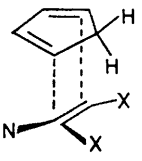
o-Quinonoid Compounds. Part X.[1] *endo*-Selectivity in the Diels–Alder Additions of Non-conjugated Olefins to *o*-Quinodimethanes

By **David W. Jones** * and **Geoffrey Kneen**, Department of Organic Chemistry, The University, Leeds LS2 9JT

The addition of cyclopentene, *cis*-but-2-ene, norbornadiene, and 1,4-dihydro-1,4-methanonaphthalene to 2-benzopyran-3-one (4) gives mainly *endo*-adducts; the addition of cycloheptene and norbornadiene to 1-methyl-2-benzopyran-3-one (5) is also *endo*-selective. *endo*-Addition predominates in the additions of cyclopentene to the valence tautomers (23; R = CN) and (23; R = CO_2Me) of 1-cyano- and 1-methoxycarbonyl-1,2-dihydrobenzocyclobutene. Only *endo*-adducts were isolated by trapping benzo[*c*]furan with cyclopentene, cyclopentadiene, and cycloheptene, but with norbornadiene as trap the *exo*-adduct predominated. An attractive interaction between an *endo*-alkyl group and the diene system will explain these observations.

THE preferred formation of *endo*-adducts in the Diels–Alder reactions of unconjugated olefins [2] can be taken as evidence for an attractive interaction between the diene and an alkyl group in the *endo*-transition state (TS).[3] However for the known reactions unequal steric or torsional effects in the *endo*- and *exo*-TS's make interpretation of the results difficult. Thus *exo*-addition to cyclopentadiene is probably inhibited by steric interaction between a methylene hydrogen atom of the diene and an *exo*-substituent (X) on the olefin as shown in structure (1).[4] A further disadvantage of cyclopentadiene as substrate in testing for diene–alkyl group interaction is that torsional interactions are different in the *exo*- and *endo*-TS's; the C(1)–H bond of the diene does not bisect the NCX angle of the olefin in the TS (2). Both these effects would be absent or at least reduced in additions to six-membered ring diene systems like (3) in which Y and Z are heteroatoms or carbonyl groups. Unfortunately additions to *o*-quinones are complicated by competing additions to the heterodiene system [5] as well as hydrogen transfer from the olefin, *e.g.* cyclopentene,[6] to the quinone. Additions to α-pyrones appear to provide rather unstable initial adducts.[7] We therefore tested [8] for attractive diene–alkyl group interactions in a study of the additions of simple olefins to the very reactive *o*-quinonoid diene system present in 2-benzopyran-3-one (4). Our earlier work [9] had shown that adducts of (4) were stable under the conditions used for generation of the diene.

2-Benzopyran-3-one (4), generated by dehydration of *o*-formylphenylacetic acid in acetic anhydride (140 °C) [9] or benzene containing dicyclohexylcarbodi-imide (80 °C),



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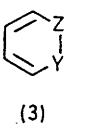

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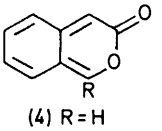
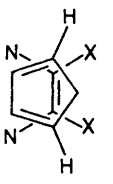


(4) R = H
(5) R = Me



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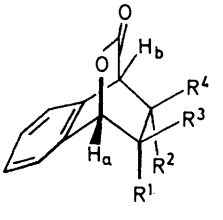
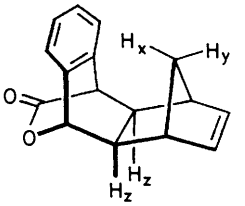


(6) $R^1R^2=[CH_2]_3$, $R^3=R^4=H_c$
(7) $R^1=R^2=H_c$, $R^3R^4=[CH_2]_3$
(8) $R^1=R^2=Me$, $R^3=R^4=H_c$
(9) $R^1=R^2=H_c$, $R^3=R^4=Me$
(10) $R^1=R^4=Me$, $R^2=R^3=H$
(11) $R^1=R^4=H$, $R^2=R^3=Me$



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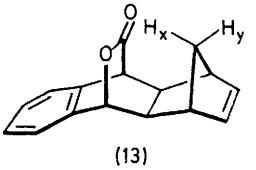

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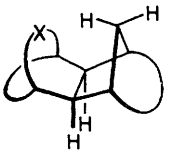

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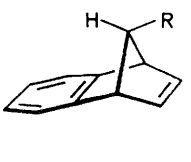


(15)

reacted with cyclopentene to give the *endo*-adduct (6) and the *exo*-adduct (7) in the ratio 6.5 : 1.† The *endo*-

† *endo* : *exo* Ratios were measured for the isolated adducts cleanly separated by short column chromatography.[10] The minor adduct was shown to be stable under the conditions of the addition reaction.

[1] Part IX, D. W. Jones and G. Kneen, *J.C.S. Perkin I*, 1975, 175.
[2] K. B. Wiberg and W. J. Bartley, *J. Amer. Chem. Soc.*, 1960, **82**, 6375; S. J. Cristol, W. K. Siefert, and S. B. Soloway, *ibid.*, p. 2351; N. A. Belikova, V. G. Berezkin, and A. F. Plate, *J. Gen. Chem.* (*U.S.S.R.*), 1962, **32**, 2896; G. L. Closs, L. E. Closs, and W. A. Boll, *J. Amer. Chem. Soc.*, 1963, **85**, 3796; M. A. Battiste and T. J. Barton, *Tetrahedron Letters*, 1968, 2951; R. Muneyuki, T. Yano, and H. Tanida, *J. Amer. Chem. Soc.*, 1969, **91**, 2408; A. Hassner and D. J. Anderson, *ibid.*, 1972, **94**, 8255.
[3] 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.
[4] K. N. Houk and L. J. Luskus, *J. Amer. Chem. Soc.*, 1971, **93**, 4606; J. M. Mellor and C. F. Webb, *J.C.S. Perkin II*, 1974, 17, 22, 26; D. W. Jones, *Ann. Reports* (*B*), 1974, 104, and cited references.
[5] R. Epbinder and W. Friedrichsen, *Tetrahedron Letters*, 1973, 2059, and cited references.
[6] D. W. Jones and R. L. Wife, *J.C.S. Perkin I*, 1974, 1.
[7] T. Imagawa, M. Kawanisi, and K. Sisido, *Chem. Comm.*, 1971, 1292.
[8] Preliminary communication, D. W. Jones, and G. Kneen, *J.C.S. Chem. Comm.*, 1973, 420.
[9] J. M. Holland and D. W. Jones, *J. Chem. Soc.* (*C*), 1970, 536.
[10] B. J. Hunt and W. Rigby, *Chem. and Ind.*, 1967, 1868.

adduct was identical with the reduction product (H_2–Pt) of the single adduct obtained from (4) and cyclopentadiene. The configurations of the adducts followed from their n.m.r. spectra. For the *endo*-adduct the three methylene protons directed towards the phenylene ring are shielded (δ 0.85) whereas the three methylene protons *anti* to the phenylene ring are less shielded (δ 1.5). In the *exo*-adduct the signals for all six methylene protons appear as a broad multiplet centred at δ 1.75. For the *endo*-adduct the H_a and H_b signals appear as cleanly resolved doublets (J 4.5 and 3 Hz) whereas for the *exo*-adduct this coupling is reduced and unresolved as a consequence of the *trans*-periplanar arrangement of the protons H_c and the electronegative lactone unit.[11] Similar addition of (4) to *cis*-but-2-ene gave the *endo*- and *exo*-adducts, ratio 4 : 1. Again the *exo*- and *endo*-adducts were clearly distinguished by the shielding effects produced by the phenylene ring. In the *endo*-adduct (8) the methyl groups are shielded (δ 0.6) relative to their position in the *exo*-adduct (9) (δ 1.2). As expected the protons H_c are more shielded in the *exo*-adduct (9) (δ 1.2) than in the *endo*-adduct (8) (δ 2.6).

Addition of *trans*-but-2-ene to (4) gave approximately equal quantities of the adducts (10) and (11). The n.m.r. spectra of these adducts (Experimental section) fully support the above assignments. The formation of equal quantities of (10) and (11) suggests that any impediment to *exo*-addition (see below) is the same whether a methyl group is opposed to the carbonyl or to the oxygen atom of the lactone unit.

Both norbornadiene and 1,4-dihydro-1,4-methanonaphthalene add to (4) to give *ca.* 6 : 1 mixtures of *endo*- and *exo*-adducts. In the *endo*-norbornadiene adduct (12) one of the methylene protons (H_x or H_y) is strongly shielded (δ −0.46) and the other less strongly shielded (δ 0.62), whereas in the *exo*-adduct (13) the methylene protons are relatively deshielded (δ 1.45 and 2.16). In a variety of molecules of general type (14) the signal for the methylene proton *syn* to the group X (X=O,[12a] C=C,[12b] or AcN·C:O [12c]) appears at lower field as a result of van der Waals deshielding. However for the adduct (12) irradiation at the frequency of the lower field methylene proton produced a simplification of the signal of the protons H_z consistent with removal of **W**-coupling. This suggested that for (12) the H_y signal appears at lower field than that of H_x. This was confirmed by preparation of the adducts of (4) with 1,4-dihydro-1,4-methanonaphthalene (15; R = H), and its monodeuterio-derivative (15; R = D).[13] The *endo*-adduct (16; R = H) presented broadened doublets for the methylene protons at δ −0.1 and 0.94. In the spectrum of the deuteriated *endo*-adduct (16; R = D) the higher field doublet was not present and that at δ 0.94 was a singlet. The situation was reversed in the *exo*-adducts. Here the *lower field* methylene doublet (δ 2.49) from (17; R = H) had disappeared in the spectrum of (17; R = D). It appears therefore that for a phenylene ring (14; X = *o*-phenylene) the shielding of a *syn*-proton outweighs the deshielding due to steric compression whereas for the lactone system (14; X = CO·O) and the carbon–carbon double bond there is an overall deshielding.

These preferred *endo*-additions as well as the related preference in the addition of cyclopentene and norbornadiene to 1-methyl-2-benzopyran-3-one (5) (see Experimental section) can either be attributed to attractive diene–alkyl group interactions, or possibly to repulsion between the alkyl substituents and the lactone unit in the *exo*-TS. The absence of a pronounced impediment to *exo*-addition was shown by the addition of (4) and (5) to tropone, which produced [6 + 4] π-adducts (18; R = H) and (18; R = Me). The spectroscopic properties of these adducts (Experimental section) demonstrate that they have analogous structures and rule out their formulation as [4 + 2] π-adducts. They are assigned the expected[14] *exo*-stereochemistry on the following grounds. Addition of 4-phenyl-1,2,4-triazoline-3,5-dione to an *exo*-adduct (18; R = Me) would be expected to occur from the direction indicated [see (18)] to give (19) in which the olefinic protons have different environments. For an *endo*-adduct of [6 + 4] π-type, addition of the dienophile to the less hindered face of the diene would give an adduct (20) in which the olefinic protons should be strongly shielded by the phenylene ring and have similar chemical shifts. In the triazolinedione adduct of our [6 + 4] π-addition product the olefinic protons have significantly different chemical shifts and are not strongly shielded (δ 6.34 and 6.83). This adduct is accordingly assigned structure (19), derived from the *exo*-structure (18; R = Me). The $A_2X_2Y_2$ spin system of (18; R = H) and (18; R = Me) appears at δ 3.6 (A_2) and 5.9 (X_2Y_2). In the [6 + 4] π-adduct from tropone and 2,5-dimethyl-3,4-diphenylcyclopenta-2,4-dienone, where the *exo*-stereochemistry is established,[15] the A_2 and X_2Y_2 parts of the spin system have these same chemical shifts; the triazolinedione adduct of this product (21) also showed unshielded olefinic resonance (δ 6.7). Photolysis of (18; R = Me) gave a cyclobutene tentatively formulated as (22) since the olefinic protons have significantly different shifts (δ 5.93 and 6.33).

Further evidence in favour of diene–*endo*-alkyl group attraction as opposed to lactone–*exo*-alkyl group repulsion was sought by a study of the addition of cyclopentene to the *o*-quinonoid nitrile (23; R = CN) and ester (23; R = CO_2Me). These dienes were generated

[11] N. S. Bhacca and D. H. Williams, *J. Amer. Chem. Soc.*, 1964, **86**, 2742; H. Booth, *Tetrahedron Letters*, 1965, 411.

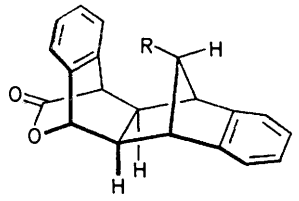
[12] (*a*) M. P. Cava and F. M. Scheel, *J. Org. Chem.*, 1967, **32**. 1304, and cited references; (*b*) W. P. Lay, K. Mackenzie, and J. R, Telford, *J. Chem. Soc.* (*C*), 1971, 3199; R. McCulloch, A. R. Rye, and D. Wege, *Austral. J. Chem.*, 1974, **27**, 1929; *Tetrahedron Letters*, 1969, 5163; (*c*) P. J. Machin, A. E. A. Porter, and P. G. Sammes, *J.C.S. Perkin I*, 1973, 404.

[13] W. T. Ford, *J. Org. Chem.*, 1971, **36**, 3979.

[14] R. B. Woodward and R. Hoffmann, ' The Conservation of Orbital Symmetry,' Academic Press, 1970.

[15] R. B. Woodward and K. N. Houk, *J. Amer. Chem. Soc.*, 1970, **93**, 4145.

by heating the corresponding dihydrobenzocyclobutenes (24). Conrotatory opening of (24; R = CN or CO_2Me) would be expected to proceed in the direction placing the group R on the outside of the diene system.[16] In agreement, (24; R = CN) reacted with *N*-phenylmaleimide, and cyclopentadiene, to give single adducts formulated as (25) and (26), respectively. The most reasonable mode of genesis of these adducts involves *endo*-addition of *N*-phenylmaleimide and cyclopentadiene to the *E*-nitrile (23; R = CN).



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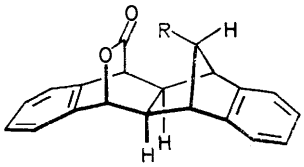

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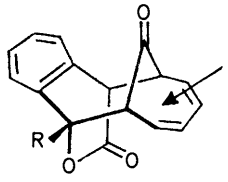

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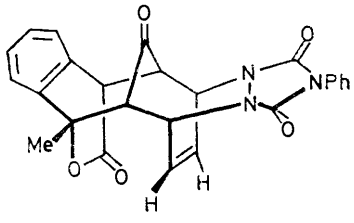

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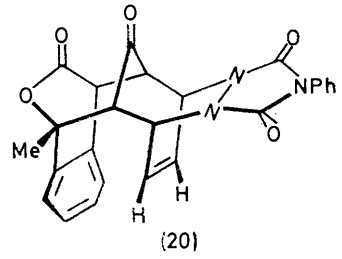

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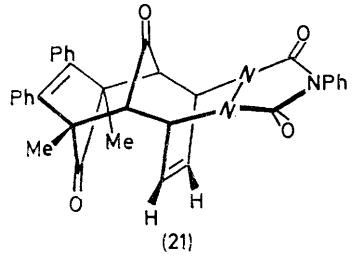

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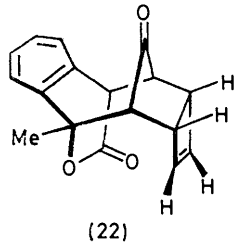


(22)

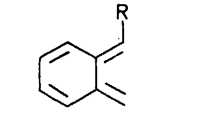
Addition of cyclopentene to (23; R = CN) gave a *ca.* 2 : 1 mixture of the *endo*-adduct (27) and the *exo*-adduct (28). Neither chromatography on silica nor g.l.c. separated these adducts. Accordingly the approximate *endo* : *exo* ratio was obtained by integration of the n.m.r. signals for the protons α to the cyano-group. These appear at δ 3.77 (*endo*-isomer) and 3.44 (*exo*-isomer); in the limited number of examples we have studied this benzylic resonance appears at lower field in the *cis* (*endo*)-isomer and shows a slightly lower vicinal coupling constant. Catalytic reduction of the *endo*-cyclopentadiene adduct (26) gave the major product (27) from the cyclopentene addition. Hydrolysis of the 2 : 1 mixture of (27) and (28) with strong sodium hydroxide solution was accompanied by epimerisation at the cyano-substituted carbon atom; esterification of the product gave the presumably more stable *trans*-ester (30) (see below).

Similar reaction of (24; R = CO_2Me) with cyclopentene gave a 3.3 : 1 mixture of the adducts (29) and (30) which was separated by both silica chromatography and g.l.c. The structure of the *exo*-adduct (30) was confirmed by its preparation from the *endo*-cyclopentene–2-benzopyran-3-one adduct (6) by hydrogenolysis (H_2,Pd–C,HOAc) followed by esterification. Related *intramolecular* addition of simple olefins to *o*-quinodimethanes has been observed by Oppolzer.[16] However for these additions it appears that conformational factors, arising from the presence of a chain of atoms connecting diene and olefin, determine whether *endo*- or *exo*-addition predominates.

Since at present one can only speculate regarding the

[16] W. Oppolzer, *J. Amer. Chem. Soc.*, 1971, **93**, 3833, 3834; *Tetrahedron Letters*, 1974, 1001.

detailed geometry of Diels–Alder TS's * we interpret our results on the commonly assumed basis [14,17a] of parallel approach of diene and dienophile. On this basis steric effects should be similar for *endo*- and *exo*-addition of cyclopentene to (4) and (5) and may well favour *exo*-addition to (23; R = CN and CO_2Me). That in all these cases *endo*-addition is preferred speaks for a small



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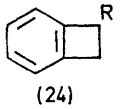

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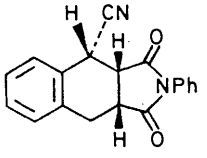

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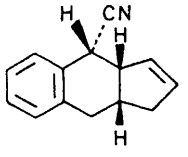

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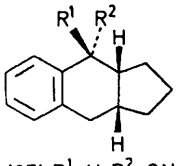
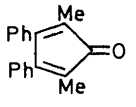


(27) R^1=H, R^2=CN
(28) R^1=CN, R^2=H
(29) R^1=H, R^2=CO_2Me
(30) R^1=CO_2Me, R^2=H



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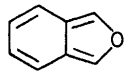

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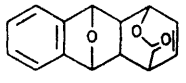

(33)

but well defined attractive diene–alkyl group interaction. The addition of cyclopropene and cyclopentene to the tropylium cation is also *endo*-selective, and the *endo*-selectivity likewise attributed to diene–alkyl group attraction.[18] Although the nature of the attractive interaction is unknown one may speculate that it is of the orbital interaction type, arising as a consequence of ' conjugation ' between the allylic hydrogen atoms and the π-system of the olefin. The allylic hydrogen atoms in the highest occupied molecular orbitals (HOMO) of cyclopropene, cyclopentene, and cyclobutene carry small coefficients of appropriate phase for bonding interaction with C-2 and C-3 of a diene lowest unoccupied molecular orbital (LUMO).[19] For the Diels–Alder reactions with inverse electron demand discussed herein this should be the dominant frontier-orbital interaction. This effect, termed ' steric-attraction ' is held to be at least partly responsible for the contrathermodynamic stereoselectivity observed in the addition of unsymmetrical carbenes to *cis*-olefins.[20] Dispersion forces were earlier proposed to explain related Diels–Alder selectivity.[3]

The preferred *endo*-addition of simple olefins observed in our work contrasts with the formation of almost equal amounts of *endo*- and *exo*-adducts in the addition of cyclopentene to 2,5-dimethyl-3,4-diphenylcyclopentadienone (31),[21] and the addition of cyclopropene to furan.[22] We have already shown [23] that steric effects associated with noncoplanarity of the phenyl groups and diene system in (31) destabilise the *endo*-TS for cyclopentene addition. The increased importance of *exo*-addition in the reaction of furan with cyclopropene may be associated with the small van der Waals radius of oxygen, or may even indicate an attractive interaction between a methylene hydrogen of cyclopropene and the furan oxygen; the HOMO of cyclopropene and the LUMO of furan carry appropriate coefficients at hydrogen and oxygen respectively.[19] We find that the addition of norbornadiene to benzo[*c*]furan (32) [generated by heating the lactone (33)] [24] is *exo*-selective. A close approach of a methylene hydrogen atom of norbornadiene and the furan oxygen is also possible in this addition. When such an interaction is less likely, as in the addition of cyclopentene and cycloheptene to (32), the *endo*-adducts are the main products (Experimental section).

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 (20—100 mg ml^{-1}) measured with a Varian A60 spectrometer. Mass spectra were obtained with an A.E.I. MS902 instrument. Petroleum refers to light petroleum, b.p. 60—80°, and chromatography on silica to short-column chromatography [10] over Kieselgel G (Merck).

Additions to 2-Benzopyran-3-one.—(*a*) Cyclopentene (1.5 ml), *o*-formylphenylacetic acid (110 mg), and acetic anhydride (6 ml) were heated in a steel bomb placed in an oil-bath at 130 °C (18 h). The crude product was evaporated under reduced pressure on a water-bath and the residue chromatographed on silica in benzene–ether (95 : 5) to give first a mixture of *exo*- and *endo*-adducts (35 mg), and then the pure endo-*adduct* (6) (2,3,3a,4,9,9a-*hexahydro*-1H-*cyclopenta*[b]*naphthalene*-4,9-*carbolactone*) (64 mg), m.p.

* Recent MINDO/3 calculations suggest that the addition of butadiene to ethylene proceeds *via* a very unsymmetrical diradical TS. [17b] Whereas the *exo*-TS for the dimerisation of cyclopentadiene is thought to involve a parallel approach, in the corresponding *endo*-TS the addends may approach at a 60° angle. [17c] However one of the authors of this view now appears to regard it with less enthusiasm.[17d]

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115—116° (from benzene–petroleum) (Found: C, 78.65; H, 6.6. $C_{14}H_{14}O_2$ requires C, 78.5; H, 6.6%), $\nu_{max.}$ 1 740 cm^{-1}, δ 0.38—1.22 (3 H, m), 1.25—1.98 (3 H, m), 2.5—3.26 (2 H. m) 3.79 (1 H, d, *J* 3 Hz), 5.4 (1 H, d, *J* 4.5 Hz), and 7.1—7.5br (4 H, s, aromatic). Rechromatography of the above mixture of *endo*- and *exo*-adducts (35 mg) under the same conditions gave the pure *endo*-adduct (20 mg) and the pure exo-*adduct* (7) (13 mg), m.p. 115—118° (from benzene–petroleum) (Found: C, 78.2; H, 6.5%), $\nu_{max.}$ 1 740 cm^{-1}, δ 1.3—2.2 (6 H, m), 2.2—2.6 (2 H, m), 3.8br (1 H, s), 5.42 (1 H, s), and 7.28br (4 H, s, aromatic). The *exo*-adduct was unchanged after treatment with boiling acetic anhydride (3 h).

(*b*) Cyclopentene (1.5 ml), *o*-formylphenylacetic acid (110 mg), dicyclohexylcarbodi-imide (0.5 g), and benzene (6 ml) were heated in a steel bomb immersed in an oil-bath at 80 °C (17 h). The crude product was chromatographed on silica in benzene to give the *exo*-adduct (7) (6 mg), and the *endo*-adduct (6) (50 mg).

(*c*) Cyclopentadiene (1.5 ml), *o*-formylphenylacetic acid (110 mg), and acetic anhydride (6 ml) were treated as in (*a*) above. The n.m.r. spectrum of the adduct fraction obtained by work-up and chromatography as described in (*a*) indicated the presence of only the endo-*adduct* (109 mg), m.p. 154—156° (from benzene–petroleum) (Found: C, 79.15; H, 5.85. $C_{14}H_{12}O_2$ requires C, 79.2; H, 5.7%), $\nu_{max.}$ 1 750 cm^{-1}, δ 1.42—2.0 (1 H, m, CH_2), 2.0—2.8 (1 H, m, CH_2), 3.0—3.7 (2 H, m), 3.95 (1 H, d, *J* 3 Hz), 5.22br (2 H, s, olefinic), 5.41 (1 H, d, *J* 4 Hz), 6.97—7.49 (4 H, m, aromatic).

This product (40 mg) and 10% palladium–charcoal (10 mg) in ethyl acetate (7 ml) were shaken in hydrogen (30 min). Evaporation of the filtered product gave the *endo*-cyclopentene–2-benzopyran-3-one adduct identical (m.p., mixed m.p., and i.r. spectrum) with that prepared in (*a*).

(*d*) *cis*-But-2-ene (3 ml; condensed at −70 °C), *o*-formylphenylacetic acid (110 mg), and acetic anhydride (6 ml) were heated in a steel bomb in an oil-bath at 130 °C (15.5 h). Work-up and chromatography as described in (*a*) gave first the exo-*adduct* (1,2,3,4-*tetrahydro*-2,3-*dimethylnaphthalene*-1,4-*carbolactone*) (9) (20 mg), m.p. 112—113° (from petroleum) (Found: C, 77.05; H, 6.95. $C_{13}H_{14}O_2$ requires C, 77.2; H, 7.0%), $\nu_{max.}$ 1 745 cm^{-1}, δ (90 MHz) 1.11—1.33 (6 H, 3 lines, *J ca.* 6 Hz), 2.1 (2 H, m), 3.6br (1 H, s), 5.24 (1 H, s), and 7.3 (4 H, s, aromatic). Continued elution gave the endo-*adduct* (8) (75 mg), m.p. 96—97° (from petroleum) (Found: C, 77.4; H, 6.75%), $\nu_{max.}$ 1 740 cm^{-1}, δ 0.6 (6 H, 2 lines, *J* 7 Hz, CH_3), 2.6 (2 H, m), 3.66 (1 H, d, *J* 3 Hz), 5.25 (1 H, d, *J* 4 Hz), and 7.32 (4 H, s, aromatic).

(*e*) *trans*-But-2-ene (2 ml), *o*-formylphenylacetic acid (180 mg), and acetic anhydride (5 ml) were heated in a steel bomb placed in an oil-bath at 140 °C (16 h). Evaporation of acetic anhydride under reduced pressure on the water-bath left a crude product (234 mg) which was separated into three fractions by chromatography on silica in benzene–ether (97.5 : 2.5). The first fraction (100 mg) was crystallised from petroleum with difficulty at low temperature (acetone–CO_2 bath) to give the *adduct* (11), m.p. 65—67° (Found: C, 77.45; H, 6.75%), $\nu_{max.}$ 1 745 cm^{-1}, δ 0.75 (3 H, d, *J* 7 Hz), 1.28 (3 H, apparent s), 1.28 (1 H, m), 1.8 (1 H, m), 3.6 (1 H, d, *J* 3 Hz), and 5.2 (1 H, s). The n.m.r. spectrum of this fraction indicated the presence of an impurity, which was removed by crystallisation. The intermediate fraction (9 mg) was a mixture not further examined. The third fraction (70 mg) crystallised readily from petroleum to give the *adduct* (10), m.p. 114—116° (Found: C, 77.25; H, 7.0%), $\nu_{max.}$ 1 745 cm^{-1}, δ 0.73 (3 H, d, *J* 7 Hz), 1.27 (3 H, s), 1.27 (1 H, m), 2.05 (1 H, m), 3.63 (1 H, d, *J ca.* 1.5 Hz), 5.25 (1 H, d, *J* 3.5 Hz), and 7.33 (4 H, s, aromatic).

(*f*) Norbornadiene (4 ml), *o*-formylphenylacetic acid (200 mg), and acetic anhydride (8 ml) were boiled under reflux (internal temperature 110 °C) for 1 h. The product was worked up and chromatographed as in (*a*). The exo-*adduct* (1,4,4a,9,10,10a-*hexahydro*-1,4-*methanoanthracene*-9,10-*carbolactone*) (13) (35 mg) was eluted first, m.p. 133—135° (from methanol) (Found: C, 80.75; H, 6.05. $C_{16}H_{14}O_2$ requires C, 80.6; H, 5.9%), $\nu_{max.}$ 1 755 cm^{-1}, δ 1.45br (1 H, d, *J* 10.5 Hz, CH_2), 1.95br (2 H, s), 2.16br (1 H, d, *J* 10.5 Hz, CH_2), 2.93br (2 H, s, $W_{\frac{1}{2}}$ 7 Hz), 3.82br (1 H, s, $W_{\frac{1}{2}}$ 3 Hz), 5.55 (1 H, s), 6.29 (2 H, m, olefinic), and 7.29 (4 H, s, aromatic). Continued elution gave the endo-*adduct* (12) (200 mg), m.p. 134—135° (Found: C, 81.0; H, 5.75%), $\nu_{max.}$ 1 745 cm^{-1}, δ −0.46br (1 H, d, *J* 10 Hz, CH_2), 0.62br (1 H, d, *J* 10 Hz, CH_2), 2.2 (1 H, ddd, *J* 9, 3, and *ca.* 1.5 Hz), 2.46 (2 H, m), 2.54 (1 H, d of br d, *J* 9 and 4 Hz), 3.92 (1 H, d, *J* 3 Hz), 5.48 (1 H, d, *J* 4 Hz), 6.19 (2 H, m, olefinic), and 7.3 (4 H, m, aromatic). In a double irradiation experiment irradiation at the frequency of the lower field CH_2 proton (60 Hz) caused the signal at δ 2.2 to collapse to a dd (removal of **W**-coupling). Irradiation at the frequency of the higher field CH_2 proton (−42 Hz) did not produce this effect.

(*g*) 1,4-Dihydro-1,4-methanonaphthalene (200 mg), *o*-formylphenylacetic acid (80 mg), and acetic anhydride (4 ml) were boiled under reflux (1 h). Evaporation under reduced pressure on a water-bath, addition and evaporation of ethanol, and chromatography on silica in benzene–ether (95 : 5) gave first the exo-*adduct* (5,5a,6,11,11a,12-*hexahydro*-5,12-*methanotetracene*-6,11-*carbolactone*) (17; R = H) (13 mg), m.p. 218—220° (from methanol) (Found: C, 83.45; H, 5.6. $C_{20}H_{16}O_2$ requires C, 83.3; H, 5.6%), δ (90 MHz) 1.79 (1 H, d, *J* 10.5 Hz, CH_2), 2.01br (2 H, s), 2.49 (1 H, d, *J* 10.5 Hz), 3.48 (2 H, 2 lines), 3.99 (1 H, d, *J ca.* 1 Hz), 5.7 (1 H, s), and 6.9—7.4 (8 H, m, aromatic). Continued elution gave the endo-*adduct* (16; R = H) (80 mg), m.p. 189—190° (from benzene–petroleum) (Found: C, 83.55; H, 5.5%), $\nu_{max.}$ 1 752 cm^{-1}, δ −0.1 (1 H, d, *J* 10 Hz), 0.94 (1 H, d, *J* 10 Hz), 2.3 (1 H, dd, *J* 9 and 3 Hz), 2.68 (1 H, dd, *J* 9 and 4 Hz), 3.05br (2 H, s), 4.05 (1 H, d, *J* 3 Hz), 5.62 (1 H, d, *J* 4 Hz), and 7.0—7.5 (8 H, m, aromatic). The experiment was repeated with 1,4-dihydro-1,4-methanonaphthalene specifically labelled with deuterium in the 9-*anti*-position [13] and the labelled adducts were separated as before. This gave the endo-*adduct* (16; R = D) (60 mg), m.p. 188—191° (from benzene–petroleum) [Found: C, 83.0; H (D), 5.85. $C_{20}H_{15}DO_2$ requires C, 83.0; H (D), 5.9%]. The n.m.r. spectrum differed from that described above in that the signal at δ −0.1 had disappeared, and that at δ 0.94 had collapsed to a br s at δ 0.94. The corresponding exo-*adduct* (17; R = D) (10 mg) had m.p. 219—220° (from methanol) [Found: C, 82.85; H (D), 5.5%]. The 90 MHz n.m.r. spectrum differed from that of the protium compound in that the signal at δ 2.49 was missing, and the doublet at δ 1.79 was replaced by a br s in the same position.

(*h*) Tropone (100 mg), *o*-formylphenylacetic acid (100 mg), and acetic anhydride (2 ml) were boiled under reflux in a nitrogen atmosphere (1 h). Evaporation of the product under reduced pressure on the water-bath, and

chromatography of the residue on silica in benzene–ether (23 : 3) gave the *adduct* (18; R = H) (*5,6,11,12-tetrahydro-13-oxo-6,11-methanobenzocyclodecene-5,12-carbolactone*) (43 mg, 28%), m.p. 225—227° (from chloroform–ethanol) (Found: C, 75.9; H, 4.8. $C_{16}H_{12}O_3$ requires C, 76.2; H, 4.8%), $\nu_{max.}$ 1 740 and 1 705 cm^{-1}, $\lambda_{max.}$ 216, 248, 257, and 267.5 nm (ε 10 350, 4 036, 5 001, and 4 650), δ 3.95—3.45 (2 H, m), 4.13 (1 H, d, *J* 7 Hz), 6.35—5.5 (5 H, m, including HC·O·CO resonance at 5.61, d, *J* 4.5 Hz), and 7.33br (4 H, s, aromatic).

Additions to 1-Methyl-2-benzopyran-3-one.—(*a*) Cycloheptene (300 mg), *o*-acetylphenylacetic acid (107 mg), and acetic anhydride (3 ml; freshly distilled from quinoline) were boiled under reflux in a nitrogen atmosphere (2.5 h). Evaporation of the product under reduced pressure on a water-bath and chromatography of the residue on silica in benzene–ether (24 : 1) gave the endo-*adduct* (116 mg, 75%), m.p. 104—107° (from benzene–petroleum) (Found: C, 79.9; H, 7.8. $C_{17}H_{20}O_2$ requires C, 79.65; H, 7.9%), $\nu_{max.}$ 1 740 cm^{-1}, δ 0.1—2.08 (13 H, m, including Me resonance at 1.84), 2.08—2.8 (2 H, m), 3.64 (1 H, d, *J* 1.9 Hz), and 7.29br (4 H, s, aromatic).

(*b*) Cycloheptatriene (600 mg), *o*-acetylphenylacetic acid (200 mg), and acetic anhydride (10 ml; freshly distilled from quinoline) were boiled under reflux in a nitrogen atmosphere (3 h). Evaporation under reduced pressure on the water-bath gave an oily residue which was hydrogenated over Adams catalyst (30 mg) in ethyl acetate (20 ml) (5.5 h). Evaporation of the filtered product and chromatography on silica in benzene–ether (47 : 3) gave first a product tentatively identified as the exo-*adduct* (18 mg, 6.3%), m.p. 198—201° (from benzene–petroleum) (Found: C, 79.5; H, 7.8%), δ 0.6—2.7 (15 H, m, including Me resonance at 1.88), 3.77 (1 H, m), and 7.29br (4 H, s, aromatic). Further elution gave the *endo*-adduct (182 mg, 63.5%) identical (mixed m.p., i.r., and n.m.r. spectra) with the sample described above.

(*c*) Norbornadiene (2 ml), *o*-acetylphenylacetic acid (82 mg), and acetic anhydride (4 ml; freshly distilled from quinoline) were boiled under reflux in a nitrogen atmosphere (2.5 h). Evaporation under reduced pressure on a water-bath and chromatography of the residue on silica in benzene–ether (9 : 1) gave the *endo*-adduct (57 mg), m.p. 98—103° (from benzene–petroleum) (Found: C, 80.65; H, 6.5. $C_{17}H_{16}O_2$ requires C, 80.9; H, 6.4%), $\nu_{max.}$ 1 740 and 1 750 cm^{-1}, δ −0.42 (1 H, d, *J* 10 Hz), 0.66 (1 H, d, *J* 10 Hz), 1.90 (3 H, s), 2.32br (2 H, s), 2.46 (2 H, m), 3.9br (1 H, s), 6.20br (2 H, s, olefinic), and 7.31br (4 H, s, aromatic).

(*d*) Tropone (120 mg), *o*-acetylphenylacetic acid (120 mg), and acetic anhydride (5 ml; freshly distilled from quinoline) were boiled under reflux in a nitrogen atmosphere (3 h). Evaporation under reduced pressure on a water-bath and chromatography on silica in benzene–ether (19 : 1) gave the exo-*adduct* (18; R = Me) (40 mg, 22%), m.p. 203—205° (from chloroform–ethanol) (Found: C, 76.7; H, 5.35. $C_{17}H_{14}O_3$ requires C, 76.7; H, 5.3%), $\nu_{max.}$ 1 753 and 1 704 cm^{-1}, $\lambda_{max.}$ 218, 248, 257.5, and 268 nm (ε 8 312, 3 804, 4 861, and 4 791), δ 1.97 (3 H, s), 3.4—3.9 (2 H, m), 4.14 (1 H, d, *J* 7 Hz), 5.6—6.5 (4 H, m, olefinic), and 7.1—7.6 (4 H, m, aromatic).

(*e*) *N*-Ethoxycarbonylazepine (200 mg), *o*-acetylphenylacetic acid (178 mg), and acetic anhydride (2.5 ml; freshly distilled from quinoline) were boiled under reflux in a nitrogen atmosphere (3 h). Evaporation under reduced pressure on a water-bath and crystallisation of the residue from chloroform–ethanol gave the *adduct* (110 mg, 34%), m.p. 139—141° (Found: C, 70.15; H, 5.8; N, 4.3. $C_{18}H_{19}NO_4$ requires C, 70.1; H, 5.9; N, 4.3%), $\nu_{max.}$ 1 750 and 1 720 cm^{-1}, δ 1.21 (3 H, t, *J* 7 Hz), 1.93 (3 H, s), 3.4—2.9 (2 H, m), 3.71 (1 H, d, *J* 2 Hz), 4.04 (2 H, q, *J* 7 Hz), 4.5—5.05 (2 H, m), 6.49 (2 H, d, *J* 10 Hz), and 7.21br (4 H, s, aromatic). Evaporation of the mother liquor and chromatography on silica in benzene–ether (43 : 7) gave more of this adduct (100 mg, total 65%).

Additions to Methyl 1,2-Dihydrobenzocyclobutene-1-carboxylate.—This ester was prepared by the reaction of diazomethane with the corresponding acid. The latter was prepared by hydrolysis of the corresponding nitrile, obtained by the addition of benzyne (generated *in situ* by aprotic diazotisation of anthranilic acid) to acrylonitrile. The purity of the product was shown by n.m.r.: δ 3.5 (2 H, d, *J* 4.5 Hz), 3.73 (3 H, s, OMe), 4.32 (1 H, t, *J* 4.5 Hz), and 7.2 (4 H, m, aromatic).

(*a*) Cyclopentene (1.5 ml), xylene (3.5 ml), and the ester (100 mg) were heated in a steel bomb in an oil-bath at 150 °C (24 h). The evaporated product was chromatographed on silica in benzene and the adduct fraction (100 mg) was thereby obtained free of starting material. The product was shown to be a 3.26 : 1 mixture of the adducts (29) and (30) by g.l.c. comparison with authentic samples prepared as described below. G.l.c. was performed on a 5 ft × 2.2 mm column of 5% Carbowax on Supersorb (80—100 mesh) at 151 °C. Careful chromatography of the reaction product on silica in benzene–petroleum (70 : 30) gave pure *methyl* cis-*2,3,3a,4,9,9a-hexahydro-1H-cyclopenta*[b]*naphthalene*-cis-*4-carboxylate* (29) (65 mg) as an oil (Found: M^+, 230.1300. $C_{15}H_{18}O_2$ requires *M*, 230.1306), $\nu_{max.}$ (film) 1 728, 1 735, and 1 742 cm^{-1}, δ 0.7—2.1br (8 H, m, CH_2 and CH envelope), 2.4—2.8 (2 H, m, benzylic), 3.71 (3 H, s, OMe), *ca.* 3.75 (1 H, presumed d, *H*C·CO_2Me), and 7.16 (4 H, m, aromatic). Further elution gave a mixture of the adducts (29) and (30) (12 mg) and then the pure trans-*ester* (30) (15 mg), m.p. 48—49° [from petroleum (b.p. 40—60°) at low temperature (CO_2–Me_2CO bath)] (Found: C, 78.15; H, 8.05%), $\nu_{max.}$ 1 726 cm^{-1}, δ 0.8—3 (10 H, m, CH_2 and CH envelope), 3.45 (1 H, d, *J* *ca.* 6 Hz, *H*C·CO_2Me), 3.7 (3 H, s, OMe), and 7.12 (4 H, m, aromatic). This ester was unchanged after being heated in boiling xylene (6 h).

Additions to 1,2-Dihydrobenzocyclobutene-1-carbonitrile.—(*a*) *N*-Phenylmaleimide (100 mg), the cyclobutene (200 mg), and xylene (4 ml) were boiled under reflux (17 h). On cooling the product deposited the *adduct* (25) (140 mg), m.p. 185—187° (from chloroform–ethanol) (Found: C, 75.5; H, 4.7; N, 9.35. $C_{19}H_{14}N_2O_2$ requires C, 75.5; H, 4.7; N, 9.3%), $\nu_{max.}$ 1 595, 1 705, 1 780, and 2 220w cm^{-1}, δ 3.0—3.9 (4 H, complex m), 4.26 (1 H, d, *J* 4.6 Hz), 6.8—7.15 (2 H, m, aromatic), and 7.2—7.7 (7 H, m, aromatic).

(*b*) Cyclopentene (1.5 ml), the cyclobutene (200 mg), and xylene (3 ml) were heated in a sealed tube at 140—145 °C (18 h). Evaporation under reduced pressure on a water-bath gave a crude product (200 mg). The adduct fraction (90 mg) was isolated by chromatography on silica in benzene and shown to be a *ca.* 2 : 1 mixture of adducts (27) and (28), δ 0.6—3.1 (10 H, complex), 3.4 (0.33 H, d, *J* 7 Hz), 3.77 (0.66 H, d, *J* 5 Hz), and 7.2 (4 H, m, aromatic). This product (90 mg) and sodium hydroxide solution (20%; 3 ml) were heated on a water-bath (18 h). Dilution with water, acidification with hydrochloric acid, and extraction into ether, followed by drying of the extract ($MgSO_4$) and

evaporation gave an acid. With ethereal diazomethane this gave the *trans*-ester (30) (n.m.r. spectrum).

(*c*) The addition to cyclopentadiene was conducted as described for the cyclopentene addition. Evaporation of the product under reduced pressure on a water-bath and chromatography on silica in benzene gave first a *cyclopentadiene dimer adduct* (110 mg), m.p. 116—117° (from petroleum) (Found: C, 87.1; H, 7.3; N, 5.55. $C_{19}H_{19}N$ requires C, 87.3; H, 7.3; N, 5.4%). Continued elution of the column gave a second *cyclopentadiene dimer adduct* (45 mg), m.p. 109—110° (from petroleum) (Found: C, 87.5; H, 7.45; N, 5.3%). Further elution of the column gave the *cyclopentadiene adduct* (26) (60 mg), m.p. 65—66° (from petroleum) (Found: C, 85.95; H, 6.8; N, 7.25. $C_{14}H_{13}N$ requires C, 86.1; H, 6.7; N, 7.2%), δ 1.85 (1 H, dm, *J ca.* 15 Hz), 2.3—3.2 (4 H, complex), 3.5 (1 H, m, allylic), 3.85 (1 H, d, *J* 6 Hz, HC·CN), 5.7 (2 H, m, olefinic), and 7.3 (4 H, m, aromatic). Hydrogenation of this adduct (60 mg) in ethyl acetate (7 ml) over platinum oxide (10 mg) (1 h) gave the pure cis-*adduct* (27) (60 mg), m.p. 54—56° (from petroleum) (Found: C, 85.35; H, 7.75; N, 7.2. $C_{14}H_{15}N$ requires C, 85.2; H, 7.7; N, 7.1%), $\nu_{max.}$ 2 225w cm^{-1}, δ 0.6—2.2 (6 H, complex m), 2.4—3.0 (4 H, complex m), 3.80 (1 H, d, *J* 5 Hz), and 7.2 (4 H, m, aromatic).

Dimerisation of 1,2-*Dihydrobenzocyclobutene*-1-*carbonitrile*.—The benzocyclobutene (200 mg) in xylene (3.5 ml) was heated in a bomb in an oil-bath at 150 °C (24 h). Evaporation under reduced pressure on a water-bath and chromatography on silica in benzene–ether (95 : 5) gave one diastereoisomer of 5,6,11,12-*tetrahydrodibenzo*[a,e]*cyclooctene*-5,6-*dicarbonitrile* (70 mg), m.p. 172—174° (from benzene–petroleum) (Found: C, 83.9; H, 5.6; N, 10.7. $C_{18}H_{14}N_2$ requires C, 83.7; H, 5.5; N, 10.85%), δ 3.2 (4 H, s, CH_2), 4.55 (2 H, s, CHCN), and 7.05 (8 H, m, aromatic). Further elution gave a second *diastereoisomer* (55 mg), m.p. 158° (from benzene–petroleum) (Found: C, 83.75; H, 5.4; N, 10.95%), δ 3.1 (4 H, s, CH_2), 4.85 (2 H, s, CHCN), and 7.0—7.6 (8 H, m, aromatic).

Hydrogenolysis of the endo-*Cyclopentene*-2-*Benzopyran*-3-*one Adduct*.—The adduct (6) (60 mg), and 10% palladium–carbon (60 mg) in acetic acid (4 ml) were shaken in hydrogen (24 h). This filtered product was evaporated under reduced pressure on a water-bath, dissolved in ether, and extracted into saturated sodium hydrogen carbonate solution. The acidified extract was extracted with ether, and the extract dried ($MgSO_4$) and evaporated to give an acid (45 mg), $\nu_{max.}$ 1 709 and 2 360—3 200 cm^{-1}. With ethereal diazomethane this gave the *trans*-4-methoxycarbonylhydrindane (30) identical with the sample described above (i.r. spectrum)

Reactions of the Tropone-1-*Methyl*-2-*benzopyran*-3-*one Adduct*.—(*a*) The adduct (18; R = Me) (40 mg), platinum oxide (10 mg), and ethyl acetate (7 ml) were shaken in hydrogen (1.5 h). Filtration and evaporation gave the *tetrahydro-derivative* (33 mg, 81%), m.p. 190—192° (from chloroform–ethanol) (Found: C, 75.4; H, 6.7. $C_{17}H_{18}O_2$ requires C, 75.5; H, 6.7%), $\nu_{max.}$ 1 739 and 1 699 cm^{-1}, δ 1.5—2.2 (11 H, m, including Me resonance at 1.82), 2.75—3.2 (2 H, m, HC·CO), 3.78 (1 H, d, 6.5 Hz, HC·CO·O), and 7.15—7.4 (4 H, m, aromatic).

(*b*) The adduct (18; R = Me) (13 mg), 4-phenyl-1,2,4-triazoline-3,5-dione (10 mg), and benzene (2 ml) were stirred under nitrogen in the dark (20 h). Evaporation left the *adduct* (19) (16 mg, 78%), m.p. 270—272° (from chloroform–ethanol) (Found: C, 68.3; H, 4.5; N, 9.4. $C_{25}H_{19}N_3O_5$ requires C, 68.0; H, 4.3; N, 9.5%), $\nu_{max.}$ 1 775, 1 731, and 1 703 cm^{-1}, δ[$(CD_3)_2SO$] 1.99 (3 H, s), 3.5—3.9 (2 H, m, HC·CO), 4.23 (1 H, d, *J* 7.5 Hz), 5.71 (2 H, dd, *J* 18 and 7.5 Hz), 6.34 (1 H, t, *J* 7.5 Hz, olefinic), 6.83 (1 H, t, *J* 7.5 Hz, olefinic), and 7.43br (9 H, s, aromatic).

(*c*) The adduct (18; R = Me) (175 mg) was irradiated in deoxygenated benzene (175 ml) (1.5 h) in a Hanovia photochemical reactor with a medium-pressure (100 W) mercury lamp, while a slow nitrogen stream was bubbled through the solution (mercury bubbler at exit). Evaporation, and chromatography of the residue on silica in benzene–ethyl acetate (22 : 3) gave the *cyclobutene* (22) (35 mg, 20%), m.p. 188—191° (from benzene–petroleum) (Found: C, 76.65; H, 5.3. $C_{17}H_{14}O_3$ requires C, 76.7; H, 5.3%), $\nu_{max.}$ 1 740 cm^{-1}, δ 1.9 (3 H, s), 2.45—3.1 (2 H, m, HC·CO), 3.15—3.55 (2 H, m), 3.92 (1 H, d, *J* 9.5 Hz, HC·CO·O), 5.93 (1 H, d, *J* 2.5 Hz), 6.33 (1 H, d, *J* 2.5 Hz), and 7.2—7.5 (4 H, m, aromatic).

Reaction of the Tropone-2,5-*Dimethyl*-3,4-*diphenylcyclopenta*-2,4-*dienone Adduct with* 4-*Phenyl*-1,2,4-*triazoline*-3,5-*dione*.—The adduct [15] (55 mg), 4-phenyl-1,2,4-triazoline-3,5-dione (30 mg), and benzene (5 ml) were stirred under nitrogen in the dark (30 h). Evaporation left the *adduct* (21) (75 mg, 92%), m.p. 264—266° (from chloroform–ethanol) (Found: C, 75.55; H, 5.05; N, 7.7. $C_{34}H_{27}N_3O_4$ requires C, 75.4; H, 5.0; N, 7.8%), $\nu_{max.}$ 1 773, 1 732, and 1 704 cm^{-1}, δ[$(CD_3)_2SO$] 1.14 (6 H, s), 3.77 (2 H, d *J* 8 Hz, HC·CO), 5.4—5.8 (2 H, m), 6.7 (2 H, dd, *J* 5 and 3 Hz), and 6.85—7.6 (15 H, m, aromatic).

Additions to Benzo[c]*furan*.—(*a*) Cyclopentene (2 ml), toluene (4 ml), and the lactone (33) (200 mg) were heated in a bomb in an oil-bath at 100 °C (1 h). The product was evaporated and the residue chromatographed on silica in benzene–ether (95 : 5) to give the endo-*benzo*[c]*furan adduct* (80 mg), m.p. 80—82° (from petroleum) (Found: C, 84.05; H, 7.4. $C_{13}H_{14}O$ requires C, 83.8; H, 7.6%), δ −0.6 (1 H, m, CH_2), 0.5—1.8 (5 H, complex m, CH_2), 3.0 (2 H, m, *H*C·CH_2), 5.15 (2 H, 4 lines, *J* 6 and 2.5 Hz, HCO), and 7.2 (4 H, m, aromatic). T.l.c. of the crude product indicated the possible presence of a very small quantity of the *exo*-adduct.

(*b*) Cycloheptene (1 ml), toluene (2.5 ml), and the lactone (33) (200 mg) were boiled under reflux (1 h). Isolation as in (*a*) gave the endo-*benzo*[c]*furan adduct* (40 mg), m.p. 49—50° (from petroleum) (Found: C, 84.0; H, 8.3. $C_{15}H_{18}O$ requires C, 84.1; H, 8.5%), δ 0—2 (10 H, complex resonance, CH_2), 2.5 (2 H, m, HC·CO), 5.1 (2 H, d, *J* 5 Hz and weak inner lines, HCO), and 7.2br (4 H, s, aromatic). T.l.c. of the crude product indicated the possible presence of a very small quantity of the *exo*-adduct.

(*c*) The addition of cycloheptatriene and isolation of the adducts was conducted as in (*b*). The exo-*benzo*[c]*furan adduct* (30 mg) was eluted first, m.p. 82—83° (from petroleum) (Found: C, 85.45; H, 6.8. $C_{15}H_{14}O$ requires C, 85.7; H, 6.7%), δ 2.3—2.7 (4 H, m, CH_2 and HC·CO), 5.03 (1 H, s, HCO), 5.28 (1 H, s, HCO), 5.75—6.4 (4 H, m, olefinic), and 7.2br (4 H, s, aromatic). Continued elution gave the endo-*benzo*[c]*furan adduct* (50 mg) as an oil (Found: M^+, 210.1048. $C_{15}H_{14}O$ requires *M*, 210.1044), δ 0.5—1.3br (1 H, m, CH_2), 1.5—2.5br (1 H, m, CH_2), 3.0—3.5br (2 H, m, HC·CO), 5.15 (1 H, d, *J* 4.5 Hz, HCO), 5.35br (1 H, d, *J* 5.5 Hz, HCO), 5.56—6.2 (4 H, m, olefinic), and 7.2 (4 H, m, aromatic).

(*d*) Norbornadiene (1.5 ml), toluene (3.5 ml), and the lactone (33) (200 mg) were boiled under reflux (1 h). Isolation by chromatography as described in (*a*) gave first

the exo-*benzo*[c]*furan adduct* (80 mg), m.p. 82° (from benzene–petroleum) (Found: C, 85.75; H, 6.65. $C_{15}H_{14}O$ requires C, 85.7; H, 6.7%), δ 1.25br (1 H, d, *J ca.* 8 Hz, CH_2), 2.65br (1 H, d, *J ca.* 8 Hz, CH_2), 1.8br (2 H, s, HCCO), 2.8 (2 H, m, *H*C·CH_2), 5.05 (2 H, s, HCO), 6.15 (2 H, m, olefinic), and 7.11 (4 H, m, aromatic). Continued elution gave the endo-*benzo*[c]*furan adduct* (45 mg), m.p. 72—73° (from benzene–petroleum) (Found: C, 85.9; H, 6.6%), δ −0.95br (1 H, d, *J* 10 Hz, CH_2), 0.67br (1 H, d, *J* 10 Hz, CH_2), 2.26 (2 H, m, HC·CO), 2.61 (2 H, m, *H*C·CH_2), 5.1 (2 H, d, *J ca.* 4 Hz with weak inner lines, HCO), 6.2br (2 H, s, olefinic), and 7.2 (4 H, m, aromatic).

(*e*) Tropone (1 g), toluene (2.5 ml), and the lactone (33) (200 mg) were boiled under reflux (1 h). Removal of toluene and the excess of tropone under high vacuum on a steam-bath gave a partly crystalline product. Trituration with methanol gave the crystalline *benzo*[c]*furan adduct* (65 mg), m.p. 206—208° (from chloroform–methanol) (Found: C, 80.3; H, 5.4. $C_{15}H_{12}O_2$ requires C, 80.3; H, 5.4%), $\nu_{max.}$ 1 710 and 1 720 cm^{-1}, δ 3.2—3.5 (2 H, m, HC·CO), 5.4br (2 H, s, HCO), 5.6—6.4 (4 H, complex m, olefinic), and 7.25br (4 H, s, aromatic).

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