Benzoquinones and Related Compounds. Part 5.[1] Nuclear Magnetic Resonance Study of the Conformation in Solution of Some Diels–Alder Adducts between 1,4-Benzoquinones and Cyclopentadiene

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The Diels–Alder reaction of cyclopentadiene with the 5,6-double bond of benzyl-, α-hydroxybenzyl-, and α-acetoxybenzyl-1,4-benzoquinone, and of 1-hydroxy-1-phenyl-, 1-phenyl-, and 1-hydroxy-indan-4,7-quinone gives in each case a pair of diastereoisomeric *endo* adducts. For those which carry a phenyl group, the chemical shift of one of the norbornene olefinic protons in one member of each pair is significantly different from that of the corresponding proton in the other member. The conformational significance of this effect is discussed. Proton longitudinal relaxation and nuclear Overhauser relaxation techniques are used to show that the cyclopentadiene *endo* monoadducts of 1,4-benzoquinone and α-hydroxybenzyl-1,4-benzoquinone prefer to adopt an 'open' rather than a 'closed' conformation.

The dipole moment of the Diels–Alder *endo* monoadduct of 1,4-benzoquinone and cyclopentadiene indicates that the enedione ring adopts a boat conformation in which the carbonyl groups are *cis* to each other.[2,3] With respect to the norbornene moiety, two extreme conformations, 'open' (**1**), and 'closed' (**2**), are then possible. Although the closed conformation must exist, at least in an excited state, to allow formation of the cage compound (**3**; R = H) following irradiation with visible or ultraviolet light,[4–6] the electronic absorption spectra of this adduct[5,6] and of the analogous one obtained from 1,4-naphthoquinone[5] do not reveal evidence of through-space π–π interactions, suggesting a preference in solution for a conformation in which the two olefinic π-systems are well separated.

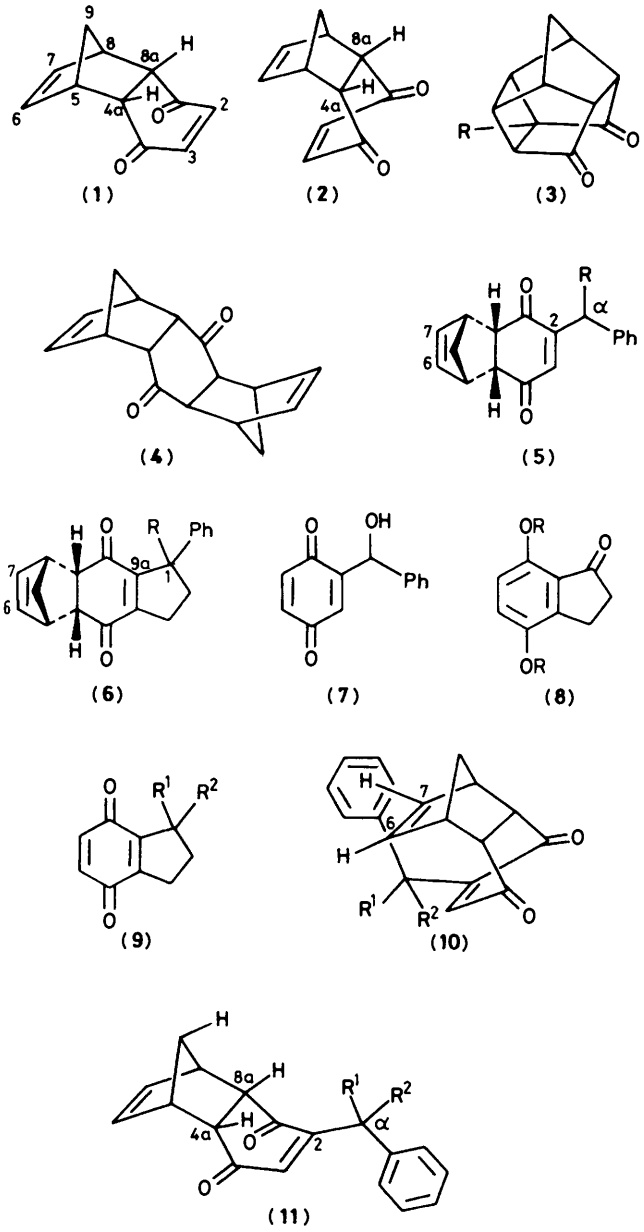
Diels–Alder addition of cyclopentadiene to the monoadduct gives the *endo-trans-endo* 1,4-benzoquinone–biscyclopentadiene adduct (**4**) exclusively,[7] suggesting addition to the closed conformation (**2**) which allows minimisation of non-bonded interactions between the 4a- and 8a-hydrogen of the monoadduct and those at the 2- and 3-position of the incoming cyclopentadiene. Stereoselective reduction of the carbonyl groups of the monoadduct has been similarly accounted for.[8] Since the activation energy for interconversion of the conformers is probably small,[5] the conformation adopted at the moment of reaction may be controlled by the incoming reagent, and the structures of the products may therefore not reflect the preferred conformation of the unperturbed adduct.

We now report on the results of an n.m.r. spectroscopic study of the 1,4-benzoquinone–cyclopentadiene monoadduct,[9] and of its homologues† (**5**; R = H), (**5**; R = OH), (**6**; R = H), and (**6**; R = OH) which were chosen with the objective of using long-range shielding by the phenyl group as a probe for the conformation of the enedione ring.

Each of the adducts (**5**; R = OH) and (**6**; R = H or OH) was obtained as a pair of diastereoisomers, subsequently referred to as isomers I and II, respectively.

Preparation of Materials.—Benzylhydroquinone was obtained by condensation[10] of cyclohexane-1,4-dione with benzaldehyde, and, in higher yield, by condensation of hydroquinone with benzyl alcohol in the presence of phosphoric acid followed by chromatographic separation from 2,5-dibenzylhydroquinone and unchanged hydroquinone. Oxidation with silver oxide gave benzyl-1,4-benzoquinone which

† The adducts were racemic. Only one enantiomer is depicted.



with cyclopentadiene afforded the monoadduct (**5**; R = H), the *endo* configuration of which was established[4] by irradiation with visible light to yield the cage compound (**3**; R = CH_2Ph).

Treatment of α-hydroxybenzyl-1,4-benzoquinone (**7**)[11] with cyclopentadiene gave a 1:1 mixture of monoadducts, both of which afforded a cage compound [**3**; R = CH(OH)Ph] when irradiated with visible light, thus establishing that they are *endo* (**5**; R = OH), and that they must differ in configuration at C-α. They were separated *via* their different solubility in carbon tetrachloride, and by chromatography. The ratio of the two adducts was essentially independent of the medium (benzene; cyclohexane; methanol; acetic acid; no solvent) in which the Diels–Alder reaction was effected.

A similar, but 1.5:1, mixture of adducts (**5**; R = OAc) was obtained from α-acetoxybenzyl-1,4-benzoquinone, suggesting that (weak) hydrogen bonding involving the hydroxy group of quinone (**7**) plays little part in controlling the ratio of diastereoisomers.

3-(2,5-Dimethoxyphenyl)propionic acid was converted into the corresponding indanone (**8**; R = Me) in high yield *via* cyclisation of the derived acid chloride with aluminium chloride (*cf.* ref. 12); demethylation[13] then gave the hydroquinone (**8**; R = H). Treatment of this with an excess of phenyl-lithium followed by oxidation of the crude product with silver oxide gave the quinone (**9**; R^1 = OH, R^2 = Ph) in moderate yield; catalytic hydrogenation–hydrogenolysis followed by oxidation afforded quinone (**9**; R^1 = H, R^2 = Ph). Both quinones (**9**; R^1 = OH or H, R^2 = Ph) formed diastereoisomeric monoadducts (**6**; R = OH or H) with cyclopentadiene; these were separated by chromatography.

Reduction of the indanone (**8**; R = H) with sodium borohydride followed by oxidation with sodium periodate (*cf.* ref 11) gave the quinone (**9**; R^1 = H, R^2 = OH), which also formed a mixture of diastereoisomeric monoadducts when treated with cyclopentadiene.

For each pair of diastereoisomers, that with the higher R_F on silica gel is designated isomer I.

Survey of ^{1}H *N.m.r. Spectra.*—The chemical shifts of corresponding protons associated with the norbornene moieties of all the adducts were similar throughout the series. However, for each of the compounds [as (**5**) and (**6**)] carrying a phenyl substituent, the chemical shifts of the two olefinic protons H-6 and -7 were almost identical for isomer I, but separated by 0.16—0.63 p.p.m. for isomer II. These results are summarised in Table 1. Sufficient data were not obtained to enable individual assignments of H-6 and -7 to be made with certainty.

The chemical shifts assigned to H-6/7 lie within a narrow range (δ 5.87—6.15) and are very close to that (δ 6.02) for the parent compound (**1**) ⇌ (**2**), suggesting that the substituents listed in Table 1 have little effect on H-6/7. However, the remaining norbornene olefinic proton H-7/6 is shielded, in isomer II only, by up to 0.63 p.p.m. Had the closed conformation [as (**2**)] of the Diels–Alder adduct predominated, a considerable divergence in the chemical shifts of both norbornene olefinic protons from that of the corresponding protons in the parent compound (**2**) would have been expected due to contributions from side-chain conformers, such as that illustrated for the benzyl series (**10**; R^1 = R^2 = H; R^1 = H, R^2 = OH or OAc); an analogous, extreme conformation would formally exist for one isomer of each of the 1-hydroxy-1-phenyl- and 1-phenyl-indan compounds (**6**) in which rotation about the C-9a–C-2 bond is prevented. The extreme 'open' conformation corresponding to (**10**) is represented by (**11**). Here the phenyl group is too far from the olefinic protons of the norbornene moiety to affect significantly the chemical shifts of either, although a rotation of 180° about C-2–C-α would place it in a position where some difference in the chemical shift of the *syn* bridge proton (shown) from that in the parent 1,4-benzoquinone–cyclopentadiene adduct would be expected. Differences in this region are relatively small (see Table 1), consistent with the much greater distance between the proton under consideration and the phenyl group. The angular protons H-4a and -8a in each compound have an almost identical chemical shift, and the range of chemical shifts for these protons in the whole series of compounds is only 0.3 p.p.m. (see Experimental section).

Long-range effects from the hydroxy and acetoxy substituents appear to be much smaller than those from the phenyl group (see, *e.g.*, the last four entries in Table 1).

These results, therefore, do not provide clear evidence for the predominance of either an 'open' or a 'closed' conformation. In order to obtain further relevant data, a detailed n.m.r. relaxation study at 300 MHz of the parent adduct (**1**) ⇌ (**2**) and of each of its diastereoisomeric α-hydroxybenzyl homologues (**5**; R = OH) was undertaken, as follows.

Relaxation Theory.—The simple problem posed in this work of distinguishing between two quite different conformations does not require the full power of density matrix relaxation theory.[14] The following simplified version of the state population treatment described by Noggle and Schirmer[15] is adequate.

For two protons *i* and *j* relaxing solely by mutual dipolar relaxation, the longitudinal relaxation of the system is governed by two coupled differential equations, whose solution gives the following expression for the longitudinal relaxation times T_{1i} and T_{1j} in the extreme narrowing limit [equation (1) where

$$T_{1i}^{-1} = T_{1j}^{-1} = \frac{3}{2}\left(\frac{\mu_o}{4\pi}\right)^2 \frac{\gamma_H^4 \hbar^2 \tau_c}{r_{ij}^6} \qquad (1)$$

$(\mu_o/4\pi)$ is the magnetic permeability of free space, γ_H is the magnetogyric ratio of the proton, r_{ij} is the internuclear distance, and τ_c is the correlation time]. However, if one proton (say *i*) is relaxed by other means of much greater efficiency than the *i–j* dipolar interaction, then the longitudinal relaxations of *i* and *j* are uncoupled, and the relaxation times are given by equations (2) where T_{1X} represents the contribution of the other sources to

$$T_{1i}^{-1} = \left(\frac{\mu_o}{4\pi}\right)^2 \frac{\gamma_H^4 \hbar^2 \tau_c}{r_{ij}^6} + T_{1X}^{-1} \qquad (2a)$$

$$T_{1j}^{-1} = \left(\frac{\mu_o}{4\pi}\right)^2 \frac{\gamma_H^4 \hbar^2 \tau_c}{r_{ij}^6} \qquad (2b)$$

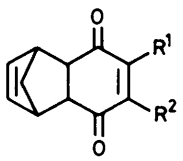
the relaxation of *i*. In the present application, these other sources are inter- and intra-molecular dipolar interactions with other nuclei. In the case that T_{1X} arises from the intramolecular dipolar interaction of *i* with a proton *k* closer to *i* than *j*, then T_{1X} is given by equation (1) with r_{ij} replaced by r_{ik}. Thus, generalising equations (1) and (2) to a multispin system, we obtain equation (3), where the structure factor Q_i is given by

$$T_{1i}^{-1} = \left(\frac{\mu_o}{4\pi}\right)^2 \gamma_H^4 \hbar^2 \tau_c Q_i + T_1^{*-1} \qquad (3)$$

$Q_i = \frac{3}{2}\sum_j r_{ij}^{-6} + \sum_k r_{ik}^{-6}$. The first summation (index *j*) runs over neighbours of *i* with similar relaxation times, while the second summation (nucleus *k*) runs over neighbours of *i* with quite different relaxation times and also over all more remote protons. T_1^* represents the relaxation contribution from intermolecular interactions. It has been assumed that the molecule is rigid and rotates isotropically, and that T_1^* is the

Table 1. Chemical shifts of norbornene olefinic and bridge protons in *endo*-5,8-methano-1,4-naphthoquinones and *endo*-5,8-methanobenz[*f*]indane-4,9-quinones ($CDCl_3$ or CCl_4; 90 or 100 MHz; 38 °C)

				Olefinic protons			Bridge protons		
	R^1	R^2	Isomer	δ(H-6/7)	δ(H-7/6)	Δδ	δ(*syn*/*anti*)	δ(*anti*/*syn*)	Δδ
A	H	H		6.02	6.02		1.52	1.44	0.08
	CH_2Ph	H		5.90	5.74	0.16	1.40	1.40	
	CH(OH)Ph	H	I	5.95	5.95		1.46	1.35	0.11
			II	5.90	5.30	0.60	1.37	1.37	
	CH(OAc)Ph	H	I	6.00	6.00		1.40	1.40	
			II	5.87	5.24	0.63	1.38	1.38	
B	Ph	OH	I	6.10	6.10		1.61	1.44	0.17
			II	6.15	5.88	0.27	1.51	1.44	0.07
	Ph	H	I	6.04	6.04		1.60	1.45	0.15
			II	6.07	5.67	0.40	1.51	1.36	0.15
	H	OH	I	6.05	6.05		1.59	1.45	0.06
			II	6.00	6.00		1.58	1.44	0.14



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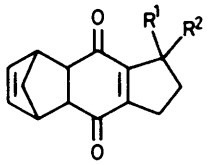

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same for all protons. Within the limitations of the model, a plot of T_{1i}^{-1} against the structure factor Q_i should therefore be linear for the correct conformation, and non-linear otherwise provided some or all of the structure factors depend on the conformation. In the present application, the internuclear distances which differ significantly in the open and closed conformations are those between the norbornene olefinic (H-6, H-7) and the enedione protons (H-2, H-3).

Nuclear Overhauser enhancements in this simplified approach are given to a good approximation by equation (4) where

$$\eta_i\{j\} = \frac{1}{2}\frac{T_{1i}}{T_{ij}} \qquad (4)$$

$\eta_i\{j\}$ is the fractional increase in the intensity of proton i on saturating proton j, and T_{ij} is the contribution of the i–j dipolar interaction to the observed longitudinal relaxation time T_{1i} of proton i. In the case that i and j are single protons, T_{ij} is given by $T_{ij}^{-1} = (\mu_o/4\pi)^2\,\gamma_H^4\hbar^2\tau_c/r_{ij}^6$. In the case that i and/or j are groups of protons, T_{ij} is given by $T_{ij}^{-1} = N_i^{-1}\,(\mu_O/4\pi)^2\,\gamma_H^4\hbar^2\tau_c\Sigma_{ij}r_{ij}^{-6}$ where N_i is the number of i protons and the summation runs over all i,j pairs.

An independent check on the correlation time τ_c can be obtained from measurements of ^{13}C longitudinal relaxation times (T_{1C}). For a $^{13}CH_n$ group (n = 1 or 2) fixed in the molecular frame, T_{1C} under proton-decoupled conditions is given by equation (5) where γ_C is the ^{13}C magnetogyric ratio

$$T_{1C}^{-1} = n\,(\mu_o/4\pi)^2\,\gamma_H^2\gamma_C^2\hbar^2\tau_c r_{CH}^{-6} \qquad (5)$$

and r_{CH} is the C–H bond length, which is known to good accuracy.

Chemical Shifts and Coupling Constants.—The parent member, (1) ⇌ (2), of the series and the two diastereoisomers I and II of its α-hydroxybenzyl homologue (**5**) were examined using acetone as solvent. All three compounds gave fairly well resolved spectra at 300 MHz. Chemical shifts and coupling constants are listed in Table 2. Their pattern is similar to that outlined above for solutions in deuteriochloroform. In particular, the notable differences cited for the norbornene olefinic protons of isomers I and II persisted.

Table 2. Chemical shifts (δ) for Diels–Alder adducts (1) ⇌ (2) and (**5**) in $(CD_3)_2CO$ at 28 °C

		(**5**)	
Proton	(1) ⇌ (2)	Isomer I	Isomer II
2	6.70		
3		6.97	6.97
5	3.53	3.53	3.48
8			3.31
6	6.16	6.18	6.05
7			5.32
4a	3.41	3.43	3.37
8a		3.33	
9a	1.62	1.59	1.56
9b	1.55	1.55	1.43
α		5.83	5.84
OH		5.01	5.04
Ph		~7.5	~7.5

The coupling constant between the hydroxy proton and α-H was 4.3 Hz in both isomers I and II. This value is consistent with free rotation of the OH group.[16] A further probe of the OH conformation is provided by the temperature coefficient of the OH chemical shift. Increasing temperature gave a low frequency shift of 6.7 × 10^{-3} p.p.m. K^{-1} in both I and II, only slightly less than the value 8.0 × 10^{-3} p.p.m. K^{-1} measured for methanol in the same solvent. Thus there is no evidence for an intramolecular hydrogen bond between the OH and the 1-carbonyl group which could have restricted rotation about the C-2–C-α bond.

Relaxation Measurements.—Inter-proton distances for use in equations (3) and (4) were taken from Dreiding molecular models. It is recognised that such models only approximate the actual molecule, but it has been found previously[17–19] that n.m.r. relaxation data for several alkaloids can be satisfactorily interpreted by geometrical data obtained from this source.

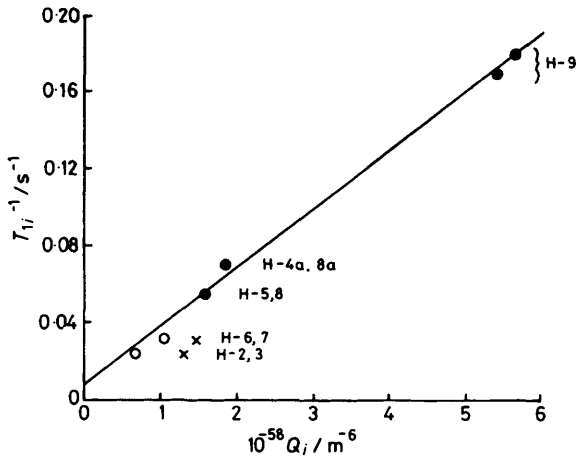

Figure. Plot of T_{1i}^{-1} *versus* Q_i [equation (3)] for the parent compound [(1) ⇌ (2)] in [$^2H_6$]acetone at 28 °C and a concentration of 10 mg ml^{-1}. ●, Coincident points for 'open' (1) and 'closed' (2) conformations; ○, points for 'open' conformation; ×, points for 'closed' conformation

The Figure shows a plot of T_{1i}^{-1} against the structure factor Q_i for the 'open' (1) and 'closed' (2) conformations of the parent member of the series. The points for the 'open' conformation fit a linear relationship reasonably well, whereas the points for the 'closed' conformation deviate considerably. As expected, Q_i for the saturated protons differ little between the two conformations whereas Q_i for the unsaturated protons display a strong conformational dependence. The slope of the line for the 'open' conformation gives a correlation time of 5.3 ps, and the intercept gives a value for T_1* of 125 s. For this compound, the ^{13}C T_1 value of a methine carbon was measured at 9.0 s, giving a correlation time from equation (5) of 5.2 ps, in excellent agreement with the result from ^1H relaxation.

As a further check on the consistency of the ^1H relaxation data, measurements were made of the n.O.e. of H-2 and -3 resulting from irradiation of H-6 and -7. The calculated enhancements from equation (5) for the 'open' and 'closed' conformations were 0.004 and 0.24, respectively. The experimental value was 0.02 ± 0.01, thus confirming the preference for the 'open' conformation.

A similar treatment of the relaxation times for the isomers of (5) is impeded by the uncertainty surrounding the side-group conformation. However, the n.O.e. of H-3 on saturation of H-6 and -7 was found to have the very low value of 0.01 in both isomers. Since the relaxation times of the framework protons in the two isomers were similar to those of the corresponding protons in (1) ⇌ (2), we may reasonably infer that these isomers also prefer the 'open' conformation. The large difference in chemical shift of H-6 and -7 must therefore arise from the difference in configuration at the α-position.

Conclusions.—Overall, a preferred conformation in which the enedione moiety of this series of Diels–Alder adducts approaches coplanarity probably accounts best for all the observations. It has the advantages of minimising dipolar repulsions between the carbonyl groups, and maximising π-orbital overlap in the enedione system, and is supported for the parent member, (1) ⇌ (2), of the series by the results of MINDO/3 calculations.[20]

Experimental

General.—Cyclopentadiene was freshly prepared. Solvents were removed under reduced pressure, usually below 50 °C. Sublimation temperatures are those of the heating bath. 60 and 90 MHz ^1H n.m.r. spectra were measured on Perkin-Elmer R12B and R32 spectrometers, respectively, for solutions containing *ca.* 50 mg ml^{-1}. Signals due to hydroxy protons were removed on addition of D_2O, and assignments were confirmed by spin decoupling.

300 MHz ^1H Spectra were recorded using a Varian Associates SC-300 spectrometer. Longitudinal relaxation times were measured using the inversion recovery sequence (π–τ–π/2) with an accuracy of ± 5%. Samples were at a concentration of 10 mg ml^{-1} in [$^2H_6$]acetone, and were degassed and sealed *in vacuo*. ^{13}C Spectra were recorded on the same instrument operating at 75.5 MHz, using samples containing 50 mg ml^{-1}.

Benzylhydroquinone.—A mixture of hydroquinone (3 g), benzyl alcohol (1.7 g), and 100% phosphoric acid (25 g) was stirred on a steam-bath for 2.5 h, and then cooled and poured into water (200 ml). The suspension was extracted with ether (3 × 50 ml), and the combined extracts were washed successively with water, saturated aqueous sodium hydrogencarbonate, and water, and dried ($MgSO_4$). Removal of the solvent and chromatography on silica gel (250 × 20 mm; 5:1 benzene–glacial acetic acid) gave benzylhydroquinone (2.9 g, 60%), m.p. 100—102 °C (lit.,[10] 105 °C), δ[$(CD_3)_2CO$; 60 MHz] 4.00 (s, CH_2), 6.3—6.6 (2 × OH), 6.7 (m, ArH_3), and 7.30 (s, Ph).

Benzyl-1,4-benzoquinone.—A mixture of benzylhydroquinone (400 mg), silver oxide (1.3 g), anhydrous magnesium sulphate (1.3 g), and dry ether (40 ml) was shaken in the dark at room temperature for 3 h, and then filtered through Celite. The solvent was removed, and the residue was chromatographed on Woelm polyamide (125 × 20 mm; benzene) to give the quinone (340 mg, 87%), m.p. 41—42 °C (lit.,[10,21] 43, 42—43 °C), δ (CCl_4; 60 MHz) 3.61 (d, *J* 1.5 Hz, CH_2), 6.28 and 6.60 (both m, H-3 + -5 + -6), and 7.20 (s, Ph).

endo-2-*Benzyl*-4a,5,8,8a-*tetrahydro*-5,8-*methano*-1,4-*naphthoquinone.*—A solution of benzyl-1,4-benzoquinone (250 mg) in cyclopentadiene (5 ml) was kept in the dark at room temperature for 25 min, and the solvent was then removed. Crystallisation of the residue from cyclohexane gave the pale yellow *adduct* (325 mg, 100%), m.p. 82—83 °C (Found: C, 81.8; H, 6.0. $C_{18}H_{16}O_2$ requires C, 81.8; H, 6.1%), $\nu_{max.}$(Nujol) 1 665 cm^{-1}, δ (CCl_4; 100 MHz) 1.33 (dt, J_1 8.0, J_2 1.2 Hz, 1 × H-9), 1.45 (dt, J_1 8.0, J_2 1.5 Hz, 1 × H-9), 3.06 (m, H-4a + -8a), 3.39 (m, H-5 + -8), 3.48 (d, *J* 1.5 Hz, 2 × H-α), 5.74 (m, H-7), 5.90 (m, H-6), 6.14 (t, *J* 1.5 Hz, H-3), and 7.12 (m, Ph).

The *endo* configuration was established by irradiation of the adduct (150 mg) in dry ethyl acetate (25 ml) at 20 °C with tungsten filament light until the yellow colour had been discharged. Removal of the solvent gave the cage compound (3; R = $PhCH_2$) (150 mg, 100%) as a gum, $\nu_{max.}$(film) 1 745 cm^{-1}, δ (CCl_4; 60 MHz) 1.77 and 1.93 (each d, *J* 10 Hz, bridge CH_2), 2.2—3.0 (m, 9 H), and 7.20 (s, Ph).

endo-2-α-*Hydrooxybenzyl*-4a,5,8,8a-*tetrahydro*-5,8-*methano*-1,4-*naphthoquinone. Isomers* I *and* II.—A solution α-hydroxybenzyl-1,4-benzoquinone[11] (100 mg) in cyclopentadiene (6 ml) was kept at room temperature for 15 min, and the excess of solvent was then removed to afford a mixture of the diastereoisomeric adducts as an oil (130 mg, 100%). Irradiation as described for the foregoing compound afforded a gum which had $\nu_{max.}$(Nujol) 3 500br and 1 750—1 755 cm^{-1}, δ ($CDCl_3$; 60 MHz) 1.6 (m, CH_2), 2.4—3.0 (m, 7 H), 4.7 (br, OH), 4.9 (m, 1 H), and 7.3 (m, Ph).

Isomer I was obtained by chromatography on silica gel (150 × 20 mm, 2:1 ether–cyclohexane). It was eluted before isomer II, and formed yellow prisms, m.p. 135—137 °C (Found:

C, 77.5; H, 5.7. $C_{18}H_{16}O_3$ requires C, 77.1; H, 5.7%); $\lambda_{max.}$ (95% EtOH) 240, 285, and 380 nm (ε 9 500, 2 500, and 102), $\nu_{max.}$(Nujol) 3 480s, 3 090w, and 1 655s cm^{-1}, δ ($CDCl_3$; 100 MHz) 1.35 (d, *J* 9 Hz, 1 × H-9), 1.46 (dt, J_1 9, J_2 1.5 Hz, 1 × H-9), 3.06 (m, H-4a + -8a), 3.18 (d, *J* 4.5 Hz, OH), 3.42 (br s, H-5 + -8), 5.58 (q, J_1 4.5, J_2 1.25 Hz, H-α), 5.95 (m, H-6 + -7), 6.65 (d, *J* 1.25 Hz, H-3), and 7.26 (s, Ph).

Isomer II was conveniently obtained by cooling the oily mixture of *endo* adducts to 0 °C until it began to solidify, and then triturating with cold dry carbon tetrachloride: it was sparingly soluble, and formed pale yellow crystals, m.p. 110—113 °C (Found: C, 77.5; H, 5.7%); $\lambda_{max.}$ (95% EtOH) 238, 283, and 380 nm (ε 10 000, 2 100, and 100), $\nu_{max.}$(Nujol) 3 400br, 3 060w, 1 660sh, and 1 655 s cm^{-1}, δ ($CDCl_3$; 100 MHz) 1.37 (m, 2 × H-9), 2.85 (br s, OH), 3.14 (m, H-4a + -8a), 3.31 (m, H-8), 3.45 (m, H-5), 5.30 (q, J_1 6.0, J_2 2.5 Hz, H-7), 5.68 (dd, J_1 4, J_2 1.5 Hz, H-α), 5.90 (q, J_1 6.0, J_2 2.5 Hz, H-6), 6.72 (d, *J* 1.25 Hz, H-3), and 7.30 (s, Ph).

α-*Acetoxybenzyl*-1,4-*benzoquinone*.—A solution of α-hydroxybenzyl-1,4-benzoquinone (100 mg) in freshly distilled acetic anhydride (6 ml) was refluxed for 1 h, the solvent was removed, and the residue was crystallised from light petroleum (b.p. 40—60 °C) to give the yellow acetate (99 mg, 80%), m.p. 73.5—74 °C (Found: C, 70.6; H, 4.7. $C_{15}H_{12}O_4$ requires C, 70.3; H, 4.7%); $\nu_{max.}$(film) 1 748s and 1 660s cm^{-1}, δ (CCl_4; 100 MHz) 2.04 (s, Me), 6.58 (m, H-3 + -α), 6.65 (m, H-5 + -6), and 7.26 (m, Ph).

endo-2-α-*Acetoxybenzyl*-4a,5,8,8a-*tetrahydro*-5,8-*methano*-1,4-*naphthoquinone*. *Isomers* I *and* II.—A solution of α-acetoxybenzyl-1,4-benzoquinone (1 g) in cyclopentadiene (10 ml) was kept in the dark for 20 min, and the solvent was then removed to give an oil (1 216 mg, 100%) which solidified. When irradiated with visible light in ethyl acetate, a portion of this adduct gave a gum with spectroscopic properties similar to those of the α-hydroxy analogue except for $\nu_{max.}$ 1 755s and 1 745s cm^{-1}, δ 2.15 (s, Me).

A portion (1 g) of the mixture of *endo* adducts was chromatographed on silica gel (250 × 20 mm, 2:1 cyclohexane–ether) giving, first, *isomer* I (480 mg) which crystallised from cyclohexane as pale yellow prisms, m.p. 85.5—86.5 °C (Found: C, 74.3; H, 5.7. $C_{20}H_{18}O_4$ requires C, 74.5; H, 5.6%), $\nu_{max.}$(film) 1 750s and 1 660s cm^{-1}, δ (CCl_4; 100 MHz) 1.33 (d, *J* 8.5 Hz, 1 × H-9), 1.47 (dt, J_1 8.5, J_2 1.5 Hz, 1 × H-9), 2.00 (s, Me), 3.00 (d, *J* 3 Hz, H-4a + -8a), 3.42 (br s, H-5 + -8), 6.00 (m, H-6 + -7), 6.48 (s, H-α + -3), and 7.22 (m, Ph).

Isomer II (460 mg) was eluted second, and crystallised from cyclohexane–ether as pale yellow prisms, m.p. 129—131 °C (Found: C, 74.4; H, 5.6%), $\nu_{max.}$(Nujol) 1 745s and 1 665s cm^{-1}, δ ($CDCl_3$; 100 MHz) 1.38 (m, 2 × H-9), 2.04 (s, Me), 3.11 (m, H-4a + -8a), 3.28 (br s, H-8), 3.42 (br s, H-5), 5.24 (q, J_1 5.5, J_2 2.5 Hz, H-7), 5.87 (q, J_1 5.5, J_2 2.5 Hz, H-6), 6.50 (d, *J* 1.5 Hz, H-3), 6.58 (d, *J* 1.5 Hz, H-α), and 7.25 (s, Ph).

4,7-*Dimethoxyindan*-1-*one*.—A mixture of 3-(2,5-dimethoxyphenyl)propionyl chloride (4 g), dry 1,2-dichloroethane (30 ml), and freshly sublimed aluminium chloride (4 g) was stirred at room temperature for 2 h, and then poured into 20% hydrochloric acid (100 ml). Extraction with chloroform, washing of the extracts with water, drying (Na_2SO_4), and evaporation afforded a solid which, on sublimation at 105—110 °C at 0.05 mmHg, gave the indanone (2.8 g, 83%) as crystals, m.p. 124—124.5 °C (lit.,[12] 124.5—125 °C), δ ($CDCl_3$; 60 MHz) 2.50—2.82 (m, 2 × H-2), 2.84—3.14 (m, 2 × H-3), 3.83 (s, OMe), 3.88 (s, OMe), 6.78 (d, *J* 8 Hz, H-6), and 6.97 (d, *J* 8 Hz, H-7).

4,7-*Dihydroxyindan*-1-*one*.—A mixture of pyridine (24 ml) and concentrated hydrochloric acid (26.5 ml) was distilled until the internal temperature reached 210 °C, and the residue was allowed to cool, under dry nitrogen, until it solidified. 4,7-Dimethoxyindan-1-one (770 mg) was added, and the mixture, which liquified, was heated at 165—170 °C under nitrogen for 1.5 h. It was then cooled, dispersed in water (100 ml), and the crude product (476 mg, 72%) isolated by extraction with ether. Sublimation at 110 °C and 0.05 mmHg gave the indanone as pale yellow needles, m.p. 197—198 °C (lit.,[13] 198 °C), δ [$(CD_3)_2CO$; 60 MHz] 2.54—2.80 (m, 2 × H-2), 2.90—3.17 (m, 2 × H-3), 6.53 (d, *J* 7.5 Hz, H-6), 6.97 (d, *J* 7.5 Hz, H-5), and 7.90—8.75 (2 × OH).

1-*Hydroxy*-1-*phenylindane*-4,7-*quinone*.—4,7-Dihydroxyindan-1-one (350 mg) in dry tetrahydrofuran (10 ml) was added during 15 min to stirred, ethereal phenyl-lithium (60 ml; 0.2M) at −75 °C, and stirring was then continued at this temperature for 15 min, during warming to room temperature, and then for a further 45 min. The solution was cooled to 0 °C, decomposed by addition of ice–water (20 ml), and the aqueous phase was then acidified with saturated aqueous oxalic acid (6 ml). The ethereal phase was separated, combined with ether (3 × 60 ml) extracts of the aqueous phase, and the combined extracts were washed with water, dried ($MgSO_4$), and concentrated to 50 ml. Anhydrous sodium sulphate (800 mg) and silver oxide (400 mg) were added, and the mixture was shaken at room temperature for 1 h. Filtration, removal of the solvent from the filtrate, and crystallisation of the residue from light petroleum (b.p. 40—60 °C) gave the yellow *quinone* (210 mg, 41%), m.p. 115—117 °C (decomp.) (Found: C, 74.6; H, 5.0. $C_{15}H_{12}O_3$ requires C, 75.0; H, 5.0%), $\nu_{max.}$($CHCl_3$) 3 560br and 1 662s cm^{-1}, δ ($CDCl_3$; 60 MHz) 2.15—2.55 (m, 2 × H-2), 2.64—3.10 (m, 2 × H-3), 3.20 (s, OH), 6.57 (d, *J* 9 Hz, H-5 or -6), 6.78 (d, *J* 9 Hz, H-6 or -5), and 7.28 (s, Ph).

endo-4a,5,8,8a-*Tetrahydro*-1-*hydroxy*-1-*phenyl*-5,8-*methano*-benz[f]*indane*-4,9-*quinone*. *Isomers* I *and* II.—A solution of the foregoing quinone (63 mg) in cyclopentadiene (2.5 ml) was kept in the dark at room temperature for 1 h, and the solvent was then evaporated leaving a pale yellow solid (81 mg, 100%), which was separated into its components by p.l.c. (silica gel, 3:1 toluene–ether). *Isomer* I (highest R_F) (39 mg) formed pale yellow needles, from hexane, m.p. 142—144 °C (Found: C, 78.1, H, 5.9. $C_{20}H_{18}O_3$ requires C, 78.4; H, 5.9%), $\nu_{max.}$($CHCl_3$) 3 550m and 1 660s cm^{-1}, δ ($CDCl_3$; 90 MHz) 1.44 (d, *J* 9 Hz, 1 × H-10), 1.61 (d, *J* 9 Hz, 1 × H-10), 2.02—2.51 (m, 2 × H-2 or 2 × H-3), 2.53—3.05 (m, 2 × H-3 or 2 × H-2), 3.28 (t, *J* 3.5 Hz, H-4a + -8a), 3.40—3.70 (m, H-5 + -8 + OH), 6.10 (t, *J* 1.5 Hz, H-6 + -7), and 7.17 (br s, Ph).

Isomer II (33 mg) formed pale yellow needles, from hexane, m.p. 147—149 °C (Found: C, 78.2; H, 6.1%), $\nu_{max.}$(Nujol) 3 370m, 1 672s, and 1 653s cm^{-1}, δ ($CDCl_3$; 90 MHz) 1.44 (dt, J_1 9, J_2 1.5 Hz, 1 × H-10), 1.57 (dt, J_1 9, J_2 1.5 Hz, 1 × H-10), 2.10—3.10 (m, 2 × H-2 + 2 × H-3), 3.30 (br s, H-4a + -8a), 3.35—3.50 (m, H-5 or -8), 3.51—3.70 (m, OH + H-8 or -5), 5.88 (dd, J_1 6, J_2 2.5 Hz, H-7 or -6), 6.15 (dd, J_1 6, J_2 2.5 Hz, H-6 or -7), and 7.10—7.48 (m, Ph).

4,7-*Dihydroxy*-1-*phenylindan*.—1-Hydroxy-1-phenylindane-4,7-quinone (70 mg) in ethanol (10 ml) containing 10% palladium–charcoal (30 mg) was hydrogenated at n.t.p. for 15 min, the mixture was filtered, and the solvent then removed. Crystallisation of the residue from ether gave the *indan* (51 mg, 77%) as needles, m.p. 125—127 °C (decomp.) (Found: $M^{+\cdot}$, 226.0996. $C_{15}H_{14}O_2$ requires *M*, 226.0994), $\nu_{max.}$($CHCl_3$) 3 580s and 3 535s cm^{-1}, δ [1:1 $(CD_3)_2CO$–$CDCl_3$; 90 MHz] 2.20—3.15 (m, 2 × H-2 + 2 × H-3 + OH), 4.51 (br t, *J* 6 Hz,

H-6), 6.29 (s, OH), 6.47 (d, *J* 8 Hz, H-5 or -6), 6.63 (d, *J* 8 Hz, H-6 or -5), and 7.16 (br s, Ph).

1-*Phenylindane*-4,7-*quinone*.—A mixture of the foregoing dihydroxyindan (47 mg), anhydrous sodium sulphate (300 mg), silver oxide (70 mg), and dry benzene (10 ml) was shaken at room temperature for 45 min, filtered, and evaporated to give the *quinone* (45 mg, 97%) as a yellow oil which decomposed on attempted distillation at 0.05 mmHg (Found: $M^{+\cdot}$, 224.0841. $C_{15}H_{12}O_2$ requires *M*, 224.0837), $\nu_{max.}$($CHCl_3$) 1 665s cm^{-1}, δ ($CDCl_3$; 90 MHz) 1.80—3.10 (m, 2 × H-2 + 2 × H-3), 4.25—4.50 (m, H-1), 6.55 (d, *J* 10 Hz, H-5 or -6), 6.70 (d, *J* 10 Hz, H-6 or -5), and 6.95—7.40 (m, Ph).

endo-4a,5,8,8a-*Tetrahydro*-1-*phenyl*-5,8-*methanobenz*[f]-*indane*-4,9-*quinone*. *Isomers* I *and* II.—A solution of the foregoing quinone (40 mg) in cyclopentadiene (2 ml) was kept in the dark at room temperature for 1.5 h, and the solvent was then removed leaving a pale yellow gum (52 mg, 100%) which was separated into its components by p.l.c. (silica gel, 3:1 toluene–ether). *Isomer* I (highest R_F) (17 mg) formed pale yellow prisms, from hexane, m.p. 90—93 °C (Found: $M^{+\cdot}$, 290.1309. $C_{20}H_{18}O_2$ requires *M*, 290.1307), $\nu_{max.}$($CHCl_3$) 1 650s and 1 616w cm^{-1}, δ ($CDCl_3$; 90 MHz) 1.35—1.70 (m, 2 × H-10), 1.75—3.04 (m, 2 × H-2 + 2 × H-3), 3.05—3.40 (m, H-4a + -8a), 3.49 (br s, H-5 + -8), 4.08—4.42 (m, H-1), 6.04 (br s, H-6 + -7), and 6.90—7.50 (m, Ph).

Isomer II (32 mg) formed pale yellow prisms, from hexane, m.p. 141—144 °C (Found: $M^{+\cdot}$, 290.1309), $\nu_{max.}$($CHCl_3$) 1 655s and 1 616w cm^{-1}, δ ($CDCl_3$; 90 MHz) 1.36 (br d, *J* 9 Hz, 1 × H-10), 1.51 (br d, *J* 9 Hz, 1 × H-10), 1.80—3.02 (m, 2 × H-2 + 2 × H-3), 3.21 (br s, H-4a + -8a), 3.32 (br s, H-5 or -8), 3.51 (br s, H-8 or -5), 4.07—4.40 (m, H-1), 5.67 (dd, J_1 6, J_2 2.5 Hz, H-7 or -6), 6.06 (dd, J_1 6, J_2 2.5 Hz, H-6 or -7), and 6.88—7.35 (m, Ph).

1-*Hydroxyindane*-4,7-*quinone*.—4,7-Dihydroxyindan-1-one (200 mg) was stirred in water (6 ml) at room temperature for 40 min to ensure wetting, and sodium borohydride (75 mg) was then added portionwise over 30 min. Further sodium borohydride (30 mg) was then added, and stirring was continued for 15 min more. The solution was cooled to 0 °C, acidified to pH 6 by careful addition of 5% sulphuric acid precooled to 0 °C, and then added to sodium periodate (0.5 g) in water (8 ml). After 15 min at 0 °C, the solution was saturated with ammonium sulphate, and extracted with chloroform (4 × 15 ml). The combined extracts were washed with water, dried (Na_2SO_4), and evaporated to give the *quinone* (170 mg, 85%) as an orange oil which decomposed on attempted distillation at 0.05 mmHg (Found: $M^{+\cdot}$, 164.0469. $C_9H_8O_3$ requires *M*, 164.0473), $\nu_{max.}$(film) 3 450b, 1 655s, and 1 585w cm^{-1}, δ ($CDCl_3$; 90 MHz) 1.73—2.15 (m, 1 × H-2 or 1 × H-3), 2.25—3.20 (m, OH + either 1 × H-2 + 2 × H-3 or 2 × H-2 + 1 × H-3), 5.22—5.47 (m, H-1), and 7.69 (s, H-5 + -6).

endo-4a,5,8,8a-*Tetrahydro*-1-*hydroxy*-5,8-*methanobenz*[f]-*indane*-4,9-*quinone*. *Isomers* I *and* II.—A solution of 1-hydroxyindan-4,7-quinone (94 mg) in cyclopentadiene was kept in the dark at room temperature for 1 h. Removal of the solvent then left a pale yellow oil (132 mg, 100%), a portion of which (60 mg) was subjected to p.l.c. (silica gel, ether). *Isomer* I (highest R_F) (36 mg) separated from hexane as pale yellow crystals, m.p. 87—88 °C (Found: C, 72.7; H, 6.3. $C_{14}H_{14}O_3$ requires C, 73.0; H, 6.1%), $\nu_{max.}$(Nujol) 3 420br and 1 655s cm^{-1}, δ ($CDCl_3$; 90 MHz) 1.45 (dt, J_1 9, J_2 2 Hz, 1 × H-10), 1.59 (dt, J_1 9, J_2 2 Hz, 1 × H-10), 1.68—2.12 (m, 1 × H-2 or 1 × H-3), 2.15—3.05 (m, OH + either 1 × H-2 + 2 × H-3 or 2 × H-2 + 1 × H-3), 3.26 (br s, H-4a + -8a), 3.52 (br s, H-5 + -8), 5.05—5.35 (m, H-1), and 6.05 (br s, H-6 + -7).

Isomer II (12.5 mg) formed pale yellow needles, from hexane, m.p. 105—107 °C (Found: C, 73.4; H, 6.3%), $\nu_{max.}$(Nujol) 3 420br and 1 650s cm^{-1}, δ ($CDCl_3$; 90 MHz) 1.44 (br d, *J* 9 Hz, 1 × H-10), 1.58 (dt, J_1 9, J_2 1.5 Hz, 1 × H-10), 2.68—3.15 (m, 2 × H-2 + 2 × H-3 + OH), 3.28 (br s, H-4a + -8a), 3.52 (br s, H-5 + -8), 5.02—5.35 (m, H-1), and 6.00 (br s, H-6 + -7).

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