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Organic and Bio-organic Chemistry

o-Quinonoid Compounds. Part VII.[1] 1,4-Diphenyl-2,3-naphthoquinone

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Oxidation of 1,4-diphenylnaphthalene-2,3-diol by addition of lead tetra-acetate results in a novel oxidative trimerisation. This probably proceeds through 1,4-diphenyl-2,3-naphthoquinone (1; R = Ph), for low-temperature oxidation by addition of the catechol to lead tetra-acetate in the presence of a variety of traps gives adducts of the expected type. Inhibition of *endo*-addition by non-planar phenyl substituents may account for the predominant formation of *exo*-adducts in the trapping experiments. The quinone (1; R = Ph) appears to be a more reactive oxidising agent than *ortho*-chloranil.

DESPITE some early experiments,[2] no simple derivative of 2,3-naphthoquinone (1; R = H) has been isolated, and apart from our own work[3] no evidence for the transient existence of 2,3-naphthoquinones has been obtained. Since *o*-benzoquinone is much more stable than *o*-quinodimethane, 2,3-naphthoquinones would be expected to be more stable than the corresponding 2,3-naphthoquinodimethanes, which are readily intercepted in trapping experiments.[4] Theory predicts considerable reactivity for the system (1; R = H).[5] Although the estimated redox potential (*ca.* 1·0 V)[6] is similar to that of 2,3-dichloro-5,6-dicyano-1,4-benzoquinone,[7] *ortho*-quinones are more reactive in hydride abstraction reactions than *para*-quinones of similar redox potential.[7] Accordingly, 2,3-naphthoquinones would be of interest as potent dehydrogenation reagents. Additional interest in structure (1; R = H) and its derivatives stems from their possible valence isomerisation to the systems (2)—(4). A structure analogous to (3) has been suggested for the colourless form of *o*-benzoquinone[8] where the gain in delocalisation energy on ring-closure would be less than for the isomerisation (1) ⟶ (3).

The diphenyl derivative (1; R = Ph) was chosen as our initial objective, for the 1,4-substituents were expected to afford conjugative,[9] and/or steric[10] stabilisation. The naphthalene-2,3-diol (5; R = H) was prepared in high yield (87%) by dehydration (HCl–HOAc) of the known[11] 1,3-diphenylbenzo[*c*]furan–vinylene carbonate adduct. Oxidation of (5; R = H) with silver oxide[12] resulted in a novel oxidative trimerisation to the *cis–trans* isomers (6; R = H) (71%) and (7; R = H) (24%).

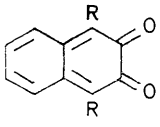
Structure of the Trimers.—Although the mass spectra of both oxidation products showed a peak of highest mass at *m/e* 621, their trimeric nature was established by ebullioscopic molecular weight determination and the mass spectra of the dimethyl ethers (6; R = Me) and (7; R = Me), which showed molecular ions (M^+ 960). The hemiacetal hydroxy-groups in (6; R = H) and (7; R = H) are in fact sufficiently acidic to undergo a slow uncatalysed reaction with diazomethane to give a mixture of mono- and di-methyl ethers.

The absence of diaryl ether linkages in the trimers was established by their reduction ($LiAlH_4$) to (5; R = H), and their oxidation (CrO_3–HOAc) to *o*-dibenzoylbenzene.

Since oxygen–oxygen coupling is unlikely[13] the trimers must be formed by carbon–oxygen coupling involving carbon atoms 1 and 4 of one molecule of (5;

[1] Part VI, J. M. Holland, and D. W. Jones, *J.C.S. Perkin I*, 1973, 927.
[2] T. Zincke and K. Fries, *Annalen*, 1904, **334**, 342; R. Willstatter and L. Schuler, *Ber.*, 1928, **61**, 366; L. F. Fieser, *J. Amer. Chem. Soc.*, 1930, **52**, 5204.
[3] D. W. Jones and R. L. Wife, *Chem. Comm.*, 1970, 1086.
[4] M. P. Cava and R. L. Shirley, *J. Amer. Chem. Soc.*, 1960, **82**, 654.
[5] H. Hopff and H. R. Schweizer, *Helv. Chim. Acta*, 1962, **45**, 312.
[6] M. E. Dyatkina and K. Syrkin, *Acta Physiochem. U.S.S.R.*, 1946, **21**, 921.
[7] L. M. Jackman, 'Hydrogenation–Dehydrogenation Reactions' in 'Advances in Organic Chemistry,' eds. R. A. Raphael, E. C. Taylor, and H. Wynberg, Interscience, New York and London, 1960, p. 333.
[8] W. M. Horspool, *Quart. Rev.*, 1969, **23**, 234.
[9] J. M. Holland and D. W. Jones, *J. Chem. Soc.* (*C*), 1970, 530.
[10] D. W. Jones and G. Kneen, *Chem. Comm.*, 1971, 1356.
[11] M. S. Newman, *J. Org. Chem.*, 1961, **26**, 2630.
[12] J. Cason, *Org. Reactions*, 1948, **4**, 305.
[13] C. K. Ingold, 'Structure and Mechanism in Organic Chemistry,' 2nd edn., Cornell Univ. Press, Ithaca, New York, 1969.

R = H). This agrees with the u.v. spectra of (6 and 7; R = H) which indicate the presence of only two chromophores of the 1,4-diphenylnaphthalene-2,3-diol type. The absence of carbonyl absorption in the i.r. spectra of the trimers suggests that they exist as bis-hemiacetals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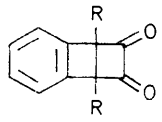
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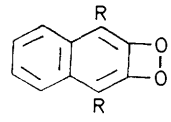
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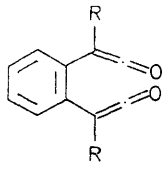
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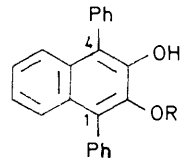
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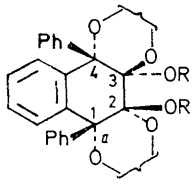
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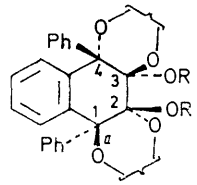
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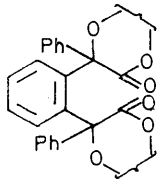
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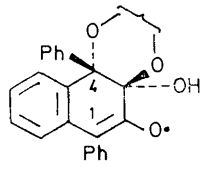
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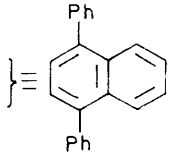
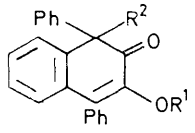


both in the solid state and in chloroform solution. In agreement, they are cleaved by lead tetra-acetate to bisdioxinones of gross structure (8). Since (6; R = H) and (7; R = H) give different bisdioxinones they must be *cis–trans* isomers at carbon atoms 1 and 4.

The further, more tentative allocation of stereochemistry shown in structures (6) and (7) accords with the failure of (7; R = H) to react with phosgene, the presence of non-equivalent hydroxy-groups shown in the n.m.r. spectrum of (6; R = H), and the conversion of both (6; R = H) and (7; R = H) in boiling benzene into a mixture of the trimers in which the *trans,anti,trans*-isomer (7; R = H) predominates. It is known that for perhydrophenanthrene the *trans,anti,trans*-arrangement is more stable than the *cis,anti,trans*.[14] Interconversion of the trimers may proceed *via* the expected ready homolysis or heterolysis of the bonds *a* in (6) and (7). Both (6; R = H) and (7; R = H) give a pale red colour in hot benzene which fades on cooling.

The trimers are produced in the same proportion by homogeneous oxidation of (5; R = H). Addition of lead tetra-acetate to a solution of the catechol in methylene chloride at room temperature results in a rapid series of colour changes terminating in pale red (*cf.* interconversion of the trimers). Predominant formation of the less stable isomer (6; R = H) is understandable if trimerisation involves coupling of a dimer radical in ring (9) or chain form with the radical (5; R = ·). The preferred side of approach to a dimer radical, *e.g.* (9), will be that remote from the pseudoaxial phenyl group.

A projected stepwise preparation of the trimers by synthesis of protected dimers, *e.g.* (11; R = Ac) and (11; R = CH_2·OMe), removal of the protecting groups, and oxidative coupling of (11; R = H) with (5; R = H) foundered on attempted removal of the protecting groups. Thus the dimer (11; R = CH_2·OMe) was readily prepared by oxidation of (5; R = CH_2·OMe)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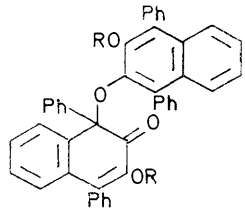
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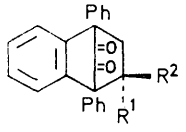


(12) R^1 = H; R^2 = CH=CH_2

(13) R^1 = CH=CH_2; R^2 = H

(14) R^2 = H; R^1 = CH(OH)·CH_2·OH

(15) R^1 = H; R^2 = CMe=CH_2

with silver oxide. However, reaction of this dimer with hydrogen chloride failed to give the desired (11; R = H). Instead the trimers (6; R = H) and (7; R = H) were obtained together with (5; R = H) and the ether (5; R = CH_2·OMe). The proportions of these products suggest that some oxidation of hydrogen chloride is brought about by a reaction intermediate. The dimer (11; R = CH_2·OMe) shows magnetic non-equivalence of the methylene protons of one of the methoxy-methyl groups (see Experimental section).

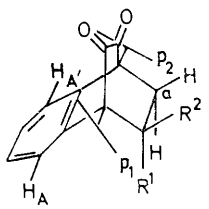
Generation of 1,4-Diphenyl-2,3-naphthoquinone.—Whereas oxidation of (5; R = H) by silver oxide may proceed by direct coupling of the radical (5; R = ·) there were indications that the oxidation with lead tetra-acetate involved initial formation of the quinone (1; R = Ph). Thus oxidation of the monomethyl ether (5; R = Me) by lead tetra-acetate gave only the acetoxylation product (10; R^1 = Me, R^2 = OAc) and no trace of the dimer (11; R = Me), which was readily formed by oxidation with silver oxide. Oxidation of (5; R = H) by addition of lead tetra-acetate to the

[14] W. S. Johnson, *Experientia*, 1951, **7**, 315; *J. Amer. Chem. Soc.*, 1953, **75**, 1498.

catechol at room temperature gave only the trimers (6 and 7; R = H) and no observable (t.l.c.) acetoxylation product.* Similar observations include the smooth reaction of (5; R = Ac) with *N*-bromosuccinimide to give the bromide (10; R^1 = Ac, R^2 = Br) and none of the dimer (11; R = Ac), available by oxidation of (5; R = Ac) with silver oxide. This contrasts with the reaction of (5; R = H) with *N*-bromosuccinimide, which gives only brominated oligomeric products. Since (5; R = H) and (5; R = Me) should be equally susceptible to oxidative coupling reactions their different behaviour with lead tetra-acetate can best be attributed to initial oxidation of (5; R = H) to the quinone (1; R = Ph), which by hydrogen abstraction gives the radical (5; R = ·) and subsequently the observed oligomeric products. A likely source of hydrogen for reduction of (1; R = Ph) to (5; R = ·) appeared to be the catechol (5; R = H). Accordingly in experiments designed to trap (1; R = Ph) the catechol (5; R = H) was added in small portions to lead tetra-acetate suspended in the trap (or the trap diluted with methylene chloride) at −30°. When butadiene was employed as solvent-trap at −40° there were obtained in addition to the trimers (33%) the two yellow adducts (12) (57%) and (13) (4%).† The spectroscopic properties of the adducts accord fully with the assigned structures (Experimental section). The assignment of *exo*-stereochemistry to the major adduct is supported by the appearance of two high-field aromatic proton resonances (τ 3·2 and 3·55) in its n.m.r. spectrum; only one shielded aromatic proton appears in the spectrum of the *endo*-adduct. The protons H_A and $H_{A'}$ in the *exo*-adduct [see (16)] will be most strongly shielded by the bridgehead phenyl groups when the planes of the phenyl rings [p_1 and p_2 in (16)] are perpendicular to the plane of the phenylene ring. Molecular models suggest that in the *exo*-adduct (16; R^1 = H, R^2 = $CH{=}CH_2$) this orientation of p_1 represents a preferred conformation, whilst for the second phenyl group a conformation in which its plane bisects the HC_aH angle may be preferred. Shielding of $H_{A'}$ will then be slightly less than that of H_A. In the *endo*-adduct (16; R^1 = $CH{=}CH_2$, R^2 = H) the orientation of p_1 shown will be unfavourable so that H_A will be unshielded. This interpretation is supported by the n.m.r. spectra of a number of related adducts.[15]

Proof of the relative stereochemistry of the adducts was obtained by hydroxylation of the double bond (with OsO_4). The *endo*-adduct formed the yellow ($\lambda_{max.}$ 453 nm) diol (14), but a colourless hemiacetal, *e.g.* (17), was obtained from the *exo*-adduct. The complex n.m.r. spectra of both this hemiacetal and the derived monoacetate did not permit a decision between the pyranose-like structure (17) and alternative formulation as a tetrahydrofuran. Either structure could exist as a mixture of epimers [*e.g.* at C_b in (17)], and so give the observed complex n.m.r. spectra. Chemical reactions that fully confirm the gross structure (12) include conversion of the *exo*-adduct into a dihydro-derivative, and into a quinoxaline derivative which on pyrolysis gave the benzo[*b*]phenazine (18). With sodium methoxide (12) underwent stereospecific benzylic ester rearrangement. The product is tentatively formulated as (19), for the methoxy-protons are slightly shielded (τ 6·57). Exclusive formation of (19) may be due to approach of methoxide ion to the less hindered face of (12) to give *e.g.* (20), which rearranges as shown (arrows).

Low temperature oxidation of (5; R = H) with lead tetra-acetate in isoprene gave the *exo*-adduct (15) (30%). To test the stereospecificity of the trapping reaction, (5; R = H) was oxidised in *cis*-but-2-ene. The n.m.r. spectrum of the crude adduct fraction indicated the presence of only one stereoisomer which, since it showed two equally shielded aromatic protons, is allocated the *cis,exo*-structure (21). Trapping with *trans*-but-2-ene was unsuccessful. The reluctance shown by (1; R = Ph) to react with dienophiles with incorporation of a substituent into the *endo*-position makes interpretation of the stereospecific reaction with *cis*-but-2-ene less



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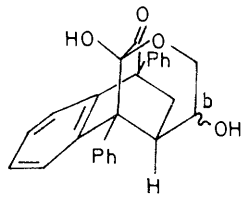

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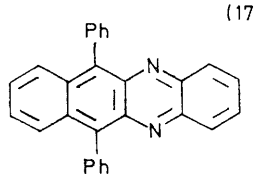

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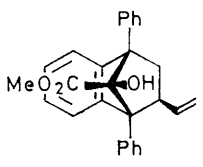

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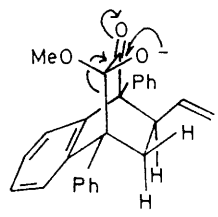

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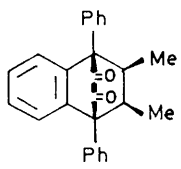

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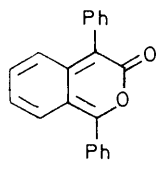


(22)

* Oxidation of (5; R = H) by addition to an excess of lead tetra-acetate at − 30° provides, *inter alia*, the monoacetoxylation product (10; R^1 = H, R^2 = OAc).

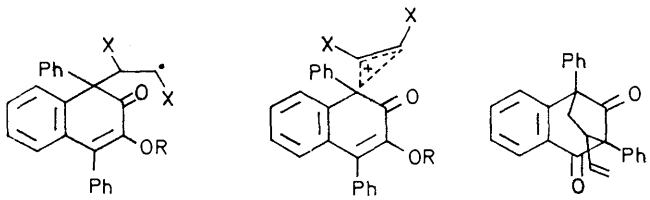
† Formulae (12)—(17), (19), and (20) show only one enantiomer of the pair under discussion.

[15] D. W. Jones and R. L. Wife, *J.C.S. Chem. Comm.*, 1973, 421.

secure. However a two-step reaction should have led in the *trans*-but-2-ene experiment to the *cis,exo*-adduct (21); this adduct was not detected. These results therefore suggest that oxidation of (5; R = H) gives (1; R = Ph), which in its Diels–Alder reactions shows an anomalous preference for *exo*-addition. Compelling analogy for this behaviour is found in the [4 + 2]π additions of the isolable pyrone (22) [9] which shows a similar preference for *exo*-addition, and at 20° reacts 2·5 times more rapidly with *cis*-but-2-ene than with the *trans*-isomer.* This *exo*-selectivity is associated with the presence of phenyl substituents which are probably not coplanar with the *ortho*-quinonoid system, and so impede the secondary interactions normally favouring *endo*-addition. In the absence of such interactions small steric effects presumably favour the *exo*-adduct.[15] In accord with this explanation, trapping of (1; R = Ph) with the more compact cyclopentadiene gives relatively more *endo*-adduct, trapping with norbornadiene gives mainly the *endo*-adduct, and with the more bulky 1,3-cyclohexadiene only the *exo*-adduct was isolated. A green solution prepared by addition of (5; R = H) to an excess of lead tetra-acetate in dichloromethane at −30° retained its colour for 1 h at −30°. The colour was rapidly destroyed by addition of either cyclopentene or 1,4-cyclohexadiene, but no adducts were obtained on attempted trapping with these compounds. The catechol (5; R = H) was recovered as the main isolable product from both experiments. It seems likely that the quinone dehydrogenates these compounds with ease; 1,4-cyclohexadiene is known to be more susceptible to dehydrogenation by quinones than the 1,3-isomer,[17] and the peculiar stability of the cyclopentenyl cation, a homocyclopropenyl cation, is well known. In related work we have shown that cyclopentene reacts with *ortho*-chloranil at 20° to give, *inter alia*, tetrachlorocatechol, and cyclopentadiene–quinone adducts. That the green solution obtained from the catechol (5; R = H) and lead tetra-acetate rapidly dehydrogenates cyclopentene at −25° provides further evidence for the presence of the quinone (1; R = Ph) and shows it to be a more powerful oxidising agent than *ortho*-chloranil. Since the catechol (5; R = H) is regenerated it may be possible to use it as a catalyst in low temperature lead tetra-acetate dehydrogenation reactions. We are exploring this possibility.

A number of experiments mitigate against adduct formation by routes not involving the quinone (1; R = Ph). For example reaction of butadiene with the radical (5; R = ·) could produce an intermediate of the type (23; R = H) which on further oxidation might give the adduct (12). However an intermediate of the type (23; R = H) or [23; R = $\dot{P}b(OAc)_2$] is not compatible with the failure of *trans*-but-2-ene, *trans,trans*-2,4-hexadiene, and *cis*-dichloroethylene as traps. Intermediates of type [23; R = H or $\dot{P}b(OAc)_2$] should with *trans*-but-2-ene give at least some of the *cis*-adduct (21); methyl radicals react more rapidly with *trans*- than with *cis*-but-2-ene.[18] Intermediates like [23; R = H or $\dot{P}b(OAc)_2$] should be particularly stable for the cases of *cis*-dichloroethylene and *trans,trans*-2,4-hexadiene. Further evidence against such a two-step process is provided by the failure of butadiene to divert the oxidation of (5; R = H) and (5; R = Ac) by silver oxide.

Although intermediates of the type [24; R = H or $\bar{P}b(OAc)_2$] could account for stereospecific formation of



(23) (24) (25)

(21), their involvement in adduct formation seems unlikely. Butadiene failed to intercept related intermediates in the acetoxylation of either the monoacetate (5; R = Ac) or 2,4-diphenylnaphthalene-1,3-diol. If an intermediate like (24) were involved in the formation of (12), a similar intermediate from the 1,3-diol would be expected to give at least some of the adduct (25); this product was not detected.

EXPERIMENTAL

M.p.s were determined with a Kofler hot-stage apparatus. Unless otherwise specified i.r. spectra refer to Nujol mulls, u.v. spectra to ethanolic solutions, and n.m.r. spectra to solutions in deuteriochloroform, measured with a Varian A60A spectrometer. Mass spectra were obtained with an A.E.I. MS 902 instrument. Petroleum refers to light petroleum, b.p. 60—80°, and chromatography on silica to short column chromatography [19] over Kieselgel G (Merck).

1,4-*Diphenylnaphthalene*-2,3-*diol* (5; R = H).—The 1,3-diphenylbenzo[*c*]furan–vinylene carbonate adduct [11] (3·04 g, 0·0086 mol), glacial acetic acid (240 ml), and concentrated hydrochloric acid (60 ml) were boiled under reflux (18 h). The solution was concentrated to 60 ml and cooled; 1,4-*diphenylnaphthalene*-2,3-*diol* (5; R = H) (2·35 g, 87%) crystallised from the solution and formed plates, m.p. 234—237° (from benzene–petroleum) (Found: C, 84·45; H, 5·4. $C_{22}H_{16}O_2$ requires C, 84·6; H, 5·2%), $\nu_{max.}$ 3680, 3540, 3420, 1600, 1310, 1210, 760, and 700 cm^{-1}, $\lambda_{max.}$ 238 and 300 nm (ε 42,750 and 8590), $\lambda_{max.}$ (C_6H_{12}) 234, 301, and 327sh nm (ε 49,330, 10,960, and 3880), τ 2·33—2·9 (14H, m) and 4·92br (2H, s, OH, exch. D_2O); *m/e* 312 (M^+), 293, 283, 265, and 252 (100, 9, 5, 30, and 12%).

Oxidation of 1,4-*Diphenylnaphthalene*-2,3-*diol by Silver Oxide*.—The phenol (5; R = H) (1·0 g, 0·0032 mol), silver oxide (1·73 g, 0·0075 mol), and anhydrous sodium sulphate (1·12 g) in dry ether (150 ml) were stirred at 20° under

* For conjugated dienophiles the *trans*-isomer is usually the more reactive.[16]

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[18] A. R. Bader, R. P. Buckley, F. Leavitt, and M. Szwarc, *J. Amer. Chem. Soc.*, 1957, **79**, 5621.
[19] B. J. Hunt and W. Rigby, *Chem. and Ind.*, 1967, 1868.

nitrogen (1 h). The product was filtered (Celite) and evaporated to dryness at 20° under reduced pressure. The crude product (980 mg) was chromatographed on silica (80 g). Elution with benzene gave 6a,10b,18a,18b-*tetrahydro*-5,6a,10b,12,17,20-*hexaphenyldinaphtho*[2,3-e:2′,3′-e′]-*naphtho*[1,2-b:3,4-b′]*bis*-p-*dioxin*-18a,18b-*diol* (7; R = H) (235 mg, 24%), m.p. 229—232° (decomp.) (from benzene–petroleum) [Found: C, 85·1; H, 5·1; *M* (osmometer), 877. $C_{66}H_{44}O_6$ requires C, 85·2; H, 4·8%; *M*, 932], $\nu_{max.}$ 3600, 1600, 1200, 1070, 1000, 770, and 700 cm^{-1}, $\lambda_{max.}$ (C_6H_{12}) 242, 307, and 331sh nm (ε 105,360, 24,080, 10,840), τ 2·25—3·50 (42H, m), and 6·96 (2H, s, OH, exch. D_2O), *m/e* 620 (*M* − $C_{22}H_{16}O_2$), 532, 328, 312, 293, and 265 (0·8, 1·3, 5, 100, 9·3, and 20%) (Found: *m/e* 620·198. $C_{44}H_{28}O_4$ requires 620·199).

Continued elution gave the *isomeric trimer* (6; R = H) (700 mg, 71%), m.p. 228—232° (decomp.) (from benzene–petroleum) [Found: C, 85·3; H, 5·2%; *M* (osmometer), 925], $\nu_{max.}$ 3500, 1600, 1210, 1100, 1080, 765, and 700 cm^{-1}, $\lambda_{max.}$ (C_6H_{12}) 242, 305, and 330sh nm (ε 104,280, 23,600, and 10,700), τ 2·25—3·5 (42H, m), 6·13 (1H, s, OH, exch. D_2O), and 7·44 (1H, s, OH, exch. D_2O), *m/e* 620, 532, 328, 312, 293, and 265 (0·5, 0·8, 6, 100, 14, and 15%) (Found: *m/e* 620·1989).

Oxidation of the Phenol (5; R = H) *with Silver Oxide in Butadiene*.—The phenol (5; R = H) (100 mg) was added in portions to a stirred suspension of silver oxide (143 mg) and anhydrous sodium sulphate (150 mg) in butadiene (15 ml) under nitrogen at −40° during 10 min. After 1 h, the mixture was allowed to warm to 20° over 3·8 h. After dilution with benzene and filtration (Celite), evaporation and chromatography on silica in benzene gave the trimers (7; R = H) (20 mg) and (6; R = H) (68 mg), identical with authentic samples (mixed m.p.s and i.r. spectra).

Oxidation of the Phenol (5; R = H) *with Lead Tetra-acetate in Methylene Chloride*.—The phenol (5; R = H) (195 mg) and lead tetra-acetate (138 mg) in dry methylene chloride (26 ml) were stirred at 20° (2 h). The product obtained after filtration and evaporation of the filtrate was chromatographed on silica in benzene. Elution with benzene gave the trimers (7; R = H) (28 mg) and (6; R = H) (96 mg) as well as the phenol (5; R = H) (53 mg).

Methylation of the Trimers (6; R = H) *and* (7; R = H) *with Diazomethane*.—The trimer (6; R = H) (200 mg) in dry ether was treated with an excess of ethereal diazomethane. The solution was kept at 0° in the dark (16 days). A portion (165 mg) of the crude product (275 mg) obtained by evaporation was chromatographed on silica (120 g). Elution with benzene–petroleum (4 : 1) gave the *dimethyl ether* (6; R = Me) (83 mg, 40%), m.p. 410—420° (from methylene chloride–methanol) (Found: *M*, 960·3430. $C_{68}H_{48}O_6$ requires *M*, 960·3451), $\nu_{max.}$ 1600, 1200, 1150, 1090, 1065, 1000, 765, 750, and 700 cm^{-1}, $\lambda_{max.}$ ($CHCl_3$) 310 and 322sh nm (ε 18,320 and 10,510), *m/e* 960, 649, 575, 480, 399, 353, 340, 312, and 310 (20, 0·8, 2, 2, 1·8, 100, 36, 4·4, and 3·8%). Further elution gave the *monomethyl ether* of (6; R = H) (70 mg, 35%), m.p. 274—276° (from benzene–petroleum) (Found: C, 85·2; H, 5·4. $C_{67}H_{36}O_6$ requires C, 85·0; H, 5·0%), $\nu_{max.}$ 1600, 1200, 1150, 1090, 1070, 1000, 760, and 700 cm^{-1}, $\lambda_{max.}$ ($CHCl_3$) 299 and 331sh nm (ε 24,820 and 11,880), $\lambda_{max.}$ (C_6H_{12}) 241, 307, and 330sh nm (ε 94,740, 20,250, and 10,640), *m/e* 636 (*M* − $C_{22}H_{14}O_2$), 576, 575, 353, 338, 325, and 312 (9·5, 7·5, 8, 48, 7, 2·3, and 100%) (Found: *m/e* 636·232. $C_{45}H_{32}O_4$ requires 636·230).

Similarly the trimer (7; R = H) after treatment with ethereal diazomethane (11 days) and chromatography on silica gave the *dimethyl ether* (7; R = Me) (43%), m.p. 340° (from methylene chloride) (Found: *M*, 960·3430), $\nu_{max.}$ 1600, 1200, 1070, 1050, 770, and 700 cm^{-1}, $\lambda_{max.}$ ($CHCl_3$) 308, 326sh nm (ε 21,170 and 10,580), *m/e* 960, 636, 576, 479, 353, 340, and 312 (12, 1·1, 1·3, 1·6, 100, 21, and 7%). Chromatography also gave the *monomethyl ether* of (7; R = H) (57 mg, 16%), m.p. 274—276° (from benzene–petroleum) (Found: C, 85·1; H, 5·2%), $\nu_{max.}$ 3600, 1600, 1200, 1150, 1090, 1070, 1000, 760, and 700 cm^{-1}, $\lambda_{max.}$ (C_6H_{12}) 304 and 330sh nm (ε 25,520 and 11,180), *m/e* 636·2302 (*M* − $C_{22}H_{14}O_2$), 575, 353, 338, 326, and 312 (16, 6, 90, 13, 26, and 100%).

Reduction of the Trimers (6; R = H) *and* (7; R = H).—The trimer (6; R = H) (80 mg, 0·086 mmol) and lithium aluminium hydride (16 mg, 0·400 mmol) in dry ether (10 ml) were boiled under reflux in a nitrogen atmosphere (0·5 h). The mixture was diluted with ether (10 ml), washed with sulphuric acid (2N), and dried ($MgSO_4$). Removal of solvent gave the phenol (5; R = H) (71 mg, 89%), identical with the material prepared previously (mixed m.p. and i.r. spectrum). Similar reduction of the trimer (7) gave the phenol (5; R = H) in 78% yield.

In an attempt to prepare a quinoxaline derivative, the trimer (6; R = H) was boiled in ethanol–benzene (1 : 1) with *o*-phenylenediamine. Chromatography of the product on silica and elution with benzene gave only the phenol (5; R = H) (60%).

Oxidation of the Trimers (6; R = H) *and* (7; R = H).—(a) *With chromium trioxide*. The trimer (6; R = H) (40 mg) and chromium trioxide (220 mg), in acetic acid (40 ml), were heated on a steam-bath (3·0 h). The solution was diluted with water (40 ml), cooled to 20°, and extracted with ether (120 ml). The extract was washed with saturated sodium hydrogen carbonate solution and water, and dried ($MgSO_4$). Removal of solvent gave *o*-dibenzoylbenzene (29 mg, 79%) (from chloroform–ethanol), identical with an authentic sample [20] (mixed m.p. and i.r. spectrum). Similar oxidation of the trimer (7; R = H) gave *o*-dibenzoylbenzene (61%).

(b) *With lead tetra-acetate*. The trimer (6; R = H) (150 mg, 0·16 mmol) and lead tetra-acetate (102 mg, 0·23 mmol) in methylene chloride (15 ml) were stirred at 20° (12 h). The solution was filtered (Celite), diluted with methylene chloride, washed with water (2 × 20 ml), and dried ($MgSO_4$). Removal of the solvent under reduced pressure gave one stereoisomer of 3,3′-o-*phenylenebis*-{3,5,10-*triphenylnaphtho*[2,3-b]-p-*dioxin*-2(3H)-*one*} (8) (145 mg, 95%), m.p. 315—320° (from benzene–petroleum) (Found: C, 84·85; H, 4·9. $C_{66}H_{42}O_6$ requires C, 85·1; H, 4·6%), $\nu_{max.}$ 1770, 1755, 1600, 1210, 1005, 765, and 700 cm^{-1}, $\lambda_{max.}$ (C_6H_{12}) 244, 294, and 301sh nm (ε 94,600, 23,410, and 22,130), *m/e* 930 (M^+), 632, 592, 576, 563, 399, 338, 312, 281, and 270 (3·8, 0·9, 5·8, 2, 1·1, 2·5, 1·7, 5·5, 100, and 33%). The n.m.r. spectrum showed only aromatic protons. Oxidation of the trimer (7; R = H) in an identical manner gave another *stereoisomer* of (8) (80%), m.p. 410—420° (from benzene–petroleum) (Found: C, 84·95; H, 4·8%), $\nu_{max.}$ 1770, 1600, 1585, 1215, 1005, 760, and 700 cm^{-1}, $\lambda_{max.}$ (C_6H_{12}) 241 and 298 nm (ε 106,340 and 16,580), *M* (osmometer) 833, *m/e* 930, 632, 592, 576, 563, 338, 312, 310, 281, and 270 (13·8, 1·9, 11·6, 1·6, 1·4, 2·2, 4, 100, and 54%). The n.m.r. spectrum showed only aromatic protons.

[20] W. Baker, J. F. W. McOmie, G. A. Pope, and D. R. Preston, *J. Chem. Soc.*, 1961, 2965.

Thermal Interconversion of the Trimers (6; R = H) *and* (7; R = H).—The trimer (7; R = H) (53 mg) and benzene (20 ml) were boiled under reflux (100 h). Chromatography on silica in benzene gave the trimer (7; R = H) (40 mg) and the trimer (6; R = H) (12 mg). Similarly the trimer (6; R = H) (61 mg), after being heated in boiling benzene (20 ml) for 54 h, gave the trimer (7; R = H) (33 mg) and trimer (6; R = H) (24 mg). In both experiments the column fractions were evaporated at 20° under reduced pressure and the identity of the components was established by mixed m.p. and i.r. comparison with authentic samples.

3-Methoxy-1,4-diphenylnaphthalen-2-ol.— 1,4-Diphenylnaphthalene-2,3-diol (400 mg) in ether (15 ml) and benzene (5 ml) was treated with ethereal diazomethane (1·28 mmol) at 20° (15 h). Evaporation of solvent gave *3-methoxy-1,4-diphenylnaphthalen-2-ol* (5; R = Me) (380 mg, 91%), m.p. 116—120° (from benzene–petroleum) (Found: C, 84·15; H, 5·7. $C_{23}H_{18}O_2$ requires C, 84·5; H, 5·6%), $\nu_{max.}$ 3480, 1600, 1590, 1290, 1205, 1005, 765, 755, and 705 cm^{-1}, τ 2·2—2·9 (14H, m), 4·0 (1H, s, OH, exch. D_2O), and 6·52 (3H, s), *m/e* 326 (M^+), 311 ($M - OCH_3$), 293, and 283 (100, 6, 7·8, and 24%).

The dimethyl ether of (5; R = H) (required as a model compound) was prepared similarly. The diol (5; R = H) (100 mg, 0·32 mmol) in ether (20 ml) was treated with an excess of ethereal diazomethane for 24 h at 20°. Evaporation of solvent and crystallisation from benzene–petroleum gave *2,3-dimethoxy-1,4-diphenylnaphthalene* (85 mg, 78%), m.p. 179—180° (Found: C, 84·6; H, 5·9. $C_{24}H_{20}O_2$ requires C, 84·7; H, 5·9%), $\nu_{max.}$ 1600, 1580, 1200, 1100, 1020, 765, 750, and 700 cm^{-1}, $\lambda_{max.}$ (C_6H_{12}) 237 and 298 nm (ε 36,600 and 11,340), τ 2·35—2·8 (14H, m) and 6·3 (6H, s), *m/e* 340 (M^+), 325 ($M - CH_3$), 310 ($M - C_2H_6$), 297, 294, and 282 (100, 2, 11, 16, 15, and 10%).

Oxidation of 3-Methoxy-1,4-diphenylnaphthalen-2-ol.— (a) *With silver oxide.* The phenol (5; R = Me) (130 mg), silver oxide (93 mg), anhydrous sodium sulphate (170 mg), and dry ether (15 ml) were stirred at 20° under nitrogen (22 h). The solution was filtered (Celite) and evaporated at 20° under reduced pressure. The resulting yellow oil was chromatographed on silica (6 g). Elution with benzene–ether (9 : 1) gave *3-methoxy-1-(3-methoxy-1,4-diphenyl-2-naphthyloxy)-1,4-diphenylnaphthalen-2(1H)-one* (11; R = Me) (98 mg, 76%), m.p. 166—169° (from ether) (Found: C, 84·65; H, 5·5. $C_{46}H_{34}O_4$ requires C, 84·9; H, 5·3%), $\nu_{max.}$ 1690, 1375, and 700 cm^{-1}, $\lambda_{max.}$ (C_6H_{12}) 237 and 335 nm (ε 74,350 and 15,750), τ 2·15—3·5 (28H, m), 6·54 (3H, s, OCH_3), and 7·12 (3H, s, OCH_3), *m/e* 650 (M^+), 622, 591, 325, 310, 293, and 283 (15, 3, 4·6, 100, 4·5, 9, and 28%).

(b) *With lead tetra-acetate.* The phenol (5; R = Me) (100 mg, 0·307 mmol) and lead tetra-acetate (136 mg, 0·307 mmol) in dry benzene (5 ml) were stirred at 20° (50 min). The mixture was diluted with chloroform, filtered (Celite), and evaporated. The residue was chromatographed on silica (20 g). Elution with benzene–ether (9 : 1) gave *1-acetoxy-3-methoxy-1,4-diphenylnaphthalen-2(1H)-one* (10; R^1 = Me, R^2 = OAc) (95 mg, 95%), m.p. 140—142° (from methanol) (Found: C, 78·0; H, 5·4. $C_{25}H_{20}O_4$ requires C, 78·1; H, 5·2%), $\nu_{max.}$ 1735, 1685, 1675, 1240, and 700 cm^{-1}, τ 2·3—3·1 (14H, m), 6·62 (3H, s), and 7·74 (3H, s, OAc), *m/e* 384 (M^+), 342 ($M - C_2H_2O$), 326, 312, 297, 282, and 270 (11·5, 22, 5·4, 7, 5·7, 100, and 20%).

3-Methoxymethoxy-1,4-diphenylnaphthalen-2-ol.— The catechol (5; R = H) (500 mg, 1·60 mmol) in ethanol (30 ml) was treated with aqueous sodium hydroxide (0·1N; 16 ml, 1·60 mmol) and the solvents were removed under high vacuum at 100° to give the monosodium salt as a yellow powder. To this salt, stirred in benzene (50 ml) under nitrogen, was added chloromethyl methyl ether (156 mg, 1·94 mmol) in portions. After 18 h the solvent was removed under reduced pressure and the product was combined with that from a second experiment (using 400 mg of the sodium salt) and chromatographed on silica (100 g). Elution with benzene–ether (19 : 1) gave the *monoether* (5; R = CH_2·OMe) (445 mg, 45%), m.p. 119—120° (from benzene–petroleum) (Found: C, 81·0; H, 5·8. $C_{24}H_{20}O_3$ requires C, 80·9; H, 5·7%), $\nu_{max.}$ 3350, 1600, 1570, 1200, 1150, 1100, 970, 930, 770, 750, and 700 cm^{-1}, τ 2·2—2·3 (14H, m), 3·33 (1H, s, OH, exch. D_2O), 5·23 (2H, s, CH_2), and 6·70 (3H, s, OCH_3), *m/e* 358 (M^+), 324, and 283 (60, 100, and 30%).

Oxidation of the Ether (5; R = CH_2·OMe) *with Silver Oxide.*—Compound (5; R = CH_2·OMe) (100 mg, 0·281 mmol), silver oxide (70 mg, 0·290 mmol), and anhydrous sodium sulphate (100 mg) in dry ether (15 ml) were stirred at 20° under nitrogen (14 h). Evaporation of the filtered product and trituration with benzene gave the *dimer* (11; R = CH_2·OMe) (93 mg, 93%), m.p. 182—184° (from benzene–petroleum), *M* (osmometer) 720, $\nu_{max.}$ 1680, 1380, 1160, 1005, and 700 cm^{-1}, $\lambda_{max.}$ (C_6H_{12}) 235 and 301 nm (ε 74,900 and 15,190), τ 2·2—3·5 (28H, m), 5·26 (2H, s), 5·53 (1H, d, *J* 5 Hz), 5·77 (1H, d, *J* 5 Hz), 7·17 (3H, s), and 7·36 (3H, s), *m/e* 355 (*M*/2), 324, and 285 (40, 100, and 43%).

Reaction of the Dimer (11; R = CH_2·OMe) *with Hydrogen Chloride.*—The dimer (55 mg) in carbon tetrachloride (50 ml) was treated with hydrogen chloride gas to saturation at 0°. The solution was washed with water, dried ($MgSO_4$), and evaporated under reduced pressure, and the product was chromatographed on silica. Elution with benzene gave the trimer (7; R = H) (2·0 mg, 4%), the trimer (6; R = H) (27 mg, 50%), the monoether (5; R = CH_2·OMe) (12 mg, 22%), and 1,4-diphenylnaphthalene-2,3-diol (12 mg, 22%). The four products were identical (mixed m.p.s and i.r. spectra) with samples previously prepared.

2-Acetoxy-1,4-diphenylnaphthalen-3-ol.—The phenol (5; R = H) (457 mg, 1·46 mmol), acetic anhydride (153 mg, 1·50 mmol), and pyridine (15 ml) were shaken at 20° (1·25 h). The product was diluted with water (100 ml) and extracted into ether (200 ml). The extract was washed with water, dried ($MgSO_4$), and evaporated to give the *monoacetate* (5; R = Ac) (389 mg, 77%), m.p. 164—166° (from benzene–petroleum) (Found: C, 81·35; H, 5·5. $C_{24}H_{18}O_3$ requires C, 81·35; H, 5·1%), $\nu_{max.}$ 3400, 1730, 1220, 1200, 1010, 940, 765, 745, and 695 cm^{-1}, $\lambda_{max.}$ (C_6H_{12}) 232, 283sh, 294, 313sh, and 329 nm (ε 67,000, 10,430, 11,470, 4750, and 5430), τ 2·3—2·9 (14H, m), 4·84br (1H, s, OH, exch. D_2O), and 8·0 (3H, s), *m/e* 354 (M^+), 312 ($M - C_2H_2O$), 293, and 283 (25, 100, 7, and 7%). Treatment of 1,4-diphenylnaphthalene-2,3-diol (50 mg) with acetic anhydride (0·5 g) in pyridine (5 ml) for 24 h (20°), and work-up as described above gave *2,3-diacetoxy-1,4-diphenylnaphthalene* (46 mg, 85%), m.p. 145—147° (from benzene–petroleum) (Found: C, 78·7; H, 5·3. $C_{26}H_{20}O_4$ requires C, 78·5; H, 5·0%), $\nu_{max.}$ 1765, 1200, 1190, and 690 cm^{-1}, $\lambda_{max.}$ (C_6H_{12}) 287 (ε 13,350), τ 2·3—2·8 (14H, m) and 8·04 (6H, s), *m/e* 396 (M^+), 354 ($M - C_2H_2O$), 312 ($M - C_4H_4O_2$), 293, and 283 (11, 32, 100, 4·5, and 5·8%).

Oxidation of 2-Acetoxy-1,4-diphenylnaphthalen-3-ol.—

(a) *With silver oxide.* The phenol (5; R = Ac) (130 mg), silver oxide (81 mg), sodium sulphate (130 mg), and dry ether (25 ml) were stirred under nitrogen at 20° (3·5 h). The mixture was filtered (Celite) and evaporated to dryness under reduced pressure to give the *dimer* (11; R = Ac) (118 mg, 92%) as a non-crystalline gum (Found: *M*, 706·2335. $C_{24}H_{34}O_6$ requires *M*, 706·2355), $\nu_{max.}$ ($CHCl_3$) 1770, 1690, 1630, 1600, and 1200 cm^{-1}, $\lambda_{max.}$ 238 and 301 nm (ε *ca.* 74,900 and 14,600), τ 2·3—3·2 (28H, m), 8·11 (3H, s, enol acetate), and 8·88 (3H, s), *m/e* 706 (M^+), 664, 622, 381, 354, 340, and 312 (5·7, 5·3, 8·7, 13, 16, 18, and 100%).

(b) *With lead tetra-acetate.* The phenol (5; R = Ac) (195 mg, 0·55 mmol) and lead tetra-acetate (242 mg, 0·545 mmol) were stirred at 20° in benzene (22 ml) in a nitrogen atmosphere (2·25 h). The mixture was diluted with water (30 ml) and extracted into ether (40 ml), and the extract was washed with saturated sodium hydrogen carbonate solution and water, dried ($MgSO_4$), and evaporated at 20° under reduced pressure to give the *acetoxy-acetate* (10; R^2 = OAc, R^1 = Ac) (170 mg, 83%), m.p. 165—166° (from benzene–petroleum) (Found: C, 75·7; H, 5·0. $C_{26}H_{20}O_5$ requires C, 75·7; H, 4·9%), $\nu_{max.}$ 1765, 1740, 1690, 1620, 1240, and 1200 cm^{-1}, $\nu_{max.}$ ($CHCl_3$) 1770, 1745, 1690, 1250, and 1200 cm^{-1}, $\lambda_{max.}$ (C_6H_{12}) 241, 263, and 316 nm (ε 18,130, 6160, and 9050), τ 2·4—3·0 (14H, m), 7·8 (3H, s), and 8·22 (3H, s, enol acetate), *m/e* 412 (M^+), 370 ($M - C_2H_2O$), 328 ($M - C_4H_4O_2$), 312, 310, and 282 (1, 25, 12, 12, and 100%).

(c) *With lead tetra-acetate in butadiene.* Lead tetra-acetate (94 mg, 0·212 mmol) and 2-acetoxy-1,4-diphenylnaphthalen-3-ol (75 mg, 0·212 mmol) were stirred together in butadiene (20 ml) at −40° in a nitrogen atmosphere. Work-up as described above gave the same acetoxy-acetate (10; R^2 = OAc, R^1 = Ac) (68 mg, 80%) as obtained in (b) (mixed m.p. and i.r. spectrum).

3-Acetoxy-1-bromo-1,4-diphenylnaphthalen-2(1H)-one (10; R^1 = Ac, R^2 = Br).—2-Acetoxy-1,4-diphenylnaphthalen-3-ol (160 mg, 0·453 mmol) and *N*-bromosuccinimide (86 mg, 0·48 mmol) in dry carbon tetrachloride (40 ml) were stirred at 20° under nitrogen (40 h). The mixture was cooled in ice and filtered, and the filtrate was evaporated at 20° under reduced pressure to give the *monobromo-acetate* (10; R^1 = Ac, R^2 = Br) (165 mg, 84%) (Found: *M*, 434·0362. $C_{24}H_{17}BrO_3$ requires *M*, 434·0342), $\nu_{max.}$ ($CHCl_3$) 1770, 1680, 1620, 1200, and 1075 cm^{-1}, $\lambda_{max.}$ (C_6H_{12}) 240sh, 332, and 345sh nm (ε *ca.* 16,500 and 5200), τ 2·3—3·1 (14H, m), and 8·04 (3H, s), *m/e* 434, 392, 390, 354, 312, 293, and 283 (2·9, 12, 12, 12, 100, 7·6, and 11%).

Oxidation of 1,4-Diphenylnaphthalene-2,3-diol with Lead Tetra-acetate.—(a) *In the presence of butadiene.* Lead tetra-acetate (1·14 g, 0·0026 mol) was suspended in dry butadiene (170 ml) at −60° in a nitrogen atmosphere. 1,4-Diphenylnaphthalene-2,3-diol (0·8 g, 0·0026 mol) was added in portions to the stirred suspension, which was allowed to warm to −40°; a strong blue colour developed. The mixture was allowed to warm to −5° over 20 min, and stirred at this temperature for 1 h then diluted with benzene and filtered (Celite). Evaporation of solvent at 20° under reduced pressure gave a yellow gum which was chromatographed on silica. Elution with benzene gave first the trimers (6; R = H) and (7; R = H) (239 mg, 33%) and secondly the racemic *1,2,3,4-tetrahydro-1,4-diphenyl-exo-2-vinyl-1,4-ethanonaphthalene-9,10-dione* (12) (412 mg, 57%), m.p. 218—221°, as yellow rosettes (from benzene–petroleum) (Found: C, 85·75; H, 5·6%; *M*, 336·1521. $C_{26}H_{20}O_2$ requires C, 85·7; H, 5·6%; *M*, 336·1514), $\nu_{max.}$ 1725, 1710, 1110, 910, 765, 740, and 700 cm^{-1}, $\lambda_{max.}$ (C_6H_{12}) 235sh, 283, and 453 nm (ε 4480, 1960, and 250), τ 2·3—3·0 (12H, m), 3·1—3·3 (1H, m, $H_{A'}$), 3·4—3·67 (1H, m, H_A), 3·96—5·07 (3H, ABX system, vinyl protons), 6·06—6·50 (1H, m, allylic proton), 6·94 (1H, dd, *J* 13·5 and 12·0 Hz), and 7·46 (1H, dd, *J* 13·6 and 4·2 Hz), *m/e* 364 (M^+), 336 (M — CO), 312, 310 ($M - C_4H_6$), 308 ($M - C_2O_2$), 293, 280, and 267 (0·21, 3·2, 4·8, 4·6, 100, 12·5, 36, and 52%).

Continued elution with benzene afforded the racemic endo-*adduct* (13) (30 mg, 4%), m.p. 237—239° (yellow rosettes from benzene–petroleum) (Found: C, 85·75; H, 5·7%), $\nu_{max.}$ 1730, 1720, and 700 cm^{-1}, $\nu_{max.}$ ($CHCl_3$) 1730, 1720, 1140, 920, and 700 cm^{-1}, $\lambda_{max.}$ (C_6H_{12}) 235sh, 282, and 453 nm (ε 4810, 1800, and 185), τ 2·34—3·0 (13H, m), 3·0—3·39 (1H, m, $H_{A'}$), 4·55—5·05 (3H, ABX system, vinyl protons), 6·05—6·45 (1H, m, allylic proton), 6·95 (1H, dd, *J* 14·5 and 10·0 Hz), and 7·52 (1H, dd, *J* 14·5 and 4·0 Hz), *m/e* 364, 336, 312, 310, 308, 293, 280, and 267 (0·37, 1·8, 1·3, 4·4, 100, 11, 37, and 50%).

(b) *In the presence of isoprene.* Lead tetra-acetate (284 mg, 0·64 mmol), 1,4-diphenylnaphthalene-2,3-diol (200 mg, 0·64 mmol), and isoprene (15 ml) reacted together under the conditions described in (a). The same colour changes were observed as the solution was allowed to warm to 20° over 0·7 h. Work-up as described in (a) and chromatography on silica in benzene gave the trimers (6; R = H) and (7; R = H) (79 mg, 40%), and the racemic exo-*adduct* (15) (84 mg, 30%), m.p. 218—223·5° (from benzene–petroleum) (Found: C, 85·6; H, 5·8. $C_{27}H_{22}O_2$ requires C, 85·75; H, 5·8%), $\nu_{max.}$ 1775, 1735, 1710, 1640, 1595, 1115, 910, 760, 740, and 700 cm^{-1}, $\lambda_{max.}$ (C_6H_{12}) 239, 285, and 454 nm (ε 4390, 1945, and 290), τ 2·1—3·1 (12H, m), 3·15—3·34 (1H, m, $H_{A'}$), 3·35—3·55 (1H, m, H_A), 5·15—5·34 (2H, m, vinyl protons), 6·4 (1H, dd, *J* 12 and 5·5 Hz, allylic proton), 6·84 (1H, dd, *J* 12 and 13 Hz), 7·6 (1H, dd, *J* 13 and 5·5 Hz), and 8·43 (3H, m, *J* <1 Hz, CH_3), *m/e* 378 (M^+), 350 (M — CO), 322 ($M - C_2O_2$), 312, and 294 (1·6, 41, 100, 14·5, and 36%).

Continued elution afforded an isomeric *adduct* (6 mg, 1·4%), m.p. 198—204° (from benzene–petroleum) (Found: C, 86·3; H, 6·1%), *m/e* 378, 350, 322, 312, and 294 (18, 36, 56, 100, and 29%).

(c) *In the presence of* cis-*but-2-ene.* The phenol (307 mg, 0·984 mmol) was added in portions to a stirred suspension of lead tetra-acetate (435 mg, 0·984 mmol) in *cis*-but-2-ene (10 ml) at −20° under nitrogen. The blue solution was stirred for 35 min as its temperature was allowed to rise to 5°. The crude product was diluted with benzene and filtered (Celite), and the filtrate was evaporated to dryness. The product was chromatographed on silica in benzene–petroleum (7 : 3), which eluted first the trimers (6; R = H) and (7; R = H) (220 mg, 56%) and then the exo-*adduct* (21) (36 mg, 10%) as yellow rosettes, m.p. 219—220° (from benzene–petroleum) (Found: C, 84·75; H, 6·05. $C_{26}H_{22}O_2$ requires C, 85·15; H, 6·0%), $\nu_{max.}$ 1745, 1720, 1600, 750, and 700 cm^{-1}, τ 2·1—2·7 (10H, m, aromatic), 2·75—3·1 (2H, m, aromatic), 3·4—3·7 (2H, m, aromatic), 6·6—7·0 (2H, m, methine), and 9·02 (6H, 4 lines, $A_3A'_3$ part of $A_3XX'A'_3$ system), *m/e* 368 (M + 2), 366 (M^+), 338 (M — CO), 310 ($M - C_2O_2$ or $M - C_4H_8$), and 295 (1·3, 0·8, 0·15, 100, and 54%).

(d) *In the presence of cyclopentadiene.* The catechol (5; R = H) (200 mg) was added in small portions during 60 min to a stirred suspension of lead tetra-acetate (284 mg) in

cyclopentadiene (10 ml) at *ca.* −30°. No green colour developed and after removal of cyclopentadiene chromatography over silica in benzene–ether (96 : 4) gave first the racemic exo-*adduct* (76 mg), m.p. 262—267° (from benzene–petroleum) (Found: C, 86·4; H, 5·4. $C_{27}H_{20}O_2$ requires C, 86·1; H, 5·4%), τ 2·5 (12H, m), 2·87 (2H, m), 3·48 (2H, m), 4·32 (2H, m, olefinic), 5·74br (1H, d, *J* 9 Hz), 6·25 (1H, dt, *J* 9 and 3·5 Hz), 7·1br (1H, dd, *J* 18·5 and 9 Hz), and 7·84br (1H, d, *J* 18·5 Hz). Continued elution gave the racemic endo-*adduct* (55 mg), m.p. 300—302° (from benzene–petroleum) (Found: C, 86·1; H, 5·3%), τ 2·45 (10H, m), 2·8 (4H, m), 4·5 (2H, m, olefinic), 5·64br (1H, d, *J* 8·5 Hz), 6·25 (1H, dt, *J* 4·5 and 8·5 Hz), 7·05 (1H, m, CH_2), and 7·9 (1H, m, CH_2).

(e) *In the presence of norbornadiene.* The catechol (5; R = H) (200 mg) was added in small portions with stirring to lead tetra-acetate (284 mg) in methylene chloride (4 ml) and norbornadiene (4 ml). The initial green colour faded rapidly at −25° and most of the catechol addition was carried out at this temperature, further additions of (5; R = H) being made after each fading of the initial green colour. After evaporation under reduced pressure on the steam-bath the product was chromatographed on silica. Elution with benzene–ether (96 : 4) gave the endo-*adduct* (84 mg), m.p. 289—290° (from chloroform–ethanol) (Found: C, 86·8; H, 5·5. $C_{29}H_{22}O_2$ requires C, 86·5; H, 5·5%), τ [$(CD_3)_2SO$] 2·2—2·9 (14H, m, aromatic), 3·5br (2H, s, olefinic), 6·8br (2H, s, allylic), 7·12 (2H, s, methine), 9·35br (1H, d, *J* 9·5 Hz, methylene), and 10·3br (1H, d, *J* 9·5 Hz, methylene).

(f) *In the presence of cyclohexadienes and cyclopentene.* Under conditions identical with those employed in (e), reaction with cyclohexa-1,3-diene gave, after chromatography over silica in benzene–ether (96 : 4), the racemic exo-*adduct* (60 mg), m.p. 220—267° (decomp.) (from chloroform–ethanol) (Found: *M*, 390·161. $C_{28}H_{22}O_2$ requires *M*, 390·162), τ 2·5 (8H, m, aromatic), 2·85 (4H, m, aromatic), 3·5 (2H, m, aromatic), 4·2br (AB system, J_{AB} 11 Hz), 6·3br (1H, d, *J* 10 Hz, allylic), 6·8 (1H, dt, *J* 10 and 5 Hz, methine), and 7·9—9 (4H, m, methylenes), $\nu_{max.}$ 1730 cm^{-1}. Under the same conditions cyclopentene gave only catechol (5; R = H) (40% recovery by chromatography). Use of cyclohexa-1,4-diene gave only catechol (5; R = H) (55% recovery by crystallisation).

Hydroxylation of the exo-*Adduct* (12).—The adduct (12) (100 mg, 0·275 mmol) and osmium tetraoxide (70 mg, 0·275 mmol) in pyridine (1·0 ml) were stirred at 20° (1·75 h). Sodium disulphite (146 mg) in water (2·2 ml) and pyridine (1·6 ml) was added and the mixture was stirred (1·25 h). The product was extracted into chloroform (40 ml); the extract was dried ($MgSO_4$) and evaporated at 30° under reduced pressure. The crude product crystallised from benzene to give the hemiacetal (17?) (103 mg, 86%), m.p. 196—200° (from benzene–petroleum) (Found: C, 78·75; H, 5·6. Calc. for $C_{26}H_{22}O_4$: C, 78·4; H, 5·6%), $\nu_{max.}$ 3530, 3500, 3470, 1730, 1600, and 700 cm^{-1}, $\nu_{max.}$ ($CHCl_3$) 3570, 3500, 1730, 1600, 1110, and 1000 cm^{-1}, *m/e* 398 (M^+), 380 ($M - H_2O$), 370 ($M - CO$), 352 ($M - CH_2O_2$), 340 ($M - C_2O_2$), 327, and 305 (3·6, 1·2, 25, 8, 4·8, 33, 100, and 60%).

Hydroxylation of the endo-*Adduct* (13).—The adduct (13) (19 mg, 0·052 mmol) and osmium tetraoxide (13 mg, 0·052 mmol) in pyridine (0·62 ml) were treated as above (1 h). Work-up with sodium disulphite (45 mg) and water (0·54 ml) (1·7 h) as before gave a gum which was chromatographed on a short column of silica (2·0 g). Elution with benzene–ether (3 : 7) gave the *diol* (14) (15 mg, 75%), m.p. 235—236°, as yellow crystals from benzene–petroleum (Found: C, 78·05; H, 5·6%), $\nu_{max.}$ 3550—3250, 1730, 1720, 1600, 740, and 710 cm^{-1}, $\nu_{max.}$ ($CHCl_3$) 3500, 3400—3150, 1730, 1720, 1595, 1585, and 1075 cm^{-1}, $\lambda_{max.}$ ($CHCl_3$) 286 and 453 nm (ε 1320 and 175), *m/e* 380 ($M - H_2O$), 342, 324, 312, and 293 (0·6, 100, 7·6, and 44%).

Acetylation of the Hemiacetal (17).—The hemiacetal (70 mg, 0·176 mmol), acetic anhydride (1·5 ml), and pyridine (5 ml) were kept at 20° for 5 days. The mixture was diluted with hydrochloric acid (2N; 50 ml) and extracted with ether. The extracts were washed with saturated sodium hydrogen carbonate solution and water, dried ($MgSO_4$), and evaporated. The product was chromatographed on silica in benzene–ether (9 : 1), which eluted the monoacetate (54 mg, 69%), m.p. 246—254° (from benzene–petroleum) (Found: C, 76·5; H, 5·5. Calc. for $C_{28}H_{24}O_5$: C, 76·35; H, 5·5%), $\nu_{max.}$ ($CHCl_3$) 3500, 1740, 1735, 1600, and 1080 cm^{-1}, *m/e* 440 (M^+), 412, 327, 308, 307, and 306 (2·2, 64, 29, 56, 71, and 100%).

Hydrogenation of the Adduct (12).—The adduct (70 mg) was hydrogenated in ethyl acetate (10 ml) over Adams catalyst (7 mg). After 0·7 h, the solution was filtered and evaporated under reduced pressure. The *dihydro-derivative* (55 mg, 78%) crystallised from benzene–petroleum as yellow rosettes, m.p. 241—242° (Found: C, 85·1; H, 6·1. $C_{26}H_{22}O_4$ requires C, 85·2; H, 6·1%), $\nu_{max.}$ 1730, 1715, 1600, 1120, 910, 760, 740, and 700 cm^{-1}, $\lambda_{max.}$ (C_6H_{12}) 237, 262, 282, and 455 nm (ε 3720, 1570, 1755, and 228), τ 1·95—3·00 (12H, m), 3·1—3·3 (1H, m, aromatic), 3·4—3·65 (1H, m, aromatic), 6·89—7·22 (2H, m), 7·62br (1H, d, *J* 10 Hz), 8·1—8·5 (2H, m), and 8·78—9·55 (5H, m), *m/e* 366 (M^+), 310 ($M - C_4H_8$), 281, and 265 (0·1, 65, 100, and 13%).

Reaction of the Adduct (12) *with* o-*Phenylenediamine.*—The adduct (12) (115 mg, 0·316 mmol) and *o*-phenylenediamine (34 mg, 0·316 mmol) in benzene–ethanol (2 : 1; 15 ml) were boiled under reflux (4·3 h). On cooling the *quinoxaline derivative* separated in two crops (78 mg, 57%), m.p. 254—256° (from chloroform–ethanol) (Found: C, 87·7; H, 5·5; N, 6·5. $C_{32}H_{24}N_2$ requires C, 88·0; H, 5·5; N, 6·4%), $\nu_{max.}$ 1640, 1600, 1180, 1120, 920, 760, and 700 cm^{-1}, $\lambda_{max.}$ (C_6H_{12}) 237, 240, 267, 276, 295, 307, 316, and 320 nm (ε 37,680, 35,500, 4800, 4610, 5545, 8845, 8590, and 10,225), τ 1·80—3·05 (16H, m), 3·05—3·28 (1H, m), 3·5—3·67 (1H, m), 4·44—5·23 (3H, ABX system, vinyl protons), 6·11—6·45 (1H, m, allylic proton), 6·95 (1H, dd, *J* 12·5 and 10·5 Hz), and 7·78 (1H, dd, *J* 12·5 and 4 Hz), *m/e* 436 (M^+), 382 ($M - C_4H_6$), and 305 (4·8, 100, and 38%), *m** 243·7 (382 ⟶ 305).

6,11-*Diphenylbenzo*[b]*phenazine* (18).—The foregoing quinoxaline derivative (23 mg) was heated at 270° under nitrogen for 3 min and the product was sublimed at 195° and 0·35 mmHg to give 6,11-*diphenylbenzo*[b]*phenazine* (18) (18 mg, 90%), m.p. 304—305° (Found: C, 87·6; H, 4·8; N, 7·3. $C_{28}H_{18}N_2$ requires C, 87·9; H, 4·7; N, 7·3%), $\lambda_{max.}$ (C_6H_{12}) 227sh, 253, 288, 362, 381, 402, 465, 494, and 529 nm (ε 19,340, 38,870, 112,830, 2510, 6340, 13,840, 3035, 5120, and 5165), *m/e* 382 (M^+) and 305 ($M - C_6H_5$) (100 and 54%), *m** 243·7 (382 ⟶ 305).

Benzylic Ester Rearrangement of the Adduct (12).—The adduct (240 mg, 0·66 mmol) and sodium methoxide (36 mg, 0·66 mmol) in bis-(2-methoxyethyl) ether (10 ml) were stirred at 20° in a nitrogen atmosphere (17 h). The solvent was removed under high vacuum and the residue was acidified with hydrochloric acid (2N) and extracted into

methylene chloride. The extract was washed with water, dried ($MgSO_4$), and evaporated. The residue was chromatographed on silica. Elution with benzene gave *methyl 1,2,3,4-tetrahydro-9-hydroxy-1,4-diphenyl-2-vinyl-1,4-methanonaphthalene-9-carboxylate* (19) (180 mg, 69%), m.p. 144—147° (from methanol) (Found: C, 81·7; H, 6·1. $C_{27}H_{24}O_3$ requires C, 81·9; H, 6·1%), $\nu_{max.}$ 3550, 1740, 1630, 1600, 1240, 750, and 700 cm^{-1}, τ 2·3—2·9 (14H, m), 3·34—4·1 (1H, m, olefinic), 4·8—5·3 (2H, m, olefinic), 6·05 (1H, s, OH, exch. D_2O), 6·57 (3H, s, $CO_2{\cdot}CH_3$), 6·7—7·4 (2H, m), and 7·72—8·2 (1H, m), *m/e* 342 ($M - C_4H_6$), 326, and 282 (35, 13, and 100%).

Elution with ether gave the corresponding *hydroxy-acid* (25 mg, 10%), m.p. 228—230° (from benzene–petroleum) (Found: C, 81·95; H, 5·8. $C_{26}H_{22}O_3$ requires C, 81·7; H, 5·8%), $\nu_{max.}$ 3500, 3200—2400, 1680, 1635, 1600, 1150, 910, 765, and 705 cm^{-1}, τ 2·2—3·0 (16H, m, aromatic and 2 OH protons; OH exch. D_2O), 3·4—4·2 (1H, m, olefinic), 4·85—5·3 (2H, m, olefinic), 6·75—7·4 (2H, m), and 7·7—8·2 (1H, m), *m/e* 328 ($M - C_4H_6$) and 282 (14 and 100%).

Oxidation of 2,4-Diphenylnaphthalene-1,3-diol with Lead Tetra-acetate.—The phenol [21] (300 mg) was added in portions to a stirred suspension of lead tetra-acetate (428 mg) in butadiene (1·5 ml) at −60°. The mixture was allowed to warm to −25° over 15 min and stirring was continued (2 h). The product was diluted with benzene and filtered (Celite), and the filtrate was evaporated under reduced pressure to give an acetoxylation product (208 mg, 60%), m.p. 155—156° (from benzene–petroleum) (Found: C, 77·95; H, 5·0. Calc. for $C_{24}H_{18}O_4$: C, 77·8; H, 5·0%), $\nu_{max.}$ 3340, 1735, 1660, 1615, 1260, and 700 cm^{-1}, $\lambda_{max.}$ 234 and 319 nm (ε 22,160 and 8865), τ 1·6—2·0 (1H, m, aromatic), 2·2—2·8 (13H, m), 3·3—3·6br (1H, s, OH, exch. D_2O), and 7·75 (3H, s, CH_3), *m/e* 370 (M^+), 328 ($M - C_2H_2O$), 312, and 282 (1, 1, 33, and 100%).

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