o-Quinonoid Compounds. Part XI.[1] *exo*-Selectivity in the Diels–Alder Reactions of Phenyl-substituted *o*-Quinonoid Dienes

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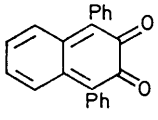
Buta-1,3-diene, isoprene, cyclopenta-1,3-diene, dimethyl maleate, norbornadiene, norbornene, *cis*-but-2-ene, and cyclopentene add to 1,4-diphenyl-2-benzopyran-3-one (2; $R^1 = R^2 = Ph$) to give mostly *exo*-adducts; only for the addition of furan is the *endo*-adduct preferred. By comparison with the preferred *endo*-addition to 2-benzopyran-3-one, its 1-phenyl derivative (2; $R^1 = Ph$, $R^2 = H$), and 1,3-diphenylinden-2-one (15) the *exo*-selectivity in additions to (2; $R^1 = R^2 = Ph$) is attributed to inhibition of secondary interactions by non-coplanar phenyl substituents.

1,4-DIPHENYL-2,3-NAPHTHOQUINONE (1) can be generated as a reactive intermediate by low temperature oxidation of the corresponding catechol and trapped by a variety of olefins and dienes.[2] However the Diels–Alder reactions of (1) are exceptional[4] in that in most cases the *exo*-adduct predominates. Although there are examples of additions in which the *exo*-adduct predominates,[5] or the *exo*- and *endo*-adducts are formed in similar amounts,[6] there appears to be little correlation between structure and tendency to *exo*-addition. In search of such correlation, and precedent for the *exo*-additions to (1), we studied the additions of dienes and olefins to the isolable[7] pyrone (2; $R^1 = R^2 = Ph$).[1b] Similar steric factors should operate in additions to (1) and (2; $R^1 = R^2 = Ph$) and both compounds would be expected to behave



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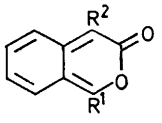


(2)

as electron-deficient dienes in Diels–Alder reactions proceeding with inverse electron demand.

With isoprene in benzene at 130 °C the pyrone (2; $R^1 = R^2 = Ph$) gives the *exo*-adduct (3) (60%), the *endo*-adduct (4) (13%), and an adduct tentatively formulated as (5) (10%). The configurations of (3) and (4) as well as the orientation of addition are assigned on the basis of the reactions of (3) and (4) with trifluoroacetic acid (20 °C). The *exo*-adduct (3) gives the lactone (6) (88%) whereas the *endo*-adduct (4) gives the indane (7) (84%). The spectroscopic properties of (6) and (7) (Experimental section) fully support the assigned structures. In particular the coupling between H_x and H_y (6.5 Hz) strongly favours a *cis*-fusion of rings A and B in both (6) and (7). Molecular models indicate that for the rigid *trans*-isomers the dihedral angle between these protons is *ca.* 100° and therefore inconsistent with the observed coupling constant. However in the more flexible *cis*-isomers conformations with dihedral angles as small as 30° are possible. The formation of (6) and (7) could involve acid-catalysed elimination of (3) and (4) to stereoisomeric acids (8) followed by protonation of the double bond [see (8)] to give stereoisomeric carbocations. In the stereoisomer from (3) neutralisation of the carbocation site by the *cis*-carboxy-group gives the lactone (6), but in the stereoisomer from (4) electrophilic attack of the carbocation on the *cis*-phenyl group gives the indane acid (7). A similar sequence triggered by protonation of the double bond in (3) and (4) is also possible.

In the n.m.r. spectra of (3) and related *exo*-adducts the signals for H_a and H_b appear at higher field (δ 6.25—6.5 and 6.5—6.8) than those of the other aromatic protons,

[1] (*a*) Part X, D. W. Jones and G. Kneen, preceding paper; (*b*) preliminary communication, D. W. Jones and R. L. Wife, *J.C.S. Chem. Comm.*, 1973, 421.

[2] D. W. Jones and R. L. Wife, *J.C.S. Perkin I*, 1974, 1; for a related observation see ref. 3.

[3] D. W. Jones and R. L. Wife, *J.C.S. Perkin I*, 1972, 2722.

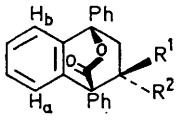
[4] J. Sauer, *Angew. Chem. Internat. Edn.*, 1967, **6**, 16.

[5] (*a*) C. M. Anderson, I. W. McCay, and R. N. Warrener, *Tetrahedron Letters*, 1970, 2735; (*b*) M. A. Battiste and C. T. Sprouse, *ibid.*, p. 4661; R. Breslow, G. Ryan, and J. T. Groves, *J. Amer. Chem. Soc.*, 1970, **92**, 988; (*c*) M. P. Cava and F. M. Scheel, *J. Org. Chem.*, 1967, **52**, 1304.

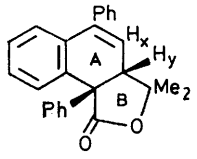
[6] (*a*) K. N. Houk, *Tetrahedron Letters*, 1970, 2621; (*b*) R. W. LaRochelle and B. M. Trost, *Chem. Comm.*, 1970, 1353; P. J. Machin, A. E. A. Porter, and P. G. Sammes, *J.C.S. Perkin I*, 1973, 404.

[7] J. M. Holland and D. W. Jones, *J. Chem. Soc.* (*C*), 1970, 530.

presumably because both phenyl rings can adopt conformations like those shown in [9; N = H, X = MeC(:CH_2)] appropriate for shielding H_a and H_b. In the *endo*-adduct [9; N = MeC(:CH_2), X = H] the required conformation of one phenyl ring is destabilised by steric clash with the *endo*-substituent and only H_b is shielded (δ 6.55—6.8). That the shielded protons are H_a and



(3) R^1 = MeC(:CH_2), R^2 = H
(4) R^1 = H, R^2 = MeC(:CH_2)
(5) R^1 = CH_2:CH, R^2 = Me
(24) R^1 = CH_2:CH, R^2 = H
(25) R^1 = H, R^2 = CH_2:CH



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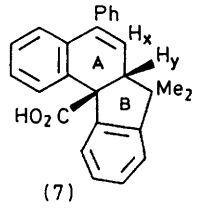

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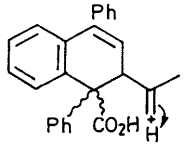

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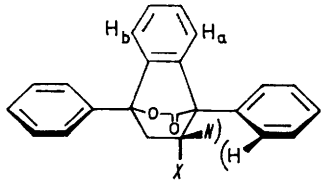

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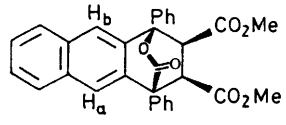
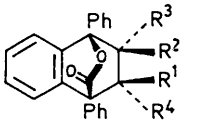
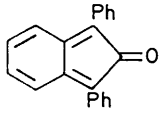


(10)

H_b is supported by the spectrum of the *exo*-adduct (10),[3] which shows signals for the shielded aromatic protons as singlets. Similar shielding effects were noted in the *exo*- and *endo*-adducts of (1) with butadiene where the configurations were established chemically.[2] This n.m.r. criterion therefore constitutes a convenient and reliable means of establishing the *endo*- or *exo*-stereochemistry of adducts derived from (2; R^1 = R^2 = Ph). It has been used extensively in the present work. For some examples other n.m.r. evidence further supports the validity of the method. For the *endo*-norbornadiene adduct the signals for the methylene protons appear at much higher field than for the *exo*-adduct [1] (Experimental section), and for the furan adducts similar though smaller shielding of *endo*-groups by the phenylene ring provides a check on the assignments based on the shielding of H_a and H_b. Furthermore for all the adduct pairs described in this and the preceding paper [1a] derived from simple olefins and dienes the *exo*-adduct has the greater mobility on silica chromatography. In contrast the *endo*-adduct has the greater R_F value when the adducts are derived from an oxygen-containing olefin (furan or dimethyl maleate). By the joint use of these criteria, configurations were assigned to the adducts from (2; R^1 = R^2 = Ph) and the following dienophiles: dimethyl maleate, buta-1,3-diene, cyclopenta-1,3-diene, cyclopentene, *cis*-but-2-ene, norbornadiene, and norbornene. In all cases the *exo*-adduct predominated. This uniform *exo* preference provides good analogy for the *exo*-addition of dienes and olefins to the putative reactive intermediate (1). There is also analogy for our ability to trap (1) with *cis*- but not with *trans*-but-2-ene. When equal quantities of *cis*- and *trans*-but-2-ene compete for (2; R^1 = R^2 = Ph) the yield of *exo,cis*-adduct (11) is three times the combined yield of the *trans*-adducts (12) and (13). More rapid reaction of *cis*- than of *trans*-but-2-ene with (2; R^1 = R^2 = Ph) contrasts with more rapid reaction of the same diene with dimethyl fumarate than with dimethyl maleate. The latter result is that expected for conjugated dienophiles.[4] Whereas the *trans*-adducts (12) and (13) are formed in similar amounts the fumarate adduct (14) is the major product. Similar behaviour is found for corresponding additions to the unsubstituted pyrone (2; R^1 = R^2 = H).[1,8] *exo*-Selectivity is associated



(11) R^1 = R^2 = Me, R^3 = R^4 = H
(12) R^1 = R^3 = Me, R^2 = R^4 = H
(13) R^1 = R^3 = H, R^2 = R^4 = Me
(14) R^1 = R^3 = CO_2Me, R^2 = R^4 = H
(22) R^1 = R^2 = CO_2Me, R^3 = R^4 = H
(23) R^1 = R^2 = H, R^3 = R^4 = CO_2Me



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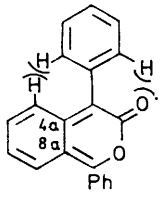
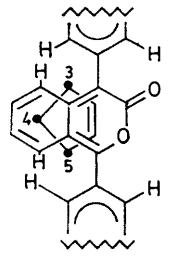


(16)

[8] J. M. Holland and D. W. Jones, *J. Chem. Soc.* (*C*), 1970, 536.

with the presence of phenyl substituents as related additions to the pyrone (2; $R^1 = R^2 = H$) are *endo*-selective.[1a] Whereas (2; $R^1 = R^2 = Ph$) reacts with dimethyl maleate to give more *exo*-adduct (58%) than *endo*-adduct (25%), the diene (2; $R^1 = Ph$, $R^2 = H$) gives more *endo*-adduct (53%) than *exo*- (9%). It is known that (2; $R^1 = R^2 = H$) gives only the *endo*-adduct with dimethyl maleate.[8] Phenyl substituents do not noticeably inhibit *endo*-addition to the five-membered ring diene system in 1,3-diphenylinden-2-one (15), which gives mainly *endo*-adducts with dimethyl maleate and cyclopentadiene.[9] In the present work we have shown that this *endo*-preference extends to cyclopentene, butadiene, and norbornadiene. It is likely therefore that the phenyl groups inhibit *endo*-addition by a steric rather than an electronic effect. Greater coplanarity of the phenyl substituents and the diene system should be possible in (15) than in (16). In the latter, steric interactions of the type shown prevent full coplanarity. The *ortho*-hydrogen atoms of *non*-coplanar phenyl groups will shield C-4a and C-8a and so impede the interactions which normally favour *endo*-addition.[1a] When such interactions are reduced the *exo*-adduct may be favoured by steric effects. Thus in the *endo*-transition state (17) three methylene hydrogen atoms of cyclopentene (●) appear to occupy more sterically demanding environments than in the *exo*-transition state (18). In agreement the *exo*-preference in addition to (2; $R^1 = R^2 = Ph$) decreases with the effective size of the olefin substituents. For *cis*-but-2-ene and cyclopentene only the *exo*-adducts are isolated. For cyclopentadiene the *exo* : *endo* ratio is 4 : 1; for norbornadiene it is 1.5 : 1; for furan the *endo*-adduct predominates; and for cyclopropene only the *endo*-adduct is reported.[10] For the norbornadiene addition steric interactions with the C-3 and C-5 hydrogen atoms would be diminished. This trend will continue for the furan addition, and for the cyclopropene addition interaction of this type will be absent. The C-4 hydrogen atom interacts mainly with the diene system and this may well be a favourable attractive interaction.[1a]

Phenyl substituents also appear to promote *exo*-selectivity in the addition of norbornadiene to 1,3-diphenylbenzo[*c*]furan. This gives only the *exo*-adduct,[5c] whereas addition of norbornadiene to benzo-[*c*]furan itself gives *exo*- and *endo*-adducts in the ratio *ca.* 1.8 : 1. This could indicate lack of complete coplanarity of the phenyl groups with this five-membered ring diene system. Nevertheless addition of cyclopentene to 1,3-diphenylbenzo[*c*]furan is strongly *endo*-selective. The major adduct obtained by Wittig and Burger [11] has the *endo*-configuration, for it is prepared by catalytic reduction of the corresponding cyclopentadiene adduct, the configuration of which rests on n.m.r. comparison with the *exo*-isomer.[9] Related effects may destabilise the *endo*-transition states in additions to 1,2-diphenylbutadiene [12] and the 3,4-diphenylcyclopentadienone (19).[5a] The latter gives mostly *exo*-adducts with certain cyclobutenes and steric destabilisation of the *endo*-transition states has been proposed as an explanation.[5a] In agreement we find that addition of the effectively smaller norbornadiene to (19) gives only the *endo*-adduct (20).[13] The configuration of (20) is supported by the appearance of the AB system for the methylene protons at very similar δ values in (20) and in the alcohol obtained by reduction with lithium aluminium hydride. That additions to (19) are subject to steric control owing to non-coplanarity of the phenyl groups and the diene system is indicated by the greater *endo*-selectivity observed in additions to (21).[14] These observations are of some importance as the diene (19) has been used to test for diene–alkyl group interactions [6a,15] and the results have been used to contest the conclusions of others.[16]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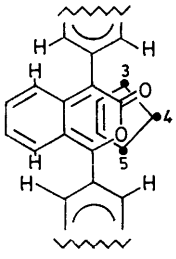
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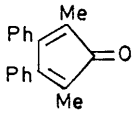
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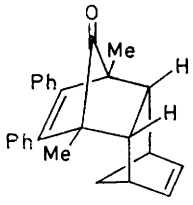
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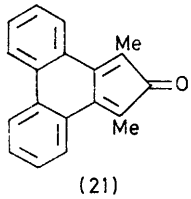
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EXPERIMENTAL

For general details see the preceding paper.[1a]

Additions to 1,4-Diphenyl-2-benzopyran-3-one.—(*a*) Dimethyl fumarate (155 mg), acetic anhydride (5 ml), and the title compound (80 mg) were boiled under reflux in a nitrogen atmosphere (2.5 h). Removal of solvent and the excess of dienophile under high vacuum at 100 °C gave a crude product that crystallised from benzene to give the *adduct* (14) (*1,2,3,4-tetrahydro-2,3-bismethoxycarbonyl-1,4-diphenylnaphthalene-1,4-carbolactone*) (85 mg, 72%), m.p. 182.5—184.5° (from methanol) (Found: C, 73.35; H, 5.2. $C_{27}H_{22}O_6$ requires C, 73.3; H, 5.2%), $\nu_{max.}$ 1 775, 1 770, 1 743, 1 600, 1 210, 1 180, and 1 150 cm^{-1}, δ 7.85—7.1 (13 H, m), 6.65—6.35 (1 H, m), 3.84 (1 H, d, *J* 6 Hz), 3.64 (1 H, d, *J* 6 Hz), and 3.62 (6 H, s); *m/e* 411 (*M* − OMe), 398, 3M9, 366, 338, and 307 (1.1, 4.6, 4.1, 15, 43, and 100%).

[8] J. M. Holland and D. W. Jones, *J. Chem. Soc.* (*C*), 1971, 608.
[9] R. E. Moerck and M. A. Battiste, *J.C.S. Chem. Comm.*, 1972, 1171.
[10] G. Wittig and T. F. Burger, *Annalen*, 1960, **632**, 85.
[11] P. C. Jain, Y. N. Mukerjee, and N. Anand, *J. Amer. Chem. Soc.*, 1974, **96**, 2996.
[12] *Cf.* K. Mackenzie, *J. Chem. Soc.*, 1960, 473.
[13] D. W. Jones, *J.C.S. Chem. Comm.*, 1975, 199.
[14] K. N. Houk and L. J. Luskus, *J. Amer. Chem. Soc.*, 1971, **93**, 4606.
[15] Y. Kobuke, T. Fueno, and J. Furukawa *J. Amer. Chem. Soc.*, 1970, **92**, 6548; Y. Kobuke, T. Sugimoto, J. Furukawa, and T. Fueno, *ibid.*, 1972, **94**, 3633.

(*b*) Dimethyl maleate (2 ml), acetic anhydride (5 ml), and the title compound (200 mg) were boiled under reflux under nitrogen (16 h). The crude product obtained by evaporation at 100 °C in high vacuum crystallised from benzene to give the exo-*adduct* (22) (132 mg, 45%), m.p. 264—267° (from benzene–petroleum) (Found: C, 73.1; H, 5.1%), $\nu_{max.}$ 1 777, 1 600, 1 585, 1 215, 1 140, 767, and 698 cm^{-1}, δ 7.9—7.0 (12 H, m), 6.9—6.6 (1 H, m), 6.6—6.35 (1 H, m), 4 and 3.98 (2 H, inner lines of AB system), 3.56 (3 H, s), and 3.4 (3 H, s); *m/e* 411 (M — OMe), 398 ($M - CO_2$), 379, 366, 338, and 307 (0.9, 2.4, 2.6, 13.5, 50, and 100%). The mother liquor (145 mg) was chromatographed on silica (35 g). Elution with benzene–ether (19 : 1) afforded the fumarate adduct (14) (30 mg, 10%), identical with the compound described in (*a*) (mixed m.p. and n.m.r. and i.r. spectra). Continued elution gave the endo-*adduct* (23) (39 mg, 13%), m.p. 216—218° (from benzene–petroleum) (Found: 73.6; H, 5.15%), $\nu_{max.}$ 1 768, 1 760, 1 757, 1 730, 1 605, 1 210, 1 017, 972, 750, and 703 cm^{-1}, δ 7.8—7.2 (14 H, m), 4.25 (2 H, apparent s), 3.54 (3 H, s), and 3.47 (3 H, s); *m/e* 411, 398, 396, 365, 338, and 307 (2.3, 15, 28, 38, 65, and 100%). The dimethyl maleate used in this experiment contained a small amount (<0.5% by g.l.c.) of dimethyl fumarate. The experiment was therefore repeated with dimethyl maleate freed of the fumarate ester by preparative g.l.c. 1,4-Diphenyl-2-benzopyran-3-one (100 mg) and dimethyl maleate (250 mg) in acetic anhydride (5 ml) were boiled under reflux (40 h). After removal of solvent and the excess of dienophile the n.m.r. spectrum of the crude product indicated the presence of the *exo*-adduct (22) (58%), the *endo*-adduct (23) (25%), and the fumarate adduct (14) (2.8%). Dimethyl maleate was not isomerised to the fumarate ester under the reaction conditions (n.m.r.). The reaction of pure dimethyl maleate with 1,4-diphenyl-2-benzopyran-3-one in refluxing xylene (22 h) under nitrogen gave a small amount of the fumarate adduct (14) (t.l.c.).

(*c*) Buta-1,3-diene (1 ml), benzene (5 ml), and the title compound (200 mg) were heated in a bomb immersed in an oil-bath at 130 °C (19 h). Chromatography of the product on silica in benzene gave the exo-*adduct* (24) (100 mg, 43%), m.p. 146—149° (from benzene–petroleum) (Found: C, 85.35; H, 5.7. $C_{25}H_{20}O_2$ requires C, 85.3; H, 5.7%), $\nu_{max.}$ 1 740, 1 635, 1 600, 1 180, 915, 760, 740, and 700 cm^{-1}, δ 7.8—7.25 (10 H, m), 7.25—6.9 (2 H, m), 6.8—6.5 (1 H, m), 6.5—6.25 (1 H, m), 6.15—5.5 (1 H, m, vinyl), 5.35—4.95 (2 H, m, vinyl), 3.65—3.2 (1 H, m, allylic), 2.88 (1 H, dd, J 13 and 10 Hz), and 2.4 (1 H, dd, J 13 and 5 Hz); *m/e* 352 (M^+), 308 ($M - CO_2$), 298 ($M - C_4H_6$), 280, and 270 (3.7, 29, 43, 15, and 100%).

Further elution gave the endo-*adduct* (25) (39 mg, 17%), m.p. 230—232° (from benzene–petroleum) (Found: C, 85.35; H, 5.7%), $\nu_{max.}$ 1 745, 1 645, 1 600, 1 210, 740, and 715 cm^{-1}, δ 7.9—7.1 (13 H, m), 6.85—6.6 (1 H, m), 5.3—5.05 (3 H, m, vinyl), 4.0—3.5 (1 H, m, allylic), 3.04 (1 H, dd, J 13.5 and 10 Hz), and 2.17 (1 H, dd, J 13.5 and 3 Hz); *m/e* 352, 308, 298, 280, and 270 (5, 100, 18, 46, and 76%).

(*d*) Isoprene (6 ml), benzene (15 ml), and 1,4-diphenyl-2-benzopyran-3-one (400 mg) were heated in a bomb immersed in an oil-bath at 130 °C (19 h). Chromatography of the product on silica in benzene gave the exo-*adduct* (3) (295 mg, 60%), m.p. 139—141° (from benzene–petroleum) (Found: C, 85.2; H, 5.8. $C_{26}H_{22}O_2$ requires C, 85.3; H, 6.0%), $\nu_{max.}$ 1 750, 1 740, 1 640, 1 595, 1 175, and 700 cm^{-1}, δ 7.9—7.25 (10 H, m), 7.25—6.9 (2 H, m), 6.8—6.5 (1 H, m), 6.5—6.25 (1 H, m), 4.9—4.75 (2 H, m, vinyl), 3.37 (1 H, dd, J 10 and 6.5 Hz, allylic), 2.91 (1 H, dd, J 13 and 10 Hz, methylene), 2.35 (1 H, dd, J 13 and 6.5 Hz, methylene), and 1.66 (3 H, t, $J < 1$ Hz, CH_3); *m/e* 366 (M^+), 348 ($M - H_2O$), 322 ($M - CO_2$), 305, 290, 280, and 270 (8.7, 0.7, 5.8, 3.3, 32, 100, and 54%). Further elution gave the exo-*adduct isomer* (5) (47 mg, 10%), m.p. 183—184° (from benzene–petroleum) (Found: C, 85.15; H, 6.1%), $\nu_{max.}$ 1 745, 1 630, 1 600, 1 192, 1 003, 752, 747, and 706 cm^{-1}, δ 7.9—6.9 (12 H, m), 6.85—6.5 (2 H, m), 6.0—4.7 (3 H, ABX system, vinyl), 2.56 (1 H, d, J 5 Hz, CH_2), 2.47 (1 H, d, J 5 Hz, CH_2), and 1.68 (3 H, s, Me); *m/e* 366, 351, 348, 333, 321, 311, 305, 298, 294, 291, and 270 (15.4, 1.0, 1.8, 0.77, 15.4, 6.3, 10.6, 71, 9.6, 8.3, and 100%).

Continued elution of the column gave the endo-*adduct* (4) (64 mg, 13%), m.p. 229—232° (from benzene–petroleum) (Found: C, 85.0; H, 6.0%), $\nu_{max.}$ 1 745, 1 640, 1 600, 1 200, 745, and 700 cm^{-1}, δ 7.8—7 (13 H, m), 6.8—6.56 (1 H, m), 4.85—4.68 (2 H, m, vinyl), 3.65 (1 H, dd, J 10.5 and 5.0 Hz, allylic), 3.05 (1 H, dd, J 13.5 and 10.5 Hz, CH_2), and 2.15 (1 H, dd, J 13.5 and 5 Hz, CH_2); *m/e* 366, 348, 320, 305, 289, 280, 276, and 270 (1.5, 0.6, 53, 100, 27, 13, 13, and 9%).

(*e*) Cyclopenta-1,3-diene (0.25 ml), benzene (5 ml), and 1,4-diphenyl-2-benzopyran-3-one (80 mg) were set aside in the dark (8 h). Chromatography of the product in benzene–ether (24 : 1) gave first the exo-*adduct* (80 mg), m.p. 257—261° (from chloroform–ethanol) (Found: C, 85.5; H, 5.75. $C_{26}H_{20}O_2$ requires C, 85.7; H, 5.5%), $\nu_{max.}$ 1 740 and 1 750 cm^{-1}, δ 8.0—7.3 (10 H, m), 7.3—7.0 (2 H, m), 6.72—6.52 (1 H, m), 6.52—6.28 (1 H, m), 5.84 (2 H, m, olefinic), 4.2—3.9 (1 H, m, allylic methine), 3.7—3.22 (1 H, m, methine), and 2.71—2.38 (2 H, m, CH_2). Continued elution gave the endo-*adduct* (20 mg), m.p. 227—231° (decomp.) (from chloroform–ethanol) (Found: C, 85.9; H, 5.65%), $\nu_{max.}$ 1 745 cm^{-1}, δ (90 MHz) 7.77—7.31 (10 H, m), 7.31—7.12 (2 H, m), 7.12—6.94 (1 H, m), 6.94—6.81 (1 H, m), 5.55 (1 H, m, olefinic), 5.34 (1 H, m, olefinic), 4.29 (1 H, dquint, J 9 and *ca.* 2 Hz, allylic methine), 3.86 (1 H, td, J 9 and 4 Hz, methine), 2.84 (1 H, ddq, J 17, 9, and 2 Hz), and 1.95 (1 H, dm, J 17 and *ca.* 1.5 Hz).

(*f*) Cyclopentene (2 ml), benzene (8 ml), and 1,4-diphenyl-2-benzopyran-3-one (75 mg) were kept in the dark (48 h). The n.m.r. spectrum ([$^2H_5$]pyridine) of the crude product obtained by evaporation under reduced pressure showed the presence of only one adduct. Crystallisation from methylene chloride–methanol gave the exo-*adduct* (76 mg, 82%), m.p. 254—257° (Found: C, 85.0; H, 6.2. $C_{26}H_{22}O_2$ requires C, 85.1; H, 6.1%), $\nu_{max.}$ 1 745, 1 600, 975, 755, and 700 cm^{-1}, δ 8.0—7.3 (10 H, m), 7.25—6.9 (2 H, m), 6.8—6.6 (1 H, m), 6.6—6.4 (1 H, m), 3.3—2.9 (2 H, m, methine), 2.25—1.2 (6 H, m, CH_2).

(*g*) *cis*-But-2-ene (1.8 ml), *trans*-but-2-ene (1.8 ml), benzene (6 ml), and 1,4-diphenyl-2-benzopyran-3-one (100 mg) were kept in a sealed bomb (15 days). Chromatography of the product on silica in benzene gave first the exo,cis-*adduct* (11) (60 mg), m.p. 225—228° (from chloroform–ethanol) (Found: C, 84.65; H, 6.35. $C_{25}H_{22}O_2$ requires C, 84.7; H, 6.3%), $\nu_{max.}$ 1 745 cm^{-1}, δ 8.0—7.28 (10 H, m), 6.9—7.28 (2 H, m), 6.9—6.55 (1 H, m), 6.45—6.13 (1 H, m), 3.2—2.6 (2 H, m, methine), 0.96 (3 H, d, J 7 Hz), and 1.13 (3 H, d, J 7 Hz). Continued elution gave the trans-*adduct* (12) (11 mg), m.p. 202—204° (from chloroform—ethanol) (Found: C, 84.8; H, 6.2%), $\nu_{max.}$ 1 735 and 1 745 cm^{-1}, δ 7.91—7.29 (10 H, m), 7.25—7.0 (3 H, m), 6.18—6.44 (1 H, m), 2.9—2.39 (1 H, m, methine), 2.39—1.9 (1 H, m, methine), 1.28 (3 H, d, J 7 Hz), and 0.94

(3 H, d, *J* 7 Hz); then the trans-*adduct* (13) (11 mg), m.p. 185—187° (from chloroform–ethanol) (Found: C, 84.8; H, 6.2%), $\nu_{max.}$ 1 755 cm^{-1}, δ 7.86—7.32 (10 H, m), 7.32—7.0 (3 H, m), 6.9—6.6 (1 H, m), 2.95—2.4 (1 H, m, methine), 2.4—1.79 (1 H, m, methine), 1.08 (3 H, d, *J* 7 Hz), and 0.87 (3 H, d, *J* 7 Hz). Further elution gave *o*-dibenzoylbenzene (8 mg) and 1,4-diphenyl-2-benzopyran-3-one (6 mg).

The separate reactions of *cis*- and *trans*-but-2-ene with 1,4-diphenyl-2-benzopyran-3-one gave the *cis*-adduct (11), and a mixture of the *trans*-adducts (12) and (13), respectively.

(*h*) Norborna-2,5-diene (0.5 g), benzene (5 ml), and 1,4-diphenyl-2-benzopyran-3-one were kept in the dark (18 h). Chromatography of the product on silica in benzene gave the exo-*adduct* (60 mg), m.p. 236—239° (from chloroform–ethanol) (Found: C, 86.15; H, 5.7. $C_{28}H_{22}O_2$ requires C, 86.1; H, 5.7%), $\nu_{max.}$ 1 750 cm^{-1}, δ 7.85—7.3 (10 H, m), 6.84—7.3 (2 H, m), 6.6—6.84 (1 H, m), 6.25—6.6 (3 H, m, overlapping, olefinic and aromatic H), 3.09br (1 H, s), 2.98—2.5 (3 H, m), 2.24br (1 H, d, *J* 10.5 Hz, CH_2), and 1.3 (1 H, d, *J* 10.5 Hz, CH_2). Continued elution gave the endo-*adduct* (42 mg), m.p. 195—198° (decomp.) (from chloroform—ethanol) (Found: C, 86.25; H, 5.75%), $\nu_{max.}$ 1 748 cm^{-1}, δ 8.0—7.34 (10 H, m), 7.34—6.9 (4 H, m), 6.7—6.2 (2 H, m, olefinic), 2.8—3.2 (4 H, m, methine), 0.71br (1 H, d, *J* 10 Hz, CH_2), and −0.55br (1 H, d, *J* 10 Hz, CH_2).

(*i*) Norborn-2-ene (0.5 g) and 1,4-diphenyl-2-benzopyran-3-one (100 mg) were treated as described in (*h*). Chromatography of the product on silica in benzene–ether (24 : 1) gave the exo-*adduct* (100 mg), m.p. 250—252° (from chloroform–ethanol) (Found: C, 85.75; H, 6.15. $C_{28}H_{24}O_2$ requires C, 85.7; H, 6.2%), $\nu_{max.}$ 1 743 cm^{-1}, δ 7.8—7.3 (10 H, m), 7.25—6.98 (2 H, m), 6.8—6.5 (1 H, m), 6.5—6.25 (1 H, m), 2.8—2.32 (2 H, m), 2.32—1.82 (2 H, m), 1.82—1.09 (5 H, m), and 0.9 (1 H, d, *J* 10.5 Hz, CH_2). Continued elution gave the endo-*adduct* (34 mg), m.p. 250—255° (decomp.) (from chloroform–ethanol) (Found: C, 85.7; H, 6.0%), $\nu_{max.}$ 1 740 cm^{-1}, δ 8.0—7.35 (10 H, m), 6.9—7.35 (4 H, m), 3.0 and 2.81 (2 H, AB system, *J* 8 Hz), 2.38br (2 H, s, bridgehead methine), 1.73—1.21 (4 H, m), 0.35br (1 H, d, *J* 10 Hz), and −0.82br (1 H, d, *J* 10 Hz).

(*j*) Furan (2.5 ml), benzene (5 ml), and 1,4-diphenyl-2-benzopyran-3-one (100 mg) were kept in the dark (3 weeks), and the product was chromatographed on silica in benzene–ether (97.5 : 2.5) to give first the endo-*adduct* (64 mg), m.p. 250—254° (decomp.) (from chloroform–ethanol) (Found: C, 82.3; H, 4.7. $C_{25}H_{18}O_3$ requires C, 82.0; H, 4.95%), $\nu_{max.}$ 1 750 cm^{-1}, δ 6.7—8.0 (14 H, m, aromatic), 5.91 (1 H, dd, *J* 3 and 2 Hz, vinyl HCO), 5.66 (1 H, d, *J* 10 Hz, HCO), 4.85 (1 H, dd, *J* 3 and 2 Hz, vinyl HC·CO), and 4.45 (1 H, dt, *J* 10 and 2 Hz, HC·CO); then the exo-*adduct* (9 mg), m.p. 242—243° (from benzene–petroleum) (Found: C, 82.15; H, 5.05%), $\nu_{max.}$ 1 757 cm^{-1}, δ (90 MHz), 7.41 (10 H, m), 7.08 (2 H, m), 6.66 (1 H, m), 6.41 (2 H, m, aromatic and vinylic HCO), 5.41 (1 H, d, *J* 9.75 Hz, HCO), 4.95br (1 H, s, vinylic HC·CO), and 4.25br (1 H, d, *J* 9.75 and 1.5 Hz).

Reaction of the Adduct (3) *with Trifluoroacetic Acid.*—The *exo*-adduct (3) (20 mg) was kept in trifluoroacetic acid (0.5 ml) (15.3 h). The product was diluted with water (20 ml) and extracted into methylene chloride (100 ml). The extracts were washed with saturated sodium hydrogen carbonate solution and water, dried ($MgSO_4$), and evaporated to give 3a,9b-*dihydro*-3,3-*dimethyl*-5,9b-*diphenylnaphtho*[1,2-c]*furan*-1(3H)-*one* (6) (17.5 mg, 88%), m.p. 195—196° (from benzene–petroleum) (Found: C, 85.4; H, 5.9. $C_{26}H_{22}O_2$ requires C, 85.3; H, 6.0%), $\nu_{max.}$ 1 750, 1 260, and 700 cm^{-1}, $\nu_{max.}$ ($CHCl_3$) 1 760 cm^{-1}, $\lambda_{max.}$ 231, 262sh, 264, and 272sh nm (ε 22 100, 6 050, 6 525, and 6 450), δ 7.9—7.6 (1 H, m), 7.5—6.9 (13 H, m), 5.72 (1 H, d, *J* 6.5 Hz, vinyl), 3.3 (1 H, d, *J* 6.5 Hz), 1.6 (3 H, s, Me), and 1.26 (3 H, s, Me); *m/e* 366 (M^+), 322 ($M - CO_2$), 320 ($M - CH_2O_2$), 307, 291, and 280 ($M - C_4H_6O_2$) (1.5, 0.75, 0.33, 1.1, 1.2, and 100%).

Reaction of the Adduct (4) *with Trifluoroacetic Acid.*—The *endo*-adduct (4) (60 mg) was set aside with trifluoroacetic acid (5 ml) (15.3 h) and the product worked up as described above. Acidification of the sodium hydrogen carbonate extract gave 7,11b-*dihydro*-7,7-*dimethyl*-5-*phenyl*-6aH-*benzo*[c]*fluorene*-11b-*carboxylic acid* (7) (50 mg, 84%), m.p. 251—259° (from benzene–petroleum) (Found: C, 85.05; H, 6.0%), $\nu_{max.}$ 2 600—2 400, 1 700, and 1 690 cm^{-1}, $\lambda_{max.}$ 230, 259sh, 265, and 272 nm (ε 24 600, 5 245, 6 370, and 6 710), δ 10.93—10.53br (1 H, s, exch. D_2O), 7.95—7.7 (1 H, m), 7.6—6.85 (12 H, m), 6.05 (1 H, d, *J* 6.5 Hz, vinyl), 3.6 (1 H, d, *J* 6.5 Hz), 1.45 (3 H, s, Me), and 0.8 (3 H, s, Me); *m/e* 366 (M^+), 348 ($M - H_2O$), 338 (M — CO), 333, 320, 305, and 291 (39, 10, 2, 8.5, 100, 52, and 50%).

Addition of 1-*Phenyl*-2-*benzopyran*-3-*one to Dimethyl Maleate.*—Dimethyl maleate (260 mg), *o*-benzoylphenylacetic acid (200 mg), and acetic anhydride (5 ml) were boiled under reflux in a nitrogen atmosphere (4 h). The solvent and the excess of dienophile were removed at 100 °C in high vacuum and the residue was chromatographed on silica in benzene–ether (9 : 1) to give the endo-*adduct* (173 mg, 53%), m.p. 141—142° (from benzene–petroleum) (Found: C, 69.15; H, 4.9. $C_{21}H_{18}O_6$ requires C, 68.9; H, 4.9%), $\nu_{max.}$ 1 775, 1 750, 1 740, 1 225, and 985 cm^{-1}, δ 7.8—6.95 (9 H, m), 4.36 (1 H, d, *J* 2 Hz, HC·CO·O), 4.08 (1 H, d, *J* 11 Hz, methine), 3.66 (1 H, dd, *J* 11 and 2 Hz, methine), 3.56 (3 H, s), and 3.5 (3 H, s); *m/e* 366 (M^+), 334, 322, 320, 306, 289, 275, and 262 (1.8, 12.5, 6.5, 10, 4.3, 100, 16, and 22.5%). Continued elution gave the exo-*adduct* (30 mg, 9%), m.p. 135—137 and 160—162° (from benzene–petroleum) (Found: C, 68.85; H, 5.1%), $\nu_{max.}$ 1 775, 1 760, 1 740, and 1 230 cm^{-1}, δ 7.8—7.0 (8 H, m), 6.9—6.65 (1 H, m), 4.42 (1 H, d, *J* 1.5 Hz, HC·CO·O), 3.83 (1 H, d, *J* 11 Hz, methine), 3.2 (1 H, dd, *J* 11 and 1.5 Hz, methine), 3.72 (3 H, s), and 3.38 (3 H, s); *m/e* 366, 324, 321, 293, 289, 263, and 262 (6.7, 25, 50, 82, 6.4, 99, and 100%).

Addition of Buta-1,3-*diene to* 1,3-*Diphenylinden*-2-*one.*—1,3-Dibromo-1,3-diphenylindan-2-one (600 mg), sodium iodide (1.16 g), and butadiene (12 ml) in acetone (30 ml) were heated under nitrogen in a bomb immersed in an oil-bath at 60—70 °C (8 h). The product was diluted with methylene chloride, and washed with sodium thiosulphate solution and water. Evaporation of the dried ($MgSO_4$) solution and chromatography of the residue on silica in benzene gave the endo-*adduct* (123 mg, 75%), m.p. 170—172° (from methanol) (Found: C, 89.0; H, 6.2. $C_{25}H_{20}O$ requires C, 89.25; H, 6.0%), $\nu_{max.}$ 1 770, 1 645, 930, 750, 740, and 700 cm^{-1}, δ 7.6—6.7 (14 H, m), 5.45—5.0 (3 H, m, vinyl), 4.0—3.5 (1 H, m, allylic), 3.0 (1 H, dd, *J* 12 and 10 Hz, CH_2), and 1.75 (1 H, dd, *J* 12 and 5 Hz, CH_2); *m/e* 336 (M^+), 308 (M — CO), 293, 280, 267, and 252 (3, 100, 13, 35, 55, and 20%).

The earlier fractions from the column were impure; purification was achieved by chromatography on silica in benzene–petroleum (3 : 7) which gave the exo-*adduct* (10 mg, 2.3%) as a gum (Found: M^+, 336.152. $C_{25}H_{20}O$ requires M, 336.151), $\nu_{max.}$(film) 1 770, 1 645, 1 610, and 700 cm^{-1}, δ 7.73—7.1 (12 H, m), 6.9—6.72 (2 H, m), 5.95—5.45 (1 H, m, vinyl), 5.22—4.95 (2 H, m, vinyl), 3.28—2.89

(1 H, m, allylic), and 2.49 and 2.4 (2 H, s and d, *J* 1 Hz, deceptively simple AB part of ABX system).

Addition of Cyclopentene to 1,3-*Diphenylinden*-2-*one*.—The 1,3-diphenylinden-2-one dimer [9] (110 mg), cyclopentene (1.5 ml), and xylene (6 ml) were heated in a bomb placed in an oil-bath at 156 °C (18 h). Evaporation of the product and chromatography of the residue on silica in benzene gave the exo-*adduct* (30 mg), m.p. 124—127° (from benzene–petroleum) (Found: C, 88.9; H, 6.45. $C_{26}H_{22}O$ requires C, 89.1; H, 6.3%), $\nu_{max.}$ 1 770, 1 605, 1 598, and 1 580 cm^{-1}, δ 8.0—7.25 (10 H, m), 7.25—6.88 (2 H, m), 6.88—6.54 (2 H, m), 3.04—2.7 (2 H, m, methine), and 2.5—0.8 (6 H, complex resonance, CH_2). Continued elution gave the endo-*adduct* (77 mg), m.p. 190—192° (from benzene–petroleum) (Found: C, 89.4; H, 6.45%), $\nu_{max.}$ 1 770, 1 760, 1 601, and 1 580 cm^{-1}, δ 7.3—7.5 (10 H, m), 7.3—7.0 (2 H, m), 7.0—6.7 (2 H, m), 3.5—3.11 (2 H, m, methine), 2.39—1.66 (2 H, complex m, CH_2), and 1.66—0.5 (4 H, complex m, CH_2).

Addition of Norborna-2,5-*diene to* 1,3-*Diphenylinden*-2-*one*.—The 1,3-diphenylinden-2-one dimer (60 mg), norbornadiene (2 ml), and xylene (3 ml) were heated in a bomb placed in an oil-bath at 150 °C (5 h). Evaporation of the product and chromatography on silica in benzene gave the endo-*adduct* (70 mg), m.p. 183—185° (from chloroform–ethanol) (Found: C, 89.7; H, 5.85. $C_{28}H_{22}O$ requires C, 89.8; H, 5.9%), $\nu_{max.}$ 1 780, 1 604, and 1 582 cm^{-1}, δ 7.65—7.3 (10 H, m), 7.3—7.05 (2 H, m), 6.98—6.65 (2 H, m), 6.38 (2 H, m, olefinic), 3.0 (2 H, m, bridgehead methine), 2.79br (2 H, s, methine), 0.66br (1 H, d, *J* 10 Hz, CH_2), and −0.62br (1 H, d, *J* 10 Hz, CH_2).

Reduction of the Norbornadiene–1,3-*Diphenylinden*-2-*one Adduct*.—To the foregoing adduct (50 mg) in ether (10 ml), lithium aluminium hydride (100 mg) was added, and the mixture was boiled under reflux for 1.5 h. Water was added dropwise to the product until the colour changed from grey to white and the mixture was then boiled under reflux for 1 h. The product was filtered off and the filter-pad washed thoroughly with ether. The combined filtrate and washings were dried ($MgSO_4$) and evaporated to give the *alcohol* (45 mg), m.p. 223—225° (from chloroform–ethanol) (Found: C, 89.5; H, 6.5. $C_{28}H_{24}O$ requires C, 89.3; H, 6.4%), $\nu_{max.}$ 3 560, 3 460, 1 600, and 1 114 cm^{-1}, δ ($CDCl_3$–D_2O) 7.7—7.22 (10 H, m), 7.22—6.95 (2 H, m), 6.95—6.6 (2 H, m), 6.35br (2 H, s, olefinic), 4.47 (1 H, s, HCO), 3.05 (2 H, s, methine), 2.66br (2 H, s, bridgehead methine), 0.65 (1 H, d, *J* 10 Hz, CH_2), and −0.86 (1 H, d, *J* 10 Hz, CH_2). In the absence of D_2O the OH resonance appeared at 1.88br (s) and the singlet at 4.47 was broadened.

Addition of Norborna-2,5-*diene to* 2,5-*Dimethyl*-3,4-*diphenylcyclopenta*-2,4-*dienone*.—The 2,5-dimethyl-3,4-diphenylcyclopenta-2,4-dienone dimer (100 mg), norborna-2,5-diene (1 ml), and toluene (5 ml) were boiled under reflux until the solution was colourless (*ca.* 2 h). Evaporation at 100 °C under high vacuum and trituration with ethanol gave the endo-*adduct* (94 mg), m.p. 159—167° (decomp.) (from chloroform–ethanol) (Found: C, 88.3; H, 6.7. $C_{26}H_{24}O$ requires C, 88.6; H, 6.9%), $\nu_{max.}$ 1 762, 1 772, and 1 600 cm^{-1}, δ 7.35—6.9 (10 H, m), 6.29 (2 H, m, olefinic), 3.02 (2 H, quint, *J* *ca.* 2 Hz, bridgehead methine), 2.53br (1 H, d, *J* 9 Hz, CH_2), 2.0br (2 H, s, methine), 1.25 [7 H (6 H, s, 2 × Me and 1 H, d, *J* 9 Hz, CH_2)].

Reduction of this adduct as in the preceding experiment and crystallisation from chloroform–ethanol gave the *alcohol*, m.p. 193—195° (Found: C, 88.0; H, 7.4. $C_{26}H_{26}O$ requires C, 88.1; H, 7.4%), $\nu_{max.}$ 3 350br cm^{-1}, δ [$(CD_3)_2SO$] 7.4—6.9br (10 H, s), 6.3br (2 H, s, vinyl), 5.49 (1 H, d, *J* *ca.* 5 Hz, HCO), 2.71br (2 H, s, bridgehead methine), 2.46 (1 H, d, *J* 9 Hz, CH_2), 2.17 (2 H, s, methine), 1.18 (1 H, d, *J* 9 Hz, CH_2), and 0.97 (6 H, s, CH_3); the OH resonance was obscured by the peak due to water in the solvent.

Reduction of Cyclopentadiene–1,3-*Diphenylbenzo*[c]*furan Adducts*.—Hydrogenation of the *endo*-cyclopentadiene–1,3-diphenylbenzo[*c*]furan adduct over platinum at atmospheric pressure (20 °C) in the usual way gave the major cyclopentene–1,3-diphenylbenzo[*c*]furan adduct described by Wittig and Burger,[11] m.p. 134—136°. Corresponding reduction of the *exo*-cyclopentadiene–1,3-diphenylbenzo[*c*]-furan adduct gave the minor cyclopentene–1,3-diphenylbenzo[*c*]furan adduct, m.p. 207—209°. The *exo*-cyclopentene adduct was unchanged after being heated in boiling toluene (18 h) [t.l.c. over silica in benzene–petroleum (2 : 3)].

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