olefinic proton), 5.80 (1 H, m, olefinic proton), 5.12 (1 H, m, methine proton), 4.90 (1 H, m, methine proton) and 2.62 (2 H, m, methylene protons), *m/z* 476 (M), 382 and 354 (100, 60.1 and 56.1%) (Found: M, 476.177. $C_{35}H_{24}O_2$ requires M, 476.178). Further elution of the column gave the yellow *cyclopentadiene adduct* **16** (1 mg) from benzene–light petroleum; (Found: M 467, 177. $C_{35}H_{24}O_2$ requires M, 476. 178); δ_H 8.55 (2 H, d, aromatic protons), 6.80–7.80 (16 H, m, aromatic protons), 5.86 (1 H, m, olefinic proton), 5.50 (1 H, m, olefinic proton), 4.05 (2 H, m, methine protons), 2.85 (1 H, m), 2.54 (1 H, m); *m/z* 476 (M), 448 (M − CO), 420 (M − 2CO) and 380 (15.1, 51.5, 100 and 31.7%).

Irradiation of 1,4-*Diphenyltriphenylene*-2,3-*dione* **12**.—The quinone **12** (60 mg) in deoxygenated benzene (15 cm^3) was flushed with argon and irradiated in a silica flask with a 100 W Hanovia water-cooled lamp (Pyrex inner and silica outer-jacket) placed close by. After *ca.* 1.5 h the initial green colour had been replaced by brown, and concentration of the solution gave a maroon solid (24 mg). A further quantity of the solid (6 mg) was obtained by chromatography of the mother liquor on silica in light petroleum–benzene (25:75). The product recrystallised from toluene, m.p. 288–290 °C (lit.,[8] m.p. 284–286 °C) (Found: C, 90.9; H, 4.9%; M, 382.1569. Calc. for $C_{29}H_{18}O$: C, 91.1; H, 4.7%; M, 382.1565); *m/z* 382, 352, 305 and 276 (100, 14.6, 3.4 and 1.5%). Irradiation of phencyclone under the same conditions apparently failed to produce this product [TLC examination in light petroleum–benzene (25:75)].

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