

1,4-Di-*o*-tolyl-2,3-naphthoquinone

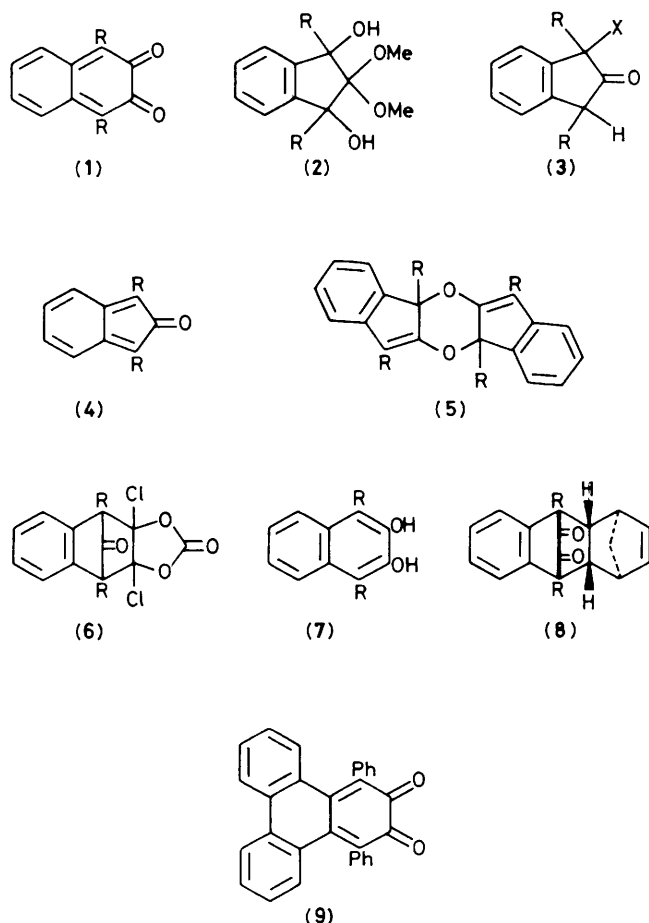
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1,4-Di-*o*-tolyl-2,3-naphthoquinone (**1**), produced by lead tetra-acetate oxidation of 1,4-di-*o*-tolynaphthalene-2,3-diol (**7**) at -30°C is sufficiently stable to allow purification involving aqueous work-up and low temperature chromatography; it has been characterised by u.v. and i.r. spectroscopy, as the adduct (**8**) formed with norbornadiene, and by a comparison of its properties with those of the stable quinone (**9**).

Both lead tetra-acetate oxidation of 1,4-diphenylnaphthalene-2,3-diol,¹ and potassium iodate oxidation of naphthalene-2,3-

diol² are believed to involve transient 2,3-naphthoquinones. In these studies the quinones were characterised as the adducts



R = *o*-tolyl throughout.

formed with dienes for in neither case was the quinone sufficiently stable to permit spectroscopic observation. We describe the preparation and spectroscopic characterisation of the sterically stabilized 1,4-di-*o*-tolyl-2,3-naphthoquinone (1).

o-Tolyl-lithium and ninhydrin dimethyl acetal gave the diol (2) which upon reduction (HI-HOAc) afforded the unstable ketone (3; X = H). Fairly clean bromination of (3; X = H) was achieved using phenyltrimethylammonium perbromide. Addition of the monobromide (3; X = Br) to sodium methoxide in methanol at -50°C produced a transient green colour which may signal formation of the inden-2-one (4). Isolation gave the dimer (5) of (4) (17%), m.p. $190-194^{\circ}\text{C}$. This had properties similar to those of a related inden-2-one dimer³ including i.r. absorption at 1650 cm^{-1} (enol ether) and a broad peak in the ^{13}C n.m.r. spectrum (δ 88.4–89.6 p.p.m.) for the sp^3 -carbons attached to oxygen. Dissociation of dimer (5) in the presence of dichlorovinylene carbonate at 140°C gave the adduct (6) of (4) (54%), m.p. $197-201^{\circ}\text{C}$. This underwent smooth dechlorination-decarbonylation ($\text{Zn-HOAc-Et}_2\text{O}$, 20°C) to the carbonate of the catechol (7), from which (7), m.p. $223-227^{\circ}\text{C}$, was obtained by acid hydrolysis ($\text{HCl-H}_2\text{O-HOAc}$).

Portionwise addition of (7) to an excess of lead tetra-acetate in CH_2Cl_2 at -40°C gave a deep green colour that persisted

apparently unchanged at -20°C over 2 h.[†] After addition of ethylene glycol to destroy the excess of lead tetra-acetate the green solution was washed (3 times) with saturated sodium hydrogen carbonate solution and chromatographed rapidly on a short silica column in $\text{CH}_2\text{Cl}_2\text{-Et}_2\text{O}$ (9:1) at -30°C . The green eluate was concentrated, and the i.r. spectrum obtained, at 20°C : ν_{max} (CH_2Cl_2) 1603m , 1629s , 1655m , 1650sh cm^{-1} . Addition of norbornadiene to the solution in the i.r. cell led to gradual (over 1 h) replacement of these bands by absorptions at 1729s , 1740sh , and 1600w cm^{-1} shown by the *endo*-norbornadiene adduct (8); (8) was independently prepared by oxidation of (7) in the presence of norbornadiene. The green ($\text{CH}_2\text{Cl}_2\text{-Et}_2\text{O}$) solution of (1) obtained after chromatography could be evaporated to small volume at 20°C when addition of hexane and cooling and scratching at -70°C led to partially crystalline (1). This material appeared stable at -40°C over 7 days and exhibited a marked solvatochromy [λ_{max} (C_6H_{14}) 636 nm , λ_{max} (CH_2Cl_2) 720 nm] and i.r. absorption (Nujol) at 1630s , 1656m , and 1650sh cm^{-1} very similar to that of the $\text{CH}_2\text{Cl}_2\text{-Et}_2\text{O}$ solution. The quinone (1) obtained in this way is probably not of analytical purity. Accordingly further evidence in support of the constitution (1) was sought by comparison with the quinone (9). This was prepared from phenylcyclohexene in the same way as (1) was prepared from (4), the terminal step involving catechol oxidation with $\text{Pb}(\text{OAc})_4$ at -40°C . In agreement with reduced 2,3-naphthoquinonoid character, (9) is stable and isolable in pure form. Like (1), (9) showed marked solvatochromy [λ_{max} (C_6H_{14}) 550 nm , λ_{max} (CH_2Cl_2) 600 nm] and low frequency carbonyl absorption [ν_{max} (Nujol) 1668m and 1648s cm^{-1}]. In common with other *ortho*-quinones⁴ both (1) and (9) show intense ($M + 2$) peaks in their mass spectra. Efforts are continuing to characterise further (1) and explore its reactions including its utility, as a high potential quinone,⁵ in dehydrogenation reactions. The evidence presented here supports the independent existence of certain 2,3-naphthoquinones and argues against the involvement of lead salts, radicals, radical cations, or semi-quinones in the earlier trapping experiments.¹

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References

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[†] The similar green colour from 1,4-diphenylnaphthalene-2,3-diol disappeared after 45 min at -20°C .

[‡] The bands of (1) appear *ca.* 15 cm^{-1} to lower frequency than those of (9). This agrees with the u.v. spectra in showing greater conjugation in the true naphthoquinone (1); 1,4-diphenyl-2-benzopyran-3-one shows ν_{max} (Nujol) 1693 cm^{-1} whereas the lactone derived by replacing one CO of (9) by oxygen has ν_{max} (Nujol) 1707 cm^{-1} , and tetraphenyl- α -pyrone has ν_{max} (Nujol) 1715 cm^{-1} .